THE ELECTROSTATIC POTENTIAL IN A FINITE IONIC CRYSTAL

by

Austin Redlack

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THE UNIVERSITY OF WATERLOO

November, 1972

I hereby declare that I am the sole author of this report.

I authorize the University of Waterloo to lend it to other institutions or individuals for the purposes of scholarly research.

Signature 

ACKNOWLEDGEMENTS

The research of this thesis was done under the supervision of Professor J. Grindlay. I wish to take this opportunity to express my gratitude for his valuable help and advice. He was always willing to discuss any problems that were encountered and aid in their solution.

I am also indebted to N.R.C. for their scholarship and the Physics Department of the University of Waterloo for their additional financial support.

ABSTRACT

This thesis is written in two parts.

In Part One, we develop a new method for evaluating three dimensional lattice summations and apply it to the evaluation of the electrostatic potential of a finite ionic crystal. We then compare our expression with those obtained using infinite crystals. Some of the effects which are not obtainable using an infinite crystal are:

1. the electrostatic potential depends on the shape of the sample when a dipole or quadrupole moment is present, and

2. the electrostatic potential at the surface of a crystal changes rapidly near the surface.

In Part Two, we use the method developed in Part One to evaluate the electrostatic potential in a deformed crystal and use the resulting expression to define the macroscopic electric field and the electric displacement field. For the case of uniform fields, the expressions for these fields reduce to those in common use.

CONTENTS

PART TWO

CHAPTER I

INTRODUCTION

A. Introduction

The electrostatic potential is a quantity which appears in most calculations related to ionic crystals. Unfortunately, it is a quantity which is difficult to evaluate. The difficulty arises from the long range nature of the coulomb potential of a point charge. If a crystal is assumed to be composed of point charges, then all the ions in the crystal contribute significantly to the electrostatic potential at any point, not just the ions in the vicinity of the point.

Since there are of the order 10^{23} ions in a finite crystal, in practice, direct summation of the contribution of each ion is impossible. What has been done in the past is to consider the case of the infinite crystal. The electrostatic potential of an infinite crystal is a periodic function of position with the periodicity of the lattice. This property aids in manipulating the expression for the electrostatic potential into more manageable forms. However, the nature of the connection between the finite crystal results and the infinite crystal results has never been made clear in the literature, at least in our opinion.

What we propose to do in this thesis is to evaluate the electrostatic potential for a finite crystal and compare the result with the expressions for the electrostatic potential of an infinite crystal obtained by other authors. The comparison of the potentials of the

infinite and finite crystals has not been done previously to our knowledge.

In Chapter II, we discuss some of the prominent methods used in the past to evaluate the electrostatic potential of an infinite crystal. In Chapter III, we evaluate the electrostatic potential due to a finite crystal. It is found convenient to consider this potential as the sum of two parts - an intrinsic and an extrinsic part. The intrinsic part is discussed in Chapter IV. We show that this quantity is related to the electrostatic potential of the infinite crystal. Chapter V is devoted to a discussion of the extrinsic part. This quantity is non-periodic and has no counter-part in the infinite crystal.

In the remainder of this chapter, we will introduce the notation and terminology that will be used throughout the thesis.

B. Notation

Before proceeding, we will introduce the notation which will be used throughout the thesis. Whenever possible, the notation of Born and Huang[1] (B&H) will be used.

The position vector of a Bravais lattice point will be denoted by $\vec{x}(\vec{l})$*1 where

$$\vec{x}(\vec{l}) = l_1 a_1 \hat{e}_1 + l_2 a_2 \hat{e}_2 + l_3 a_3 \hat{e}_3 + \vec{x}_0 \qquad 1.2.1$$

$\vec{l}$ is the triplet of integers (l_1, l_2, l_3) (which will be referred to as lattice site indices); $a_1\hat{e}_1$, $a_2\hat{e}_2$, $a_3\hat{e}_3$ are the primitive translation vectors of the Bravais lattice; and $\hat{e}_1$, $\hat{e}_2$, $\hat{e}_3$ are unit vectors. i.e.

$$|\hat{e}_i| = 1 \qquad i = 1,2,3 \qquad 1.2.2$$

a_1, a_2, a_3 will be referred to as lattice parameters. $\vec{x}_0$ is a vector, independent of $\vec{l}$, which is zero if we have chosen the origin of $\vec{x}(\vec{l})$ to be a Bravais lattice site and non-zero otherwise.

We will denote vectors in the reciprocal lattice (reciprocal to the Bravais lattice defined by (1.2.1)) by $\vec{k}$ and reciprocal lattice vectors by $\vec{y}(\vec{h})$. i.e.

$$\vec{k} = k_1\hat{e}_1 + k_2\hat{e}_2 + k_3\hat{e}_3 \qquad 1.2.3$$

and

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*1 We will be using the symbol l in three forms - $\vec{l}$ which represents the triplet (l_1, l_2, l_3), l_i which is a component of $\vec{l}$, and 1 which is the symbol for one.

$$\vec{y}(\vec{h}) = h_1 b_1 \hat{e}_{\sim 1} + h_2 b_2 \hat{e}_{\sim 2} + h_3 b_3 \hat{e}_{\sim 3} \qquad 1.2.4$$

$\vec{h}$ denotes the triplet of integers (h_1, h_2, h_3); k_1/b_1, k_2/b_2, k_3/b_3 are real numbers; $b_1 \hat{e}_{\sim 1}$, $b_2 \hat{e}_{\sim 2}$, $b_3 \hat{e}_{\sim 3}$ are the primitive translation vectors of the reciprocal lattice; $\hat{e}_{\sim 1}$, $\hat{e}_{\sim 2}$, $\hat{e}_{\sim 3}$ are unit vectors; and b_1, b_2, b_3 are reciprocal lattice parameters. The unit vectors $\hat{e}_{\sim i}$, in addition to satisfying (1.2.2), also satisfy

$$\hat{e}_i \cdot \hat{e}_{\sim j} = \delta_{ij} \qquad i,j = 1,2,3 \qquad 1.2.5$$

where δ_{ij} is the Kronecker delta.

$$\begin{aligned} \delta_{ij} &= 1 && \text{if } i = j \\ &= 0 && \text{if } i \neq j \end{aligned} \qquad 1.2.6$$

The $\hat{e}_{\sim i}$ are given in terms of the $\hat{e}_i$ by the relation

$$\hat{e}_{\sim i} = \hat{e}_j \times \hat{e}_k / \hat{e}_i \cdot (\hat{e}_j \times \hat{e}_k) \qquad 1.2.7$$

where i, j, k are cyclic permutations of 1, 2, 3.

C. The Electrostatic Potential

Before giving the expression for the electrostatic potential of a crystal, we will first have to define what we mean by a finite or by an infinite crystal. For the purposes of this thesis the following definitions will apply.

'A finite crystal is one which is constructed by associating a unique charge repetition unit (c.r.u.)*1 with each lattice point within a finite region of a Bravais lattice.'*2

The c.r.u. is the simplest group of charges (or ions) with which we may build up the finite crystal. In practice, the c.r.u. will be chosen to be electrically neutral, though many of our results hold for the case of c.r.u.'s with non-vanishing net charge.

'An infinite crystal is one which is constructed by associating a neutral charge basis unit (c.b.u.) with every lattice point of a Bravais lattice.'

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*1 There are finite crystals in which it is convenient to consider the crystals as being built up from two c.r.u.'s. This is usually done if the total number of ions in the two c.r.u.'s is less than the number of ions in the single necessary c.r.u.

*2 A more realistic definition of a finite crystal should include statements about the equilibrium conditions satisfied by the ions. We have chosen the present definition because the electrostatic potential associated with this charge array may be evaluated exactly. Equilibrium conditions are beyond the scope of this part of the thesis.

Again the c.b.u. is some group of point charges (or ions) with which the infinite crystal can be constructed. We have chosen to use c.r.u. for the finite crystal and c.b.u. for the infinite crystal to emphasis that the charge repetition group for a finite crystal is unique (for a given Bravais lattice) and that the charge repetition group for an infinite crystal is not unique.*3 (See figs. 1.1 and 1.2.) The criteria the c.b.u. must satisfy are charge neutrality and that it correctly builds up the crystal lattice. The neutrality condition is necessary if the electrostatic potential is to be finite. Some convenient c.b.u.'s are the primitive cell and other unit cells. The ions in the c.b.u. are allowed to have charges which are fractions of the ionic charge. The only criterion (but more stringent) which the c.r.u. must satisfy is that it correctly builds up the finite sample which is being considered. For a given region V in a Bravais lattice there is a different finite crystal for each c.r.u. Whereas, for the case of an infinite crystal, a number of different c.b.u.'s plus one Bravais lattice may generate the same system.

To give an example of why we wish to stress the difference between a c.b.u. and a c.r.u., we will consider the charge arrays given in figs. 1.1 and 1.2. In fig. 1.1 we show part of an infinite charge array. We see that, for each Bravais lattice we may choose, there are many different c.b.u.'s which may be used to build up the infinite crystal. A few of them are given in fig. 1.1. We note that these c.b.u.'s have

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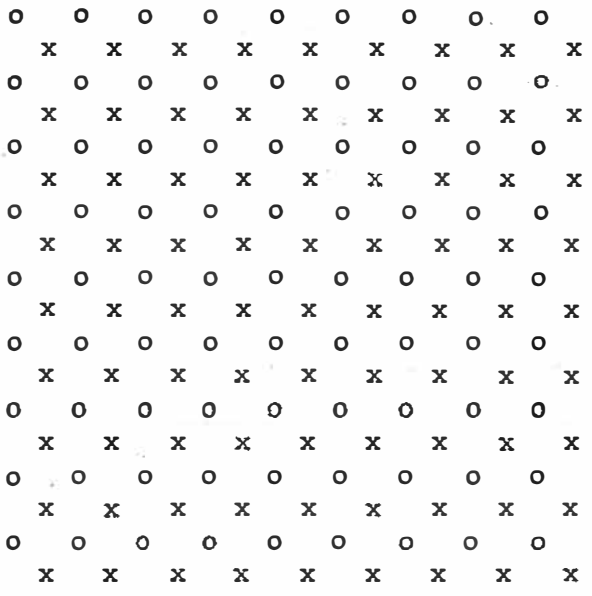
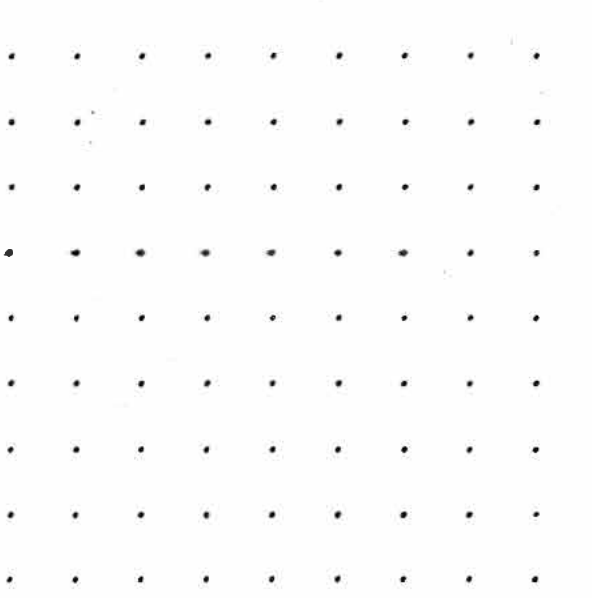
*3 We note that a single charge repetition unit may be either a c.r.u. or a c.b.u. depending on the type of crystal it is used to construct.

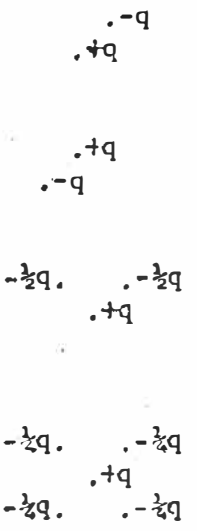


o - + q

x - - q

An infinite charge array





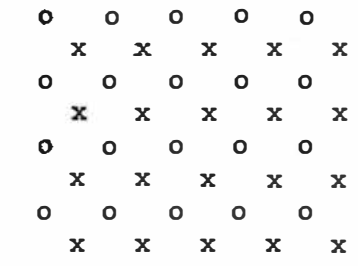
A possible Bravais lattice of the infinite crystal.

Several possible c.b.u.'s with which the infinite crystal may be constructed using the given Bravais lattice.

Figure 1.1

The Infinite Crystal

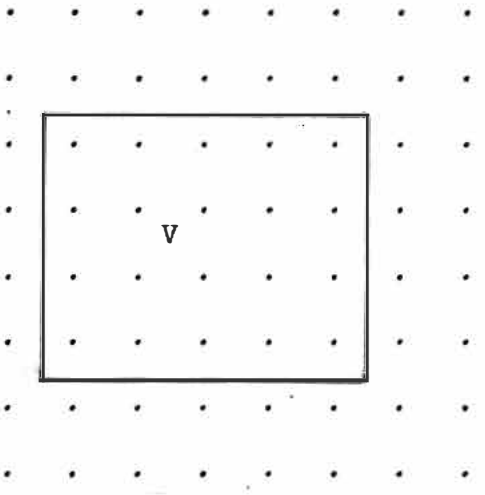
A Diatomic Crystal of Point Charges with Charges q and -q



A finite charge array

o - + q

x - - q



A Bravais lattice with which we can associate the finite crystal. A c.r.u. is associated only with each of the lattice sites within the finite region V.

The c.r.u. of the finite crystal associated with the given Bravais lattice.

Figure 1.2

A Finite Diatomic Ionic Crystal

varying dipole moments and different symmetry properties. Directing our attention to fig. 1.2, we have an example of a finite crystal. The region V is a rectangle of sides 4a by 5a. In contrast to the infinite crystal case, we see that once the Bravais lattice is chosen, there is only one charge repetition unit with which we may build this finite crystal.

In summary, we use c.r.u. because a finite crystal uniquely defines the c.r.u. whereas the infinite crystal does not uniquely define the c.b.u. Also when the term c.r.u. is being used, it is immediately obvious that a finite crystal is being considered.

The following discussion, up to eq (1.3.5), holds for both finite and infinite crystals. For simplicity we will refer only to the c.r.u. of the finite crystal explicitly.

If the c.r.u. is neutral, then the whole crystal is also neutral. Labelling each of the ions in the c.r.u. with the symbol k[*4], we have

$$\sum_{k}^{r} q^k = 0 \qquad 1.3.1$$

where q^k is the charge of the k-th type ion and k is summed over all the ions in the c.r.u. which is denoted by the r on the sum. If k is summed over a c.b.u., then we use a b instead of the r. We find it convenient to introduce a dimensionless parameter s^k, related to q^k as follows:

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*4 There should be no confusion between $\vec{k}$ denoting a vector in the reciprocal lattice and k denoting the type of ion in the c.r.u. or c.b.u. since $\vec{k}$ will always carry the vector symbol.

$$s^k = q^k/e \qquad 1.3.2$$

where e is the magnitude of the electronic charge.

If we let one of the ions (with k = 0) in the c.r.u. occupy the Bravais lattice sites, then we can define the positions of the other ions in the c.r.u. with respect to this ion. Letting the position vector of the k-th type ion be $\vec{x}^k$ relative to the k = 0 ion, then

$$\vec{x}^k = x_1^k \hat{e}_1 + x_2^k \hat{e}_2 + x_3^k \hat{e}_3 \qquad 1.3.3$$

where x_1^k/a_1, x_2^k/a_2, x_3^k/a_3 are real numbers whose magnitudes are less than one. By definition

$$\vec{x}^0 = 0 \qquad 1.3.4$$

Thus the position vector, $\vec{x}(\vec{l},k)$, of the k-th ion in the c.r.u. associated with the $\vec{l}$-th lattice site is

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k \qquad 1.3.5$$

where $\vec{x}^k$ is independent of $\vec{l}$. The choice of which ion we choose to have k = 0 is arbitrary.

The electrostatic potential, $V(\vec{z})$, at a point P (with position vector $\vec{z}$) which is not an ion site, in a finite crystal of point charges is defined by

$$V(\vec{z}) = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}\in V} \sum_{k}^{r} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 1.3.6$$

where k is summed over all the ions in the c.r.u. and $\vec{l}$ is summed over all the Bravais lattice sites within V ($\vec{l}\in V$). (See fig. 1.3.) The boundary condition that the electrostatic potential due to each ion

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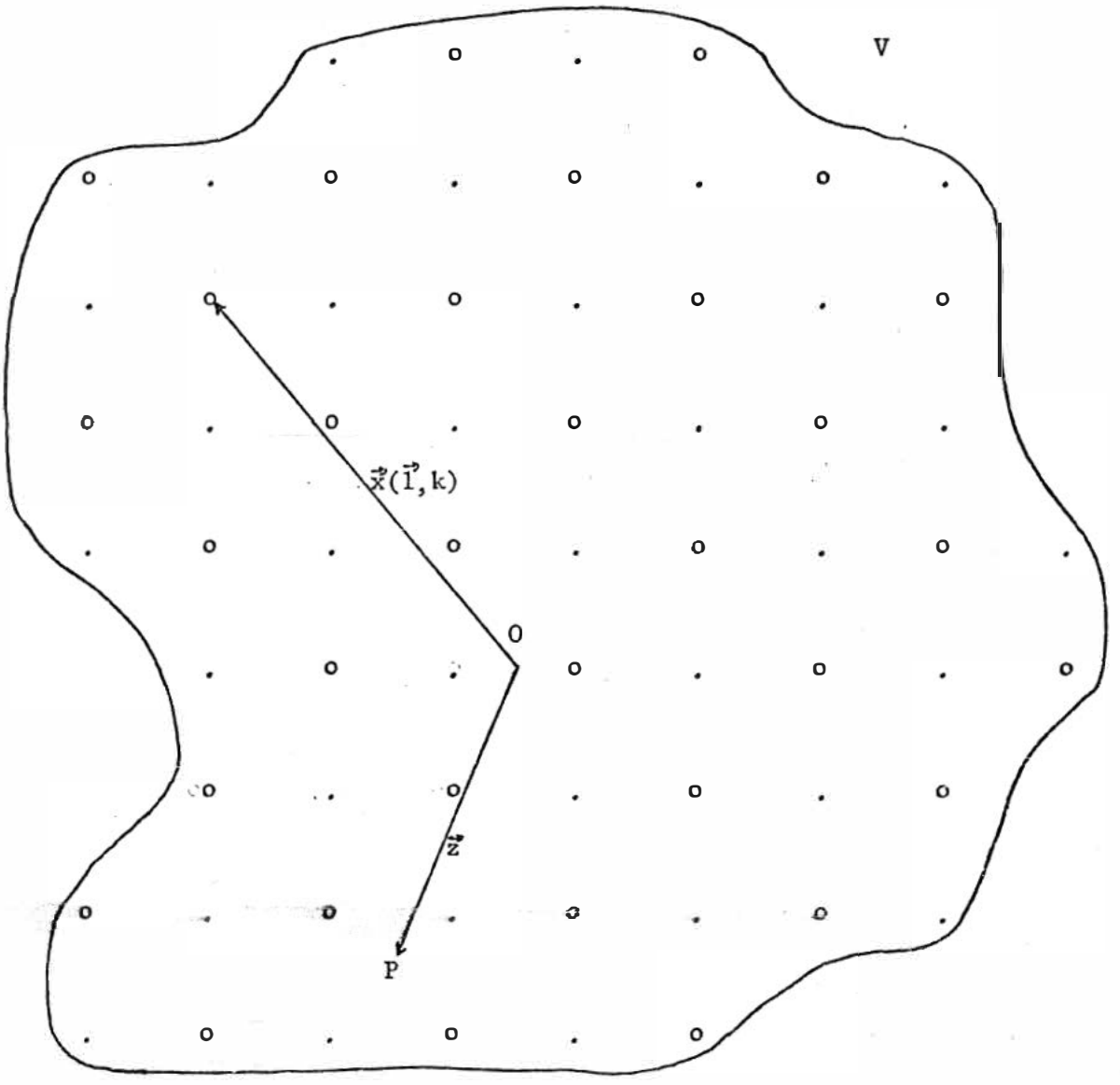
*5 We will be using M.K.S. units throughout this thesis.



$\vec{x}(\vec{l},k)$ - a lattice vector

$\vec{z}$ - position vector of an arbitrary point P

O - the origin

Figure 1.3

Position Vectors in a Finite Crystal of Volume V

must satisfy is that it vanishes far from the ion. If the point P happens to be an ion site, say $\vec{x}(\vec{l}',k')$, then the electrostatic potential at this point (called the self-potential) $V^{k'}(\vec{l}')$ is defined by

$$V^{k'}(\vec{l}') \overset{\text{defn}}{=} \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \sum_{k}^{r} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{x}(\vec{l}',k')|} \qquad 1.3.7$$

where the ' on the sum indicates that the term associated with $\vec{l} = \vec{l}'$ is to be omitted when $k = k'$. i.e. the lattice site $\vec{x}(\vec{l}',k')$ is considered to be vacant.

In the past it has been common practice to write the electrostatic potential of an infinite crystal as

$$V(\vec{z}) = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}} \sum_{k} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 1.3.8$$

where the sum over $\vec{l}$ is over the infinite lattice and the sum over k is over some charge repetition unit (usually the unit cell). Due to the conditional convergence of the R.H.S. of (1.3.8), this is not a good representation to use.

What we will mean by the electrostatic potential of an infinite crystal is

$$V^{\infty}(\vec{z}) = \frac{e}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V} \sum_{k}^{b} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 1.3.9$$

First k is summed over all the ions in the c.b.u., then $\vec{l}$ is summed over all the lattice points within the finite region V which tends to infinity. $V^{\infty}(\vec{z})$ is a periodic function of $\vec{z}$ with the periodicity of the lattice.

The self-potential, $V^{\infty}(k')$, at an ion site with position vector $\vec{x}(\vec{l}',k')$ is

$$V^{\infty}(k') = \frac{e}{4\pi\epsilon_0} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \sum_{k}^{b} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{x}^{k'}|} \qquad 1.3.10$$

where the ' on the sum over $\vec{l}$ indicates that $\vec{l} = 0$ is to be omitted when $k = k'$. For the infinite crystal, the electrostatic self-potential does not depend on the lattice site indices (i.e. on $\vec{l}'$) due to the periodic nature of $V^{\infty}(\vec{z})$.

We will denote the quantity defined by the introduction of the vanishing exponential by $V'(\vec{z})$ (this is the quantity which Ewald evaluated). i.e.

$$V'(\vec{z}) = \frac{e}{4\pi\epsilon_0} \lim_{\beta\to 0} \lim_{V\to\infty} \sum_{\vec{l}\in V} \sum_{k}^{b} \frac{s^k e^{-\beta|\vec{x}(\vec{l},k)-\vec{z}|}}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 1.3.11$$

The electrostatic self-potential associated with this definition of the electrostatic potential is

$$V'^{k'} = \frac{e}{4\pi\epsilon_0} \lim_{\beta\to 0} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \sum_{k}^{b} \frac{s^k e^{-\beta|\vec{x}(\vec{l},k)-\vec{x}^{k'}|}}{|\vec{x}(\vec{l},k) - \vec{x}^{k'}|} \qquad 1.3.12$$

The limit $V\to\infty$ and the limit $\beta\to 0$, in general, do not commute (see discussion following eq (2.4.4)). Thus the quantities $V'(\vec{z})$ and $V^{\infty}(\vec{z})$ are, in general, different.

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*6 We will use $V = V^{\infty}(k'=0)$ for the electrostatic self-potential of the k=0 ion in the infinite crystal.

D. Conditional Convergence

The electrostatic potential at a point P with position vector $\vec{z}$, due to a infinite, point charge crystal is usually written as

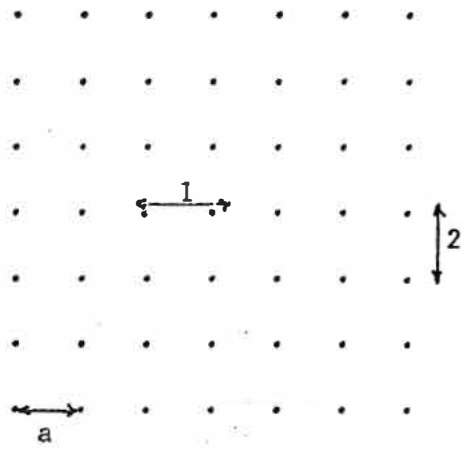
$$V^{\infty}(\vec{z}) = \frac{e}{4\pi\epsilon_0} \sum_{\vec{l}} \sum_{k}^{b} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \quad \text{(see (1.3.8))} \qquad 1.4.1$$

As (1.4.1) is written, we first sum over all the ions in the charge basis unit (c.b.u.) (the sum over k), then sum over all the Bravais lattice sites (a c.b.u. is associated with each lattice site). By choosing a particular c.b.u., we are implicitly choosing one type of order of summation. The choice of c.b.u. is not unique in a crystal. For a given Bravais lattice, there are many ways in which the same crystal structure may be built up (see fig. 1.1). If the sum (1.4.1) depends on the choice of c.b.u., then the sum is said to be c.b.u. conditionally convergent.

There is a second way in which (1.4.1) may be conditionally convergent. To obtain a better understanding of this type of conditional convergence, we write $V^{\infty}(\vec{z})$ as given by eq (1.3.9).

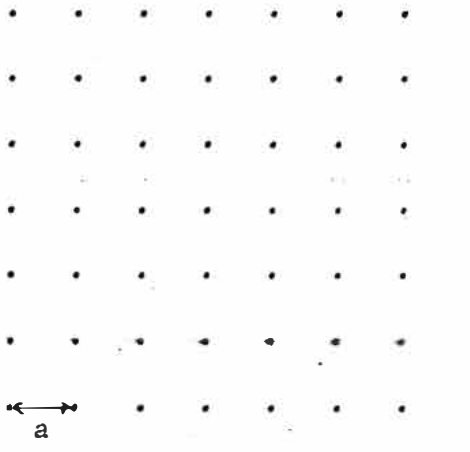
$$V^{\infty}(\vec{z}) = \frac{e}{4\pi\epsilon_0} \lim_{V\to\infty} \sum_{\vec{l}\in V} \sum_{k}^{b} \frac{s^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 1.4.2$$

where $\vec{l} \in V$ indicates that the sum is over all lattice points in the region V. If $V^{\infty}(\vec{z})$ depends on how we let the region V go to infinity, then $V^{\infty}(\vec{z})$ is said to be shape conditionally convergent. For a three dimensional lattice we could sum over lines and planes as Madelung, or



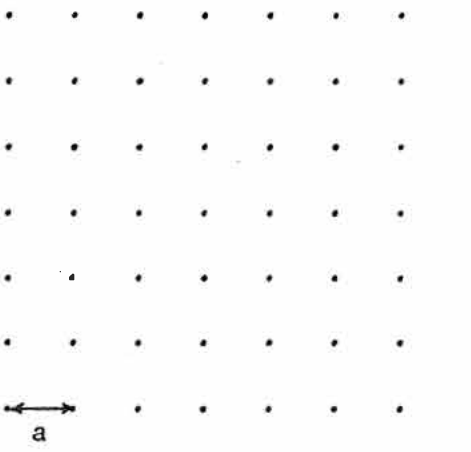
Line-wise Summation

First sum over all the points in a line ($\xleftrightarrow{1}$), then sum over all the lines ($\updownarrow 2$).



Expanding Square

First sum over all the points within the square of side 2a, then all the points on the surface of the square of side 4a, 6a, etc.



Expanding Circle

First sum over all the points within the circle of radius a, then add the points lying of the circle of radius $\sqrt{2}a$, $\sqrt{3}a$, etc.

Figure 1.4

Several possible ways one may sum over all the lattice sites in an infinite

over an expanding cube as Evjen, or over all the points within an expanding sphere (see fig. 1.4 for the case of a two dimensional array).

Previous authors have not distinguished between the two types of conditional convergence. We shall see later that the sum, eq (1.4.2), representing the electrostatic potential of an infinite crystal is always c.b.u. conditionally convergent. For some of the c.b.u.'s it will also be shape conditionally convergent. There may be c.b.u.'s such that eq (1.4.2) is not shape conditionally convergent but, in general, this is not true for all the possible c.b.u.'s of a crystal.

In Chapter IV we will show how these two kinds of conditional convergence arise when eq (1.4.2) is used to define the electrostatic potential of an infinite crystal. This conditional convergence is the principal drawback of the infinite crystal methods since the value of eq (1.4.2) is not solely a property of the crystal structure.

Since the electrostatic potential of an infinite crystal is represented by a conditionally convergent sum, the question of accepted value for this conditionally convergent sum arises. It has been our experience that previous authors have assumed that if the c.b.u. is choosen such that the infinite sum is no longer shape conditionally convergent, then this gives the accepted value for the electrostatic potential of the infinite crystal. Unfortunately, there are crystals where such a c.b.u. does not exist. We will show later that the quantity defined by the introduction of the vanishing exponential, eq (1.3.11), gives the accepted value when it exists. Thus, for the cases where there is no suitable c.b.u., the accepted value has been chosen to be the quantity which results from the introduction of the vanishing

exponential. However, given this accepted value, the problem still remains as to the meaning of this accepted value.

In Chapter IV, we will show how this accepted value is related to the actual value of the electrostatic potential for the finite crystal. In general, they are not the same.

In the discussion of the infinite crystal methods, we will refer to the methods as valid or correct if the methods give the accepted value for the infinite crystal (as defined on the previous page). We do not mean they are valid or correct for the case of finite crystals. For finite systems, the electrostatic potential is a well defined quantity for each sample, although it may vary from sample to sample of the same crystal.

CHAPTER II

HISTORICAL SUMMARY

A. Introduction

There have been many methods developed for evaluating the sums associated with the electrostatic potential of a point charge, ionic crystal. They all considered the mathematically simple case of the infinite crystal.

The first method was developed by Madelung[2] in 1918*1. He first obtained the fourier series solution of two electrostatic potential problems (a) lines of periodic neutral charge groups, and (b) planes of periodic neutral charge groups. He then considered the infinite crystal as composed of (001) planes each composed of (100) lines. He was then able to evaluate the total electrostatic potential at an ion site by using his solutions to the linear and planar problems to evaluate the contribution of each plane of charge.

Another method, which relies on special ordering of the terms (with charge neutrality as the criterion), was developed by Evjen[3].

Other methods have been developed by Ewald[4], Born*1, and Harris and Monkhorst[5] (H&M). All three methods are based on the introduction of a vanishing exponential term to remove the conditional convergence inherent in the original sum. Ewald was the only one who discussed

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*1 The discussions of the methods of Madelung and Born are based on the review article by J. Sherman[6].

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this point but it is implicit in the other two methods. Ewald introduced the theta-function transformation to simplify the resulting expression whereas H&M introduced fourier transforms. Born used Ewald's results in his method. The methods of Ewald and H&M have been successfully applied to a variety of problems.

In yet another approach, Tosi considered the problem of an infinite array of similar point charges embedded in a uniform background of charge of opposite sign. In this way he was able to associate a finite electrostatic potential with a Bravais lattice whose lattice sites are occupied by similar point charges. The electrostatic potential of the ions without the background charge is infinite.

This chapter will be devoted to giving a brief description of these various methods.

B. Madelung's Method

One of the problems Madelung considered was the electrostatic potential of an infinite row of periodic neutral charge groups with period a. The electrostatic potential $V^L(\bar{z})$ of such a line of point charges is periodic in one dimension. Thus he assumed a fourier series representation for the solution at a point P, of the form

$$V^L(x,r,\theta) = \frac{q}{4\pi\epsilon_o} \sum_m A(r,m) e^{i2\pi mx/a} \qquad 2.2.1$$

where (x,θ,r) are the cylindrical coordinates of the point P relative to the origin chosen to be at ion k (see fig. 2.1 for the special case of a line of alternating point charges). m is to be summed over all integers. The R.H.S. of (2.2.1) is independent of the angular coordinate θ due to the symmetry of the problem. The conditions Madelung imposed on the electrostatic potential of this system were that it must be a solution of Poisson's equation and must vanish as $r \to \infty$.

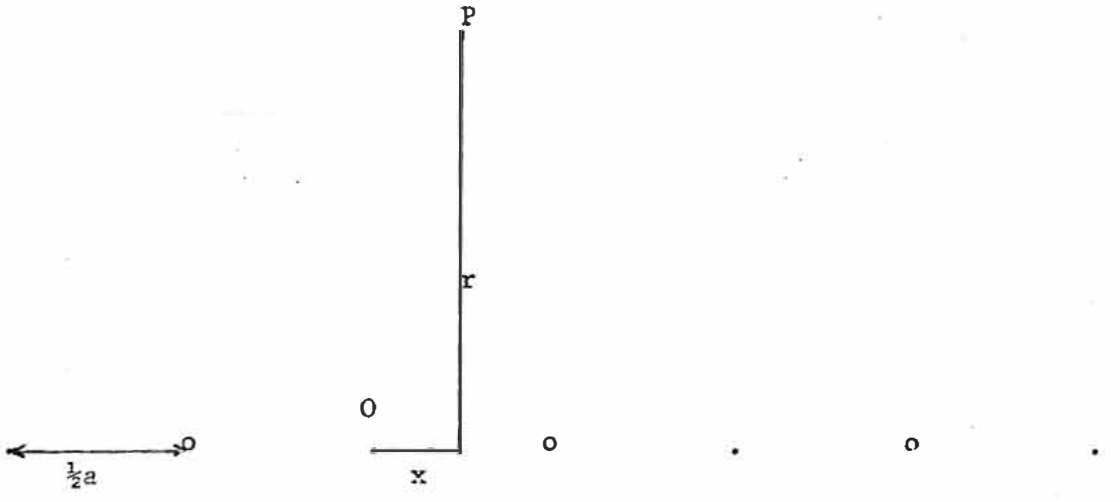
The solution he found, for an electrically neutral line of alternating point charges $(q',-q')$ (see fig. 2.1), was

$$V^L(x,r) = \frac{8q'}{4\pi\epsilon_o a} \sum_{\substack{m=1 \\ \text{odd}}}^{\infty} K(2\pi mr/a)\cos(2\pi mx/a) \qquad 2.2.2$$

where

$$K(z) = \tfrac{1}{2}i\pi H_0^{(1)}(iz) \qquad 2.2.3$$

and $H_0^{(1)}(z)$ is a Hankel function of the first kind. However, this



. - ion of charge q'

o - ion of charge -q'

O - origin of coordinate system

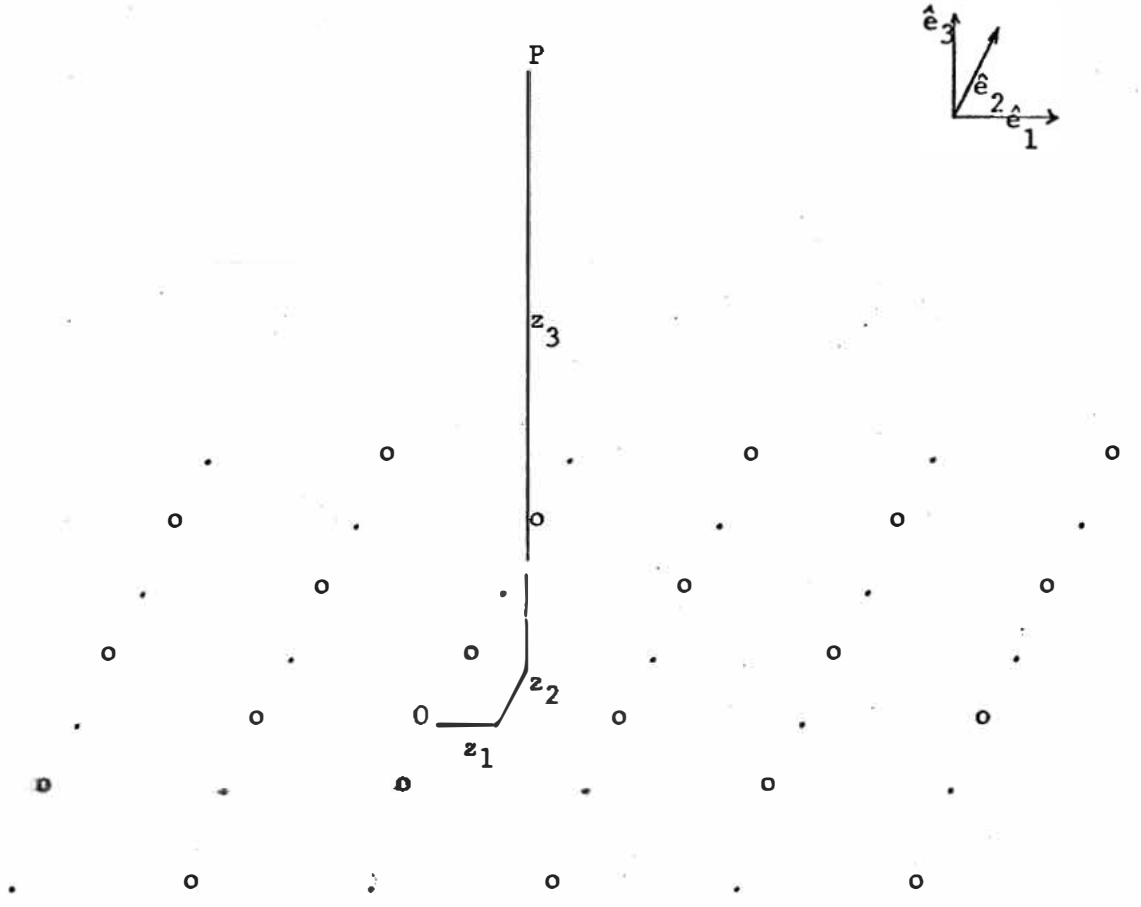
P - point of interest

r, x - cylindrical coordinates of point P

Figure 2.1

A One Dimensional System

An infinite line of alternating point charges with period a. The coordinates of an arbitrary point P are shown.



. - ion of charge q'

o - ion of charge - q'

0 - origin of coordinate system

P - point of interest

z_1, z_2, z_3 - cartesian coordinates of the point P

Figure 2.2

A Two Dimensional System

An infinite plane of alternating point charges with periods a_1, a_2 in the $\hat{e}_1$ and $\hat{e}_2$ directions respectively. The coordinates of an arbitrary point P are shown.

solution is not valid for $r \to 0$ since it includes the contribution of the ion at $x = 0$. For $r = 0$,

$$V^{L}(x;0) = \frac{2q'}{4\pi\epsilon_o a} \sum_{m=1}^{\infty} \frac{(-1)^m}{|m - x/a|} \qquad 2.2.4$$

where we have excluded the contribution due to the ion at $x = 0$. This may also be represented by a fourier series for $-\frac{1}{2}a \leq x \leq \frac{1}{2}a$ but the coefficients are numbers which are not readily available.

The other problem Madelung considered was the potential at a point P due to a plane array of neutral charge groups (see fig. 2.2 for the special case of a plane of alternating charges). Extending the fourier method, the electrostatic potential for a plane of charges, $V^{P}(\vec{z})$, is

$$V^{P}(\vec{z}) = \frac{16q'}{4\pi\epsilon_o a_1 a_2} \sum_{\substack{m_1,m_2=1 \\ \text{odd}}}^{\infty} \frac{e^{-2\pi z_3((m_1/a_1)^2+(m_2/a_2)^2)^{\frac{1}{2}}}}{((m_1/a_1)^2+(m_2/a_2)^2)^{\frac{1}{2}}} \cos(2\pi m_1 \frac{z_1}{a_1}) \cos(2\pi m_2 \frac{z_2}{a_2}) \qquad 2.2.5$$

where

$$\vec{z} = z_1\hat{e}_1 + z_2\hat{e}_2 + z_3\hat{e}_3 \qquad 2.2.6$$

In terms of reciprocal lattice notation (2.2.5) may be rewritten as

$$V^{P}(\vec{z}) = \frac{4\pi q'}{4\pi\epsilon_o a_1 a_2} \sum_{\substack{h_1,h_2 \\ \text{odd}}} \frac{e^{-z_3|\vec{y}(\vec{h})|}}{|\vec{y}(\vec{h})|} e^{i\vec{y}(\vec{h}).\vec{z}} \qquad 2.2.7^{*1}$$

where

---

*1 This function is of the same form as the potential calculated in Chapter V (see eq (5.4.1i)).

$$\vec{\gamma}(\vec{h}) = h_1 b_1 \hat{e}_1 + h_2 b_2 \hat{e}_2 \qquad \text{(see eq (1.2.4))} \qquad 2.2.8$$

and $b_1 = 2\pi/a_1$, $b_2 = 2\pi/a_2$. This expression is not valid for $z_3 = 0$ since it includes the contribution of the point charge a $z_1 = z_2 = 0$.

As a sample calculation, we will describe the evaluation of the electrostatic potential at a Na ion site in NaCl. We will consider the ion as occupying a lattice site in a (001) plane. This plane will be referred to as the zero plane. The other planes are at a distance na (n integral) from the zero plane. The contribution, V_3, to the total electrostatic potential from the planes at a distance na from the zero plane, may be found from (2.2.5) with $z_3 = na$, $z_1 = z_2 = 0$, $q' = (-1)^n q$ (where q is the charge of the Na ion), and $a_1 = a_2 = a$. Thus

$$V_3 = \sum_n V^P(0,0,na)$$

$$= \frac{16q}{4\pi\epsilon_o a} \sum_{n=1}^{\infty} \sum_{\substack{m_1,m_2=1 \\ \text{odd}}} (-1)^n \frac{e^{-2\pi n(m_1^2+m_2^2)^{\frac{1}{2}}}}{(m_1^2+m_2^2)^{\frac{1}{2}}} \qquad 2.2.9$$

The contribution of the zero plane to the total potential consists of two parts: V_1 and V_2. V_1 is the contribution of the charges which lie on the line in the (100) direction which passes through the ion site and V_2 is the contribution of the remaining lines of charge in the (001) plane. To evaluate V_2 we use (2.2.2) with $x = 0$, $r = na$, and $q' = (-1)^n q$. Thus

$$V_2 = \frac{16q}{4\pi\epsilon_o a} \sum_{n=1}^{\infty} \sum_{\substack{m=1 \\ \text{odd}}}^{\infty} (-1)^n K(2\pi nm) \qquad 2.2.10$$

and setting $x = 0$ in (2.2.4) to obtain V_1 we get

$$V_1 = V^L(0;0)$$

$$= \frac{2q}{4\pi\epsilon_o a} \sum_{m=1}^{\infty} \frac{(-1)^m}{m}$$

$$= -2\ln 2 \frac{q}{4\pi\epsilon_o a}$$

Therefore the self-potential at an Na ion site in NaCl may be written as

$$V = V_1 + V_2 + V_3$$

$$= \frac{q}{4\pi\epsilon_o a}\left(-2\ln 2 + 16 \sum_{n=1}^{\infty} (-1)^n \left\{ \sum_{\substack{m_1=1 \\ \text{odd}}}^{\infty} \left[K(2\pi n m_1) + \sum_{\substack{m_2=1 \\ \text{odd}}}^{\infty} \frac{e^{-2\pi n (m_1^2+m_2^2)^{\frac{1}{2}}}}{(m_1^2+m_2^2)^{\frac{1}{2}}} \right] \right\}\right) \qquad 2.2.12$$

This method is restricted to those crystals which can be broken up into neutral lines and neutral planes of charge as described above. This can be easily done for m3m crystals such as NaCl or CsCl but is more difficult to do in the case of more complex crystals such as $BaTiO_3$ or cubic ZnS.

This method is principally of historical interest since without modification it is restricted to a small class of crystals. However, in the class of crystals in which it may be applied, the Madelung method is still useful in evaluating lattice sums arising in surface problems.

We stated earlier that the electrostatic potential of an infinite crystal is, in general, conditionally convergent. This means that the infinite sum associated with the electrostatic potential gives different

values depending on the order of summation. There is no guarantee that the order of summation Madelung used gives the correct physical potential other than for thin slabs where Madelung's ordering is justifiable.

C. Evjen's Method

The self-potential at a k' = 0 ion site is

$$V = \frac{1}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \sum_{k}^{b} \frac{q'^k}{|\vec{x}(\vec{l},k)|} \qquad \text{(see eq (1.3.10))}$$

$$= \frac{1}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \sum_{k}^{b} \frac{q'^k}{|\vec{x}(\vec{l}) + \vec{x}^k|} \qquad 2.3.1$$

where we have substituted for $\vec{x}(\vec{l},k)$ using eq (1.3.5). We are using q'^k to indicate that the charges used in the c.b.u. may be fractions of the ionic charge q^k.

In terms of our notation, Evjen chose to write the electrostatic potential in the form

$$V = \frac{e}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \phi(\vec{l}) \qquad 2.3.2$$

where

$$\phi(\vec{l}) = \frac{1}{e} \sum_{k}^{b} \frac{q'^k}{|\vec{x}(\vec{l}) - \vec{x}^k|} \qquad 2.3.3$$

is proportional to the electrostatic potential at the origin due to the electrically neutral charge group associated with the lattice site $\vec{l}$.

The difference between Evjen's method and other ordering methods (such as Madelung's) is his choice of unit cells (i.e. of c.b.u.'s). Normally one chooses the unit cell to have charges which are integral multiples of the ionic charge q^k. Evjen chose to consider unit cells which contained ionic charges q'^k which may be fractions of q^k.

He did this by assuming the charge of each ion in the unit cell should be multiplied by a weighting factor which depends on the position

of the ion in the unit cell. Thus the charges of the unit cell can be written

$$q'^k = e s^k w^k \qquad 2.3.4$$

where w^k is the weighting factor (for a cubic lattice w^k is just the inverse of the number of unit cells which are adjacent to the ion site - 1/8 for a corner, ¼ for an edge, ½ for a side, and 1 for inside the unit cell), s^k is the dimensionless parameter introduced by eq (1.3.2).

Introducing the dimensionless parameter e^k defined by

$$e^k = s^k w^k \qquad 2.3.5$$

$\phi(\vec{l})$ may be written as

$$\phi(\vec{l}) = \sum_k^b \frac{e^k}{|\vec{x}(\vec{l}) + \vec{x}^k|} \qquad 2.3.6$$

Evjen then divided the sum over $\vec{l}$ in (2.3.2) into two parts - a sum over all points within a sphere of radius R ($\vec{l} \in V_R$) and a sum over the rest ($\vec{l} \notin V_R$).

$$V = \frac{e}{4\pi\epsilon_o}\left[\sum_{\vec{l}\in V_R} \phi(\vec{l}) + \lim_{V\to\infty} \sum_{\substack{\vec{l}\in V \\ \vec{l}\notin V_R}} \phi(\vec{l}) \right] \qquad 2.3.7$$

where V_R is the volume of the sphere of radius R. He then set the second sum equal to Q and assumed that it may be approximated by an integral as follows:

$$Q = \lim_{V\to} \sum_{\substack{\vec{l}\in V \\ \vec{l}\notin V_R}} \phi(\vec{l})$$

$$= \lim_{V\to\infty} \sigma \iiint_{V'} d\vec{x}\phi(\vec{x}) \qquad 2.3.8$$

where V' is the region V from which the region V_R has been omitted and σ is the number of unit cells per unit volume. He gives no discussion

of the fact that the volume is made up of a sum of cubes and hence the spherical surface is not smooth. Also he does not discuss the properties of Q such as its infinite value when $\phi(\vec{x}) = 1/|\vec{x}|$ or its undefined, though finite, nature when $\phi(\vec{x}) = e^{i\vec{k}.\vec{x}}/|\vec{x}|$ ($\vec{k}$ a vector in reciprocal space (see eq (1.2.3)). The quantity Q is not referred to explicitly in the rest of the paper. He seems to assume that it is vanishingly small for large R.

Evjen then proceeded to expand $1/|\vec{x}(\vec{l})+\vec{x}^k|$ in a series of Legendre polynomials $P_n(\cos(\theta))$, as follows

$$\frac{1}{|\vec{x}(\vec{l}) + \vec{x}^k|} = \sum_{n=0}^{\infty} (x^k)^n P_n(\cos\theta^k)/x^{n+1} \qquad 2.3.10$$

where

$$x^k = |\vec{x}^k| , \quad x = |\vec{x}(\vec{l})| \qquad 2.3.11$$

$$\cos\theta^k = \left[x_1(\vec{l})x_1^k + x_2(\vec{l})x_2^k + x_2(\vec{l})x_2^k\right]/xx^k$$
$$= (a + b + c)/x^k \qquad 2.3.12$$

where

$$a = x_1(\vec{l})x_1^k/x, \; b = x_2(\vec{l})x_2^k/x, \text{ and } c = x_3(\vec{l})x_3^k/x \qquad 2.3.13$$

Substituting (2.3.10) into (2.3.3), $\phi(\vec{l})$ becomes

$$\phi(\vec{l}) = \sum_{n=0}^{\infty} A_n/x^{n+1} \qquad 2.3.14$$

where

$$A_n = \sum_{k}^{b} e^k (x^k)^n P_n(\cos\theta^k) \qquad 2.3.15$$

This expansion is not valid for the unit cell at $\vec{x}(\vec{l}) = 0$ and hence $\phi(\vec{0})$ has to be considered seperately.

The polynomial expansion for $P_n(y)$ is

$$P_n(y) = \sum_{t=0}^{n} L_t^n y^t \qquad 2.3.16$$

where L_t^n is the t-th coefficient of the Legendre polynomial of degree n (which vanishes when t is odd). Consequently

$$A_n = \sum_{k}^{b} e^k L_t^n (x^k)^t (a+b+c)^t \qquad 2.3.17$$

Therefore A_n will depend linearly on terms of the type $a^{\beta_1} b^{\beta_2} c^{\beta_3}$ where $\beta_1, \beta_2, \beta_3$ are a set of integers with the property that

$\beta_1 + \beta_2 + \beta_3 = n - t$ with t=0, or t=2, or t=4, etc.

At this point Evjen makes the following statement:

'It follows that, if we form the integral over the surface of a sphere

$$B_n = \iint_0^{4\pi} d\Omega\, A_n \qquad 2.3.18$$

then $B_{2n+1} = 0$. It is therefore sufficient to consider terms where n, $\beta_1, \beta_2, \beta_3$ are all even.'

He does not justify this statement and we are unable to give a rigorous proof of its validity.

Manipulating (2.3.17), it can be written in the form

$$A_{2n} = \sum_{t=0}^{n} L_{2t}^{2n} F_t \qquad 2.3.19$$

where

$$F_t = \sum_{\Gamma} \frac{(2(n-t))!\ M(p,q,s,t)}{(2p)!(2q)!(2s)!} [x_1(1)/x]^{2p} [x_2(1)/x]^{2q} [x_3(1)/x]^{2s} \qquad 2.3.20$$

where Γ denotes the summation over the sets of positive integers p, q,

s such that for each value of n and t

$$p + q + s = n - t \qquad 2.3.1$$

and M(p,q,s,t) is a 2n-th order electric moment of the unit cell given by

$$M(p,q,s,t) = \sum_{k}^{b} e^{k} (x^{k})^{2t} (x_1^{k})^{2p} (x_2^{k})^{2q} (x_3^{k})^{2s} \qquad 2.3.22$$

To give examples of how his method worked, Evjen evaluated the Madelung constants (see eq. (4.3.7)) for three cubic crystals - NaCl, CsCl, and cubic ZnS. The unit cells he chose and the weighting factors of each ion are given in figs. 2.3, 2.4, and 2.5. His results are given in Table 4.3.

In the calculation for CsCl, Evjen found that the electrostatic self-potential at a Cs (or Cl) site approached two different limits depending on whether the terminating surface was made up of Cs or Cl ions. Although he did not mention it, implicit in the above result is the use of two different unit cells (see fig 2.4). We will show in Section 4.5 that the two infinite crystals which are constructed using these two unit cells will have different electrostatic potentials and that the average of the two potentials gives the accepted results for CsCl.

To explain his result, Evjen incorrectly assumed that the difference was a result of his theory being valid for a sphere while the calculation used a cube. He obtained the accepted value for the Madelung constant by correctly averaging the two limiting values. Several papers[7,8,9,10] have discussed this inconsistency and used different elementary cells other than a unit cell to obtain the accepted values of the electrostatic potential without the averaging Evjen had to do.

We will also show that the value for the infinite crystal obtained for ZnS using Evjen's method is incorrect (in the sense discussed at the end of Section 1.5). In his paper, Evjen gives the accepted value without giving a clear discussion of how he obtained it. This result has not received much attention in the literature, probably because Evjen did not discuss it explicitly in his paper as he did for the CsCl result.

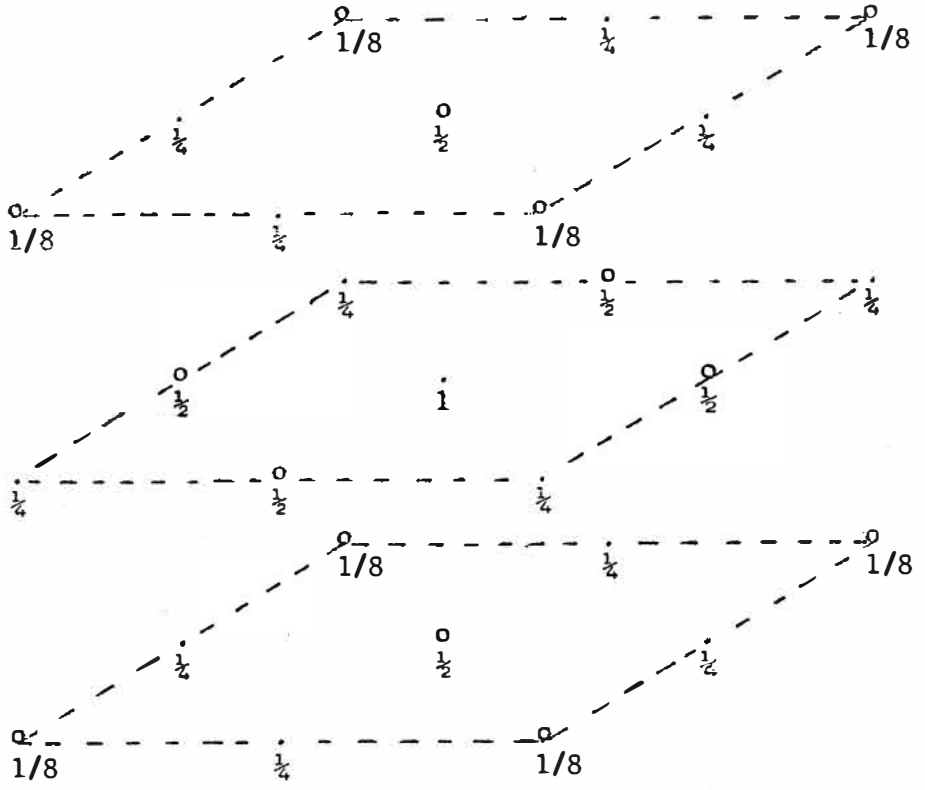
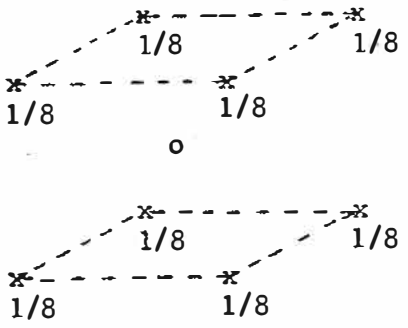


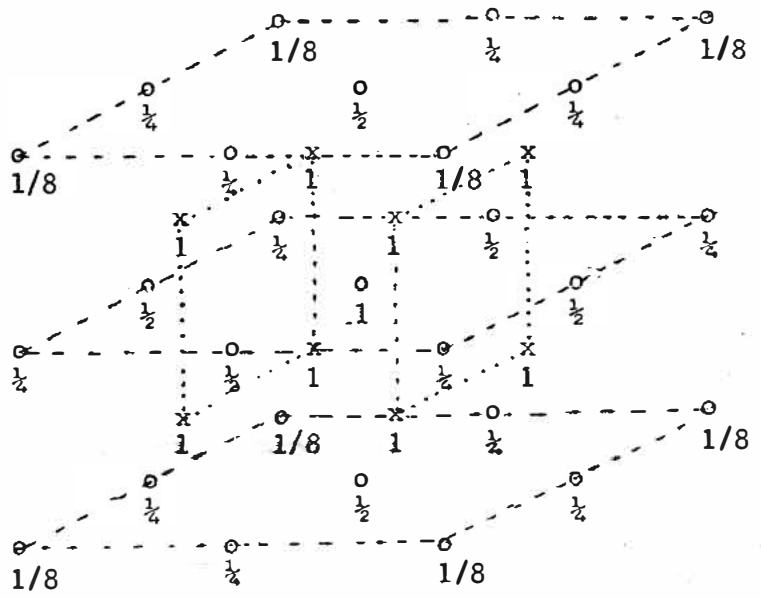
Figure 2.3

Unit Cell for NaCl

The fractions are the weighting factors Evjen assigned to each ion.



(i) A unit cell with the ions at the surface having opposite sign to the ion at the center.



(ii) A cell with the ions at the surface having the same sign as the ion at the center.

o - Cs x - Cl

Figure 2.4

Two Possible Cells for CsCl

The weighting factor Evjen assigned to each ion are given.

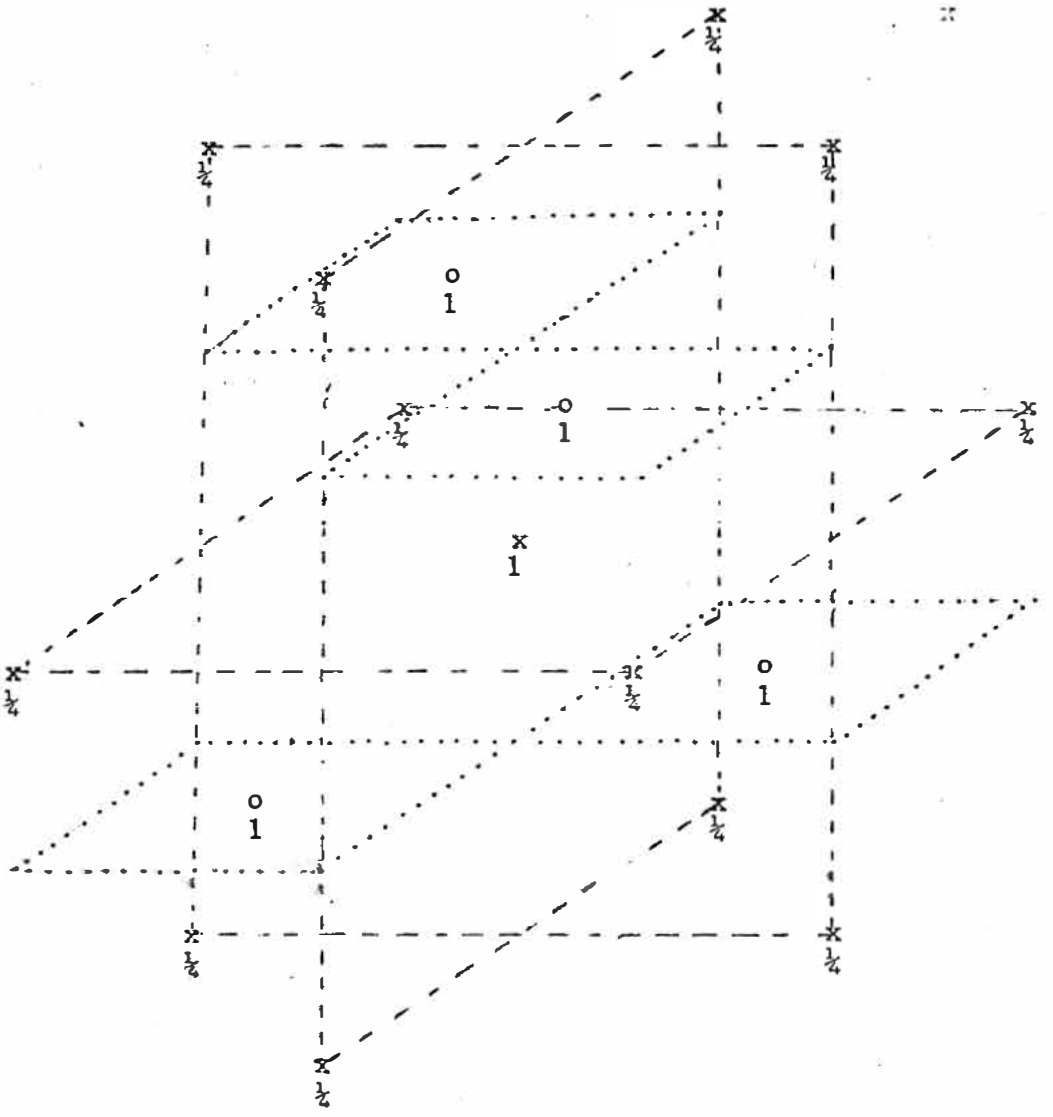


Figure 2.5

Unit Cell for ZnS

The weighting factors Evjen assigned to each ion are given.

D. Ewald's Method

The most widely used method for evaluating Coulomb sums was developed by Ewald in 1921. He was interested in potentials of the form

$$V(\vec{z},\vec{k},K_o) = \frac{1}{4\pi\epsilon_o} \sum_{k}^{b} q^k \lim_{V\to\infty} \sum_{\vec{l}\in V} \frac{e^{i\vec{k}.\vec{x}(\vec{l},k)}\, e^{iK_o|\vec{x}(\vec{l},k)-\vec{z}|}}{|\vec{x}(\vec{l},\vec{k}) - \vec{z}|} \qquad 2.4.1$$

where $\vec{k}$ is a vector in reciprocal space, $K_o = \omega/c$ (ω is an optical frequency and c the velocity of light), and $\vec{z}$ is the position of the point of interest P with respect to the origin of the c.b.u. (which will be chosen to be the unit cell). This type of potential arises in the optical theory of solids. $\vec{z}$ is assumed to be non-zero and the sum over $\vec{l}$ is over all lattice sites in the infinite Bravais lattice.

Instead of considering the sum over $\vec{l}$ given in (2.4.1), which is conditionally convergent when $\vec{k}$ and K_o are non-zero and is infinite when $\vec{k} = 0$ and $K_o = 0$, Ewald decided to consider the well defined quantity

$$V'(\vec{z},\vec{k},K_o) = \lim_{\beta\to 0} \sum_{k}^{b} \frac{q^k}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V} \frac{e^{i\vec{k}.\vec{x}(\vec{l},k)}\, e^{iK'_o|\vec{x}(\vec{l},k)-\vec{z}|}}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 2.4.2$$

where $K'_o = K_o + i\beta$. The limits $\beta\to 0$ and $V\to\infty$ do not commute. This new potential is well defined for all $\vec{k}$ and K_o. Ewald gave the following argument for the introduction of the vanishingly small exponent.

'This exponent may be very small so that no changes from the actual state occur within finite distances from the origin. It is sufficient to cause an absolute convergence of the sum over $\vec{l}$. The

crystal gets blurred, so to speak, at large distances without, however, being suddenly limited. All properties which we call properties of the material, (those which result from a certain limited environment and are therefore repeated in all equivalent points of the crystal independently of the limitation), should be calculated from the crystal "limited but without surface".

For these properties the physically correct value of the sum is that one which occurs in the limit of the vanishing of the exponential.'

The conclusion of this argument is valid.*1 The argument, however, only strongly indicates that the introduction of the vanishing exponential is valid; it is not an absolute proof. This proof will be given in Chapter 4.6.

To simplify the discussion, we will give a description of Ewald's method for $K_o = 0$. We will closely follow the description of Ewald's method given in B&H since this reference is readily available to most people. We will include the exponential term which B&H ignored.

If we define a quantity $\phi(\vec{z},\vec{k},\beta)$ by

$$\phi(\vec{z},\vec{k},\beta) = \lim_{V\to\infty} \sum_{\vec{l}\in V} \frac{e^{i\vec{k}.\vec{x}(\vec{l})}\, e^{-\beta|\vec{x}(\vec{l})-\vec{z}|}}{|\vec{x}(\vec{l}) - \vec{z}|}, \qquad 2.4.3$$

then it is easily seen that the quantity V' may be written as

$$V'(\vec{z},\vec{k},0) = \lim_{\beta\to 0} \sum_{k}^{b} \frac{q^k}{4\pi\epsilon_o} \phi(\vec{z}-\vec{x}^k,\vec{k},\beta) e^{i\vec{k}.\vec{x}^k} \qquad 2.4.4$$

where we have used the relation

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k \qquad \text{(see eq (1.3.5))} \qquad 2.4.5$$

---

*1 See discussion at the end of Section 1.5 for the meaning we give valid.

In order to manipulate (2.4.3) into a more rapidly converging expression, Ewald introduced the identity

$$\frac{e^{-\beta r}}{r} = \frac{2}{\sqrt{\pi}} \int_0^\infty d\rho\, e^{-\rho^2 r^2 - \beta^2/4\rho^2} \qquad 2.4.6$$

Substituting (2.4.6) into (2.4.3), we find

$$\begin{aligned}\phi(\vec{z},\vec{k},\beta) &= \sum_{\vec{l}}^{\infty} e^{i\vec{k}\cdot\vec{x}(\vec{l})} \frac{2}{\sqrt{\pi}} \int_0^\infty d\rho\, e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2 - \beta^2/4\rho^2} \\ &= \int_0^\infty d\rho \frac{2}{\sqrt{\pi}} \sum_{\vec{l}}^{\infty} e^{i\vec{k}\cdot\vec{x}(\vec{l})} e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2 - \beta^2/4\rho^2} \\ &= \int_0^\infty d\rho\, e^{i\vec{k}\cdot\vec{z}} \left[\frac{2}{\sqrt{\pi}} e^{-\beta^2/4\rho^2} \sum_{\vec{l}}^{\infty} e^{i\vec{k}\cdot(\vec{x}(\vec{l})-\vec{z})} e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2}\right] \end{aligned} \qquad 2.4.7$$

where we have denoted $\lim_{V\to\infty} \sum_{\vec{l}\in V}$ by $\sum_{\vec{l}}^{\infty}$ for convenience in writing.

The term enclosed by the brackets in eq (2.4.7) is a periodic function of $\vec{z}$ with the period of the lattice. Thus we may represent this term by a fourier series. i.e.

$$\frac{2}{\sqrt{\pi}} e^{-\beta^2/4\rho^2} \sum_{\vec{l}}^{\infty} e^{i\vec{k}\cdot(\vec{x}(\vec{l})-\vec{z})} e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2} = \sum_{\vec{h}} g(\vec{h}) e^{i\vec{y}(\vec{h})\cdot\vec{z}} \qquad 2.4.8$$

where

$$g(\vec{h}) = \frac{2\pi}{v_a} \frac{1}{\rho^3} e^{-[\beta^2+|\vec{y}(\vec{h})+\vec{k}|^2]/4\rho^2} \qquad 2.4.9$$

and $\vec{y}(\vec{h})$ are reciprocal lattice vectors with indices $\vec{h}$ (see eq (1.2.4)). $\vec{h}$ is the triplet of integers (h_1,h_2,h_3) which is summed over all the reciprocal lattice sites. v_a is the volume of the unit cell in real space. Equation (2.4.8) represents the well known theta function transformation.

It is evident from the series involved in eq (2.4.8) that the

series on the L.H.S. of the equation is rapidly convergent for large values of ρ and the series on the R.H.S. of the equation is rapidly convergent for small values of ρ. Thus it is convenient to split the integral in (2.4.7) into two parts as follows:

$$\phi(\vec{z},\vec{k},\beta) = \frac{2}{\sqrt{\pi}} \sum_{\vec{l}}^{\infty} \int_{R}^{\infty} d\rho \; e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2-\beta^2/4\rho^2} \; e^{i\vec{k}.\vec{x}(\vec{l})}$$

$$+ \frac{2\pi}{v_a} \sum_{\vec{h}} \int_{0}^{R} \frac{d\rho}{\rho^3} \; e^{-[\beta^2+|\vec{y}(\vec{h})+\vec{k}|^2]/4\rho^2} \; e^{i\vec{y}(\vec{h}).\vec{z}} \qquad 2.4.10$$

where R is chosen such that fast convergence of both terms is obtained.

If we want to find the potential at $\vec{z} = 0$, we must subtract the term associated with $\vec{x}(\vec{l}) = 0$ which has been included in the sum over $\vec{l}$ in eq (2.4.3). Thus

$$\phi(0,\vec{k},\beta) = \lim_{\vec{z}\to 0}\left[\frac{2}{\sqrt{\pi}} \sum_{\vec{l}}{}' \int_{R}^{\infty} d\rho \, e^{-\rho^2|\vec{x}(\vec{l})-\vec{z}|^2-\beta^2/4\rho^2} \; e^{i\vec{k}.\vec{x}(\vec{l})}\right.$$

$$\left. + \frac{2\pi}{v_a} \sum_{\vec{h}} \int_{0}^{R} \frac{d\rho}{\rho^3} \, e^{-[\beta^2+|\vec{y}(\vec{h})+\vec{k}|^2]/4\rho^2} \; e^{i\vec{y}(\vec{h}).\vec{z}}\right]$$

$$+ \lim_{\vec{z}\to 0}\left[\frac{2}{\sqrt{\pi}} \int_{R}^{\infty} d\rho \, e^{-\rho^2 z^2-\beta^2/4\rho^2} - \frac{e^{-\beta z}}{z}\right] \qquad 2.4.11$$

where the $'$ on the sum over $\vec{l}$ denotes the exclusion of the term associated with $\vec{l} = 0$ from the sum and

$$z \approx |\vec{z}|. \qquad 2.4.12$$

The $\lim_{\vec{z}\to 0}$ may be taken in the first term in square brackets since it is an analytic function of $\vec{z}$. In the second term both parts diverge and hence have to be considered carefully.

Adding and subtracting the integral over ρ from 0 to R, the last

term may be written as

$$\lim_{z\to 0}\left[\frac{2}{\sqrt{\pi}}\int_R^\infty d\rho\, e^{-\rho^2z^2-\beta^2/4\rho^2} - \frac{e^{-\beta z}}{z}\right] = \lim_{z\to 0}\left[\frac{2}{\sqrt{\pi}}\int_0^\infty d\rho\, e^{-\rho^2z^2-\beta^2/4\rho^2} - \frac{e^{-\beta z}}{z}\right]$$

$$- \lim_{z\to 0}\left[\frac{2}{\sqrt{\pi}}\int_0^R d\rho\, e^{-\rho^2z^2-\beta^2/4\rho^2}\right] \qquad 2.4.13$$

The first term in (2.4.13) vanishes identically and the second term is an analytic function of z and the limit may be interchanged with the integration to give

$$\lim_{z\to 0}\left[\frac{2}{\sqrt{\pi}}\int_R^\infty d\rho\, e^{-\rho^2z^2-\beta^2/4\rho^2} - \frac{e^{-\beta z}}{z}\right] = -\frac{2}{\sqrt{\pi}}\int_0^R d\rho\, e^{-\beta^2/4\rho^2}$$

$$= -\frac{2R}{\sqrt{\pi}}e^{-\beta^2/4R^2} - \beta + O(\beta^3) \qquad 2.4.14$$

Therefore (2.4.11) reduces to

$$\phi(0,\vec{k},\beta) = \frac{2}{\sqrt{\pi}}\sum_{\vec{l}}{}' \int_R^\infty d\rho\, e^{-\rho^2|\vec{x}(\vec{l})|^2-\beta^2/4\rho^2} e^{i\vec{k}.\vec{x}(\vec{l})} \qquad 2.4.15$$

$$+ \frac{2\pi}{v_a}\sum_{\vec{h}}\int_0^R \frac{d\rho}{\rho^3} e^{-\left[\beta^2+|\vec{y}(\vec{h})+\vec{k}|^2\right]/4\rho^2} - \frac{2R}{\sqrt{\pi}}e^{-\rho^2/4R^2} - \beta$$

Substituting eqs (2.4.10) and (2.4.15) into (2.4.4), we find that the self-potential at a vacant Bravais lattice site of the k-th ion is given by

$$V'^k(0,\vec{k},0) = \lim_{\beta\to 0}\sum_{k'}^{b}\frac{q^{k'}}{4\pi\epsilon_o}\left[\frac{2}{\sqrt{\pi}}\sum_{\vec{l}}{}'\int_R^\infty d\, e^{-\rho^2|\vec{x}(\vec{l})+\vec{x}^{k'}|^2-\beta^2/4\rho^2} e^{i\vec{k}.\vec{x}(\vec{l})}\right.$$

$$\left. + \frac{2\pi}{v_a}\sum_{\vec{h}}\int_0^R \frac{d\rho}{\rho^3} e^{-\{\beta^2+|\vec{y}(\vec{h})+\vec{k}|^2\}/4\rho^2} e^{-i\vec{y}(\vec{h}).\vec{x}^{k'}}\right] e^{ik.x^{k'}}$$

$$- \frac{q^k}{4\pi\epsilon_o}\frac{2R}{\sqrt{\pi}}e^{-\beta^2/4R^2} - \beta \qquad 2.4.16$$

The prime on the sum over $\vec{l}$ denotes the exclusion of the $\vec{l} = 0$ term from the sum when $k' = k$. The other authors discussed in this chapter all consider the simpler case of $\vec{k} = 0$. Therefore to have a formula for the same quantity the other authors evaluated, we will set $\vec{k} = 0$ in eq (2.4.16). Thus

$$V'^{k} = \lim_{\beta \to 0} \sum_{k'}^{b} \frac{q^{k'}}{4\pi\epsilon_o} \left\{ \frac{2}{\sqrt{\pi}} \sum_{\vec{l}}{}' \int_{R}^{\infty} d\rho\, e^{-\rho^2 |\vec{x}(\vec{l}) + \vec{x}^{k'}|^2 - \beta^2/4\rho^2} + \frac{2\pi}{v_a} \sum_{\vec{h}}{}' \int_{0}^{R} \frac{d\rho}{\rho^3} e^{-\{\beta^2 + |\vec{y}(\vec{h})|^2\}/4\rho^2} e^{-i\vec{y}(\vec{h}) \cdot \vec{x}^{k'}} \right\}$$

$$- \frac{q^k}{4\pi\epsilon_o} \frac{2R}{\sqrt{\pi}} e^{-\beta^2/4R^2} - \beta \qquad 2.4.17$$

The term with $\vec{h} = 0$ in (2.4.17) vanishes due to charge neutrality. We will indicate the exclusion of the term associated with $\vec{h} = 0$ by the use of the ' on the sum over $\vec{h}$. The limit $\beta \to 0$ may now be taken to obtain

$$V'^{k} = \frac{1}{4\pi\epsilon_o} \sum_{k'}^{b} q^{k'} \left\{ \frac{2}{\sqrt{\pi}} \sum_{\vec{l}}{}' \int_{R}^{\infty} d\rho\, e^{-\rho^2 |\vec{x}(\vec{l}) + \vec{x}^{k'}|^2} + \frac{2\pi}{v_a} \sum_{\vec{h}}{}' \int_{0}^{R} \frac{d\rho}{\rho^3} e^{-|\vec{y}(\vec{h})|^2/4\rho^2} e^{-i\vec{y}(\vec{h}) \cdot \vec{x}^{k'}} \right\} - \frac{q^k}{4\pi\epsilon_o} \frac{2R}{\sqrt{\pi}} \qquad 2.4.18$$

E. Born's Method

Using the vanishing exponential, we may write the Coulomb potential at a k' = 0 ion site as, eq (1.3.12),

$$V'^0 = \frac{e}{4\pi\epsilon_o} \lim_{\beta \to 0} \lim_{V \to \infty} \sum_{\vec{l} \in V}{}' \sum_k^b \frac{s^k e^{-\beta |\vec{x}(\vec{l},k)|}}{|\vec{x}(\vec{l},k)|} \qquad 2.5.1$$

where we have set $\vec{x}^{k'} = 0$. For the manipulations performed in Born's method, the exponential and $\lim_{V \to \infty}$ do not enter explicitly. Thus to simplify writing, we will use the simpler expression

$$V'^0 = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}}^{\infty}{}' \sum_k^b \frac{s^k}{|\vec{x}(\vec{l},k)|}$$

$$= \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}}^{\infty}{}' \sum_k^b \frac{s^k}{|\vec{x}(\vec{l}) + \vec{x}^k|} \qquad 2.5.2$$

where we have substituted for $\vec{x}(\vec{l},k)$ using (1.3.5) and s^k is a dimensionless parameter given by

$$s^k = q^k/e \qquad \text{(see eq (1.3.2))} \qquad 2.5.3$$

The absolute value of each of the components x_i^k (i=1,2,3) is less than the corresponding lattice parameter a_i (see eq (1.3.3)). Suppose that the crystal structure is such that

$$nx_i^k = m_i^k a_i \qquad i = 1,2,3 \qquad 2.5.4$$

for all k, where n and m_i^k are both integers and n is positive, then

$$\vec{x}^k = (m_1^k a_1 \hat{e}_1 + m_2^k a_2 \hat{e}_2 + m_3^k a_3 \hat{e}_3)/n$$

$$= \vec{x}(\vec{m}^k)/n \qquad 2.5.5$$

where $\vec{x}(\vec{m}^k)$ is a lattice vector with indices $\vec{m}^k$.

The self-potential of a k = 0 ion may now be written as

$$V'^0 = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}}{}' \sum_k^b \frac{s^k}{|\vec{x}(\vec{l}) + \vec{x}(\vec{m}^k)/n|}$$

$$= \frac{ne}{4\pi\epsilon_o} \sum_{\vec{l}}{}' \sum_k^b \frac{s^k}{|n\vec{x}(\vec{l}) + \vec{x}(\vec{m}^k)|} \qquad 2.5.6$$

Introducing the generalized Kronecker delta defined by

$$\delta_{\vec{l}',\vec{l}} = 0 \quad \text{if } \vec{l}' \neq \vec{l}$$
$$= 1 \quad \text{if } \vec{l}' = \vec{l} \qquad 2.5.7$$

the potential (2.5.6) becomes

$$V'^0 = \frac{ne}{4\pi\epsilon_o} \sum_{\vec{l}}{}' \sum_k^b \sum_{\vec{l}'}{}' \frac{s^k}{|\vec{x}(\vec{l}')|} \delta_{\vec{l}',n\vec{l}+\vec{m}^k} \qquad 2.5.8$$

where $\vec{l}'$ is to be summed over all lattice sites except $\vec{l}' = 0$ (which is indicated by the ' on the sum over $\vec{l}'$). We have used the property of lattice vectors that

$$n\vec{x}(\vec{l}) + \vec{x}(\vec{m}^k) = \vec{x}(n\vec{l}) + \vec{x}(\vec{m}^k)$$
$$= \vec{x}(n\vec{l}+\vec{m}^k) \qquad 2.5.9$$

However

$$\sum_{\vec{l}}^{\infty} \delta_{\vec{l}',n\vec{l}+\vec{m}^k} = \frac{1}{n^3} \sum_{\vec{h}=0}^{n-1} e^{i[\vec{x}(\vec{l}')-\vec{x}(\vec{m}^k)]\cdot\vec{y}(\vec{h})/n} \qquad 2.5.10$$

where $\vec{y}(\vec{h})$ is a reciprocal lattice vector (see eq (1.2.4)) and $\vec{h}$ is the triplet of integers (h_1, h_1, h_1).

The term associated with $n\vec{l}+\vec{m}^k = 0$ is omitted from the sum over $\vec{l}$ in eq (2.5.8). We may add this term to the sum over $\vec{l}$ since it contributes

$$\delta_{\vec{l}',0} = 0 \qquad 2.5.11$$

to eq (2.5.8). Interchanging the summations over $\vec{l}'$ and k with the sum over $\vec{l}$, V'^0 becomes

$$V'^0 = \frac{ne}{4\pi\epsilon_0} \sum_k^b \sum_{\vec{l}'}' \frac{s^k}{|\vec{x}(\vec{l}')|} \sum_{\vec{l}} \delta_{\vec{l}', n\vec{l}+\vec{m}^k}$$

$$= \frac{ne}{4\pi\epsilon_0 n^2} \sum_k^b \sum_{\vec{l}'}' \frac{s^k}{|\vec{x}(\vec{l}')|} \sum_{\vec{h}=0}^{n-1} e^{i\{\vec{x}(\vec{l}')-\vec{x}(\vec{m}^k)\}.\vec{y}(\vec{h})/n} \qquad 2.5.12^{*1}$$

where we have substituted for the sum over $\vec{l}$ using eq (2.5.10). Performing a further interchange of the orders of summation, (2.5.12) may be rewritten as

$$V'^0 = \frac{e}{4\pi\epsilon_0 n^2} \sum_{\vec{h}=0}^{n-1} \sum_{\vec{l}'}' \frac{e^{i\vec{x}(\vec{l}').\vec{y}(\vec{h})/n}}{|\vec{x}(\vec{l}')|} \sum_k^b s^k e^{i\vec{x}(\vec{m}^k).\vec{y}(\vec{h})/n} \qquad 2.5.13$$

Therefore the potential may be written in the form

$$V'^0 = \frac{e}{4\pi\epsilon_0 n^2} \sum_{\vec{h}=0}^{n=1} II(\vec{y}(\vec{h})/n) S_n(\vec{h}) \qquad 2.5.14$$

where

$$S_n(\vec{h}) = \sum_k^b s^k e^{i\vec{x}(\vec{m}^k).\vec{y}(\vec{h})/n} \qquad 2.5.15$$

is a structure factor and

$$II(y(h)/n) = \lim_{\beta \to 0} \lim_{V \to \infty} \sum_{\vec{l}' \in V}' \frac{e^{i\vec{x}(\vec{l}').\vec{y}(\vec{h})/n} e^{-\beta|\vec{x}(\vec{l}')|}}{|\vec{x}(\vec{l}')|} \qquad 2.5.16$$

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*1 All interchanges are valid since we are actually considering the well-defined expression (2.5.1). All interchanges are made before the $\lim \beta \to 0$ is taken.

where we have reintroduced the limits since they are relevant to the following discussion.

Born called II the 'Grundpotential'. This is the self-potential that would result at a vacant lattice site at the origin if all the other Bravais lattice sites were occupied by point charges of charge

$$e^{i\vec{x}(\vec{l}').\vec{y}(\vec{h})/n} \; e^{-\beta|\vec{x}(\vec{l}')|}.$$

Born's procedure would not be strictly valid if the vanishing exponential was not present because the $II(\vec{k})$ would not be well defined functions due to the conditional convergence of the sum over $\vec{l}'$ in eq (2.5.16). However, the sum over $\vec{l}'$ in eq (2.5.7) is the same quantity which Ewald evaluated using the theta function transformation. Thus Born was able to use Ewald's results to write the Grundpotential as the sum of two terms II_1 and II_2. i.e.

$$II(\vec{k}_n) = II_1 + II_2 \qquad 2.5.17$$

where

$$II_1(\vec{k}_n) = \frac{4\pi}{v_a} \sum_{\vec{h}}{}' \frac{e^{-|\vec{k}_n+\vec{y}(\vec{h}')|^2/4R^2}}{|\vec{k}_n+\vec{y}(\vec{h}')|^2} - \frac{2R}{\sqrt{\pi}} \qquad 2.5.18$$

and

$$II_2(\vec{k}_n) = \sum_{\vec{l}'}{}' \frac{[1-\Omega(R|\vec{x}(\vec{l}')|)]}{|\vec{x}(\vec{l}')|} e^{ix(l').k_n} \qquad 2.5.19$$

where we have set

$$\vec{k}_n = \vec{y}(\vec{h})/n \qquad 2.5.20$$

and

$$\Omega(x) = \frac{2}{\sqrt{\pi}} \int_0^x dx\, e^{-x^2} \qquad 2.5.21$$

is the error function. These formulae may be derived from (2.4.15) by

setting $\beta = 0$ and manipulating the resulting expressions.

Using these formulae Emerslebem[13] has calculated a table of Grundpotentials for n = 12 for a cubic Bravais lattice. Once the Grundpotentials are known then it is a simple matter to evaluate V'^0 due to the small number of terms (n^3) involved in eq (2.5.14). However the Grundpotentials have not been calculated for general n. Thus this method is limited at the present time to the cubic case where the ions satisfy condition (2.5.4) for n = 12.

As with Madelung's method this method is primarily of historical interest since the numbers of crystals which satisfy (2.5.4) are limited. We note that since Born's method introduces the vanishing exponential, this method will give the same values for the electrostatic potential as Ewald's method.

F. Harris and Monkhorst's Method

Harris and Monkhorst have recently developed a new method for evaluating the electrostatic potential. The basis of their method is the incorrect fourier transform*1

$$\frac{1}{r} = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}}{k^2} e^{-i\vec{k}.\vec{r}} \qquad 2.6.1$$

where

$k = |\vec{k}|$, and $r = |\vec{r}|$

The correct identity that should be used is

$$\frac{e^{-\beta r}}{r} = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{-i\vec{k}.\vec{r}}}{(k^2+\beta^2)} \qquad 2.6.2$$

We may set $\beta = 0$ but only after the integration over $\vec{k}$ has been performed. In order to use the fourier transform (2.6.2) to evaluate the electrostatic potential at a lattice site, the exponential term must be introduced (c.f. method of Ewald). Although H&M do not state this, it is implicit in their calculations. Therefore we will include

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*1 If we take the integral over all space of both sides of (2.6.1) times $e^{i\vec{k}.\vec{r}}$ (the result should be the fourier transform of 1/r), we have

$$\iiint \frac{d\vec{r}}{r} e^{i\vec{k}.\vec{r}} = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}'\, e^{i(\vec{k}-\vec{k}').\vec{r}}}{(\vec{k}')^2}$$

Evaluating both sides of the above equation we find that the R.H.S. equals $1/k^2$, however the L.H.S. is undefined (though finite).

---

the exponential term in our description of their method.

Thus, instead of considering the actual self-potential of a k'= 0 ion

$$V^{\infty}(0)= \frac{e}{4\pi\epsilon_o} \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \sum_{k}^{b} \frac{s^k}{|\vec{x}(\vec{l}) + \vec{x}^k|} \qquad 2.6.3$$

(see eq (1.3.10) with $\vec{x}^{k'}=0$), we consider the quantity

$$V'^0 = \lim_{\beta\to 0} V(\beta) \qquad 2.6.4$$

where

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}}^{\infty}{}' \sum_{k}^{b} \frac{s^k\, e^{-\beta|\vec{x}(\vec{l})+\vec{x}^k|}}{|\vec{x}(\vec{l}) + \vec{x}^k|} \qquad 2.6.5$$

(c.f. eq (2.4.3) with $\vec{k}=0$). The c.b.u. will be chosen to be the unit cell. Substituting (2.6.2) into (2.6.5), it becomes

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \sum_{\vec{l}}{}' \sum_{k}^{b} s^k \frac{1}{2\pi^2} \iiint \frac{d\vec{k}\, e^{-i\vec{k}.[\vec{x}(\vec{l})+\vec{x}^k]}}{(k^2+\beta^2)} \qquad 2.6.6$$

As stated in Section D, the introduction of the exponential term removes any conditional convergence that may have been present. Thus we may interchange the sums and integration in (2.6.6) without altering the value of $V(\beta)$. Hence

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \frac{1}{2\pi^2} \iiint \frac{d\vec{k}}{(k^2+\beta^2)} \sum_{\vec{l}}^{\infty}{}' \sum_{k}^{b} s^k\, e^{-i\vec{k}.[\vec{x}(\vec{l})+\vec{x}^k]} \qquad 2.6.7$$

Adding and subtracting the term associated with $\vec{l} = 0$ which has been excluded from the sum over $\vec{l}$ in eq (2.6.7), the potential becomes

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \frac{1}{2\pi^2} \iiint \frac{d\vec{k}}{(k^2+\beta^2)} \left\{ \sum_{\vec{l}} e^{-i\vec{k}.\vec{x}(\vec{l})} \sum_{k}^{b} s^k\, e^{-i\vec{k}.\vec{x}^k} - s^0 \right\} \qquad 2.6.8$$

where s^0 is the dimensionless parameter associated with the charge of the ions which occupy the Bravais lattice sites $\vec{x}(\vec{l})$ (see eq (1.3.2)).

This procedure is valid but since it involves introducing infinities which cancel, careful track of the terms must be kept.

H&M then introduced the identity (which is valid for cubic systems with lattice parameter a)

$$\sum_{\vec{l}} e^{-i\vec{k}.\vec{x}(\vec{l})} = (2\pi/a)^3 \sum_{\vec{h}} \delta(\vec{k} - \vec{y}(\vec{h})) \qquad 2.6.9$$

where $\delta(\vec{k} - \vec{y}(\vec{h}))$ is the Dirac delta function, $\vec{y}(\vec{h})$ is a reciprocal lattice vector (see eq (1.2.4)), $\vec{h}$ is the triplet of integers (h_1,h_2,h_3), and $\vec{h}$ is summed over all integers.

Substituting (2.6.9) into (2.6.8), we obtain

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \frac{1}{2\pi^2} \iiint \frac{d\vec{k}}{(k^2+\beta^2)} \left[\frac{8\pi^3}{v_a} \sum_{\vec{h}} \delta(\vec{k}-\vec{y}(\vec{h})) \sum_{k}^{b} s^k e^{-i\vec{k}.\vec{x}^k} - s^0 \right] \qquad 2.6.10$$

where $v_a = 1/a^3$ is the volume of the unit cell.

Hence

$$V(\beta) = \frac{e}{4\pi\epsilon_o} \frac{1}{2\pi^2} \left\{ \frac{8\pi^3}{v_a} \sum_{k}^{b} s^k \sum_{\vec{h}} \frac{e^{-iy(h).x^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} - s^0 \iiint \frac{d\vec{k}}{(k^2+\beta^2)} \right\} \qquad 2.6.11$$

The term associated with $\vec{h} = 0$ may be excluded from the sum since it vanishes by charge neutrality. Therefore, taking the limit $\beta \to 0$ in eq (2.6.11) (using the prime on the sum over $\vec{h}$ to indicate the exclusion of $\vec{h}=0$), V'^0 becomes

$$V'^0 = \lim_{\beta \to 0} V(\beta) \qquad \text{see eq (2.6.4)}$$

$$= \frac{e}{4\pi\epsilon_o} \left\{ s^0 \lim_{\beta \to 0} \left[\frac{4\pi}{v_a} \sum_{\vec{h}}' \frac{1}{\{\vec{y}(\vec{h})^2+\beta^2\}} - \frac{1}{2\pi^2} \iiint \frac{d\vec{k}}{(k^2+\beta^2)} \right] + \right.$$

cont.

$$+\sum_{k}^{b}{}' \frac{4\pi s^k}{v_a} \sum_{h}{}' \frac{e^{-i\vec{y}(\vec{h})\cdot\vec{x}^k}}{|\vec{y}(\vec{h})|^2} \Bigg\} \qquad 2.6.13$$

where the prime on the sum over k indicates the exclusion of k = 0.

Each of the terms multiplying s^0 diverge. This is a result of the cancelling infinities that were introduced in eq (2.6.8). The correct method of evaluating this term is to let the regions of summation and integration be the same, then take the limit as the region goes to infinity.

H&M have successfully applied (2.6.13) to a variety of problems [11,12].

G. Tosi's Method

Tosi considered the problem of finding the potential associated with a neutralized cubic Bravais lattice, i.e. a cubic Bravais lattice whose lattice sites are occupied by point charges of charge q with a uniform background charge of opposite sign. The charge density for a neutralized Bravais lattice is

$$\rho(\vec{r}) = q\left\{\sum_{\vec{l}} \delta(\vec{r}-\vec{x}(\vec{l})) - v_a^{-1}\right\} \qquad 2.7.1$$

where $v_a = a^3$ is the volume of a unit cell and $\vec{l}$ is to be summed over all the Bravais lattice sites.

The potential arising from the above charge density is

$$V'(\vec{z},0) = \frac{1}{4\pi\epsilon_o}\left\{\iiint_{\text{all space}} \frac{d\vec{r}'\,\rho(r')}{|\vec{r}' - \vec{z}|} + \text{constant}\right\}$$

$$= \frac{q}{4\pi\epsilon_o}\left\{\lim_{V\to\infty}\left[\sum_{\vec{l}\in V} \frac{1}{|\vec{x}(\vec{l})-\vec{z}|} - \frac{1}{v_a}\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|}\right] + \text{constant}\right\} \qquad 2.7.2$$

The limiting procedure has to be used because each of the terms diverge if taken separately. The constant is evaluated by imposing the boundary condition that the average value of $V'(\vec{z},0)$ over a unit cell must vanish. i.e.

$$\iiint_{v_a} d\vec{y}\,V'(\vec{y},0) = 0 \qquad 2.7.3$$

The previously discussed authors have all used the boundary condition that the electrostatic potential of each ion vanishes at points infinitely far from the ion.

The final expression for the electrostatic potential of a neutralized cubic Bravais lattice is

$$V'(\vec{z},0) = \frac{q}{4\pi\epsilon_o}\left\{\lim_{V\to\infty}\left[\sum_{\vec{l}\in V}\frac{1}{|\vec{x}(\vec{l})-\vec{z}|} - \frac{1}{v_a}\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|}\right] + \frac{\pi}{6a}\right\} \qquad 2.7.4$$

Tosi did not express $V'(\vec{z},0)$ in the above form since it is not convenient for calculations. We have given the expression for comparison with our result.

Instead of considering the form of the charge density given in (2.7.1), Tosi wrote $\rho(r)$ as follows

$$\rho(\vec{r}) = \rho_1(\vec{r}) + \rho_2(\vec{r}) \qquad 2.7.5$$

where

$$\rho_1(\vec{r}) = \frac{q}{\eta^3\pi^{3/2}}\sum_{\vec{l}} e^{-|\vec{r}-\vec{x}(\vec{l})|^2/\eta^2} - qv_a^{-1} \qquad 2.7.6$$

and

$$\rho_2(\vec{r}) = q\left\{\sum_{\vec{l}}\delta(\vec{r}-\vec{x}(\vec{l})) - \frac{1}{\eta^3\pi^{3/2}}e^{-|\vec{r}-\vec{x}(\vec{l})|^2/\eta^2}\right\} \qquad 2.7.7$$

Clearly $\rho(\vec{r})$ is independent of η - the gaussian half-width.

Both $\rho_1(\vec{r})$ and $\rho_2(\vec{r})$ are periodic functions of $\vec{r}$ with the period of the lattice. However it is convenient to expand only $\rho_1(\vec{r})$ as a fourier series. i.e.

$$\rho_1(\vec{r}) = \frac{q}{v_a}\left\{\sum_{\vec{h}} e^{-\eta^2|\vec{y}(\vec{h})|^2/4}\, e^{i\vec{y}(\vec{h})\cdot\vec{r}} - qv_a^{-1}\right\}$$

$$= \frac{q}{v_a}\sum_{\vec{h}}{}' e^{-\eta^2|\vec{y}(\vec{h})|^2/4}\, e^{i\vec{y}(\vec{h})\cdot\vec{r}} \qquad 2.7.8$$

where the ' indicates that the term associated with $\vec{h} = 0$ (which has be cancelled by the $-qv_a^{-1}$ term) is to be omitted from the sum. Using this charge density in Poisson's equation

$$\nabla^2 V_1'(\vec{z},0) = -\rho_1(\vec{z})/\epsilon_o \qquad 2.7.9$$

we obtain the solution

$$V_1'(\vec{z},0) = \frac{q}{4\pi\epsilon_o}\frac{4\pi}{v_a}\sum_{\vec{h}}{}' \frac{e^{-\eta^2|\vec{y}(\vec{h})|^2/4}}{|\vec{y}(\vec{h})|^2} e^{i\vec{y}(\vec{h})\cdot\vec{z}} \qquad 2.7.10$$

where we have used the boundary condition (2.7.3).

The potential associated with $\rho_2(r)$ is found by first using Gauss' theorem to obtain the electric field associated with the charge distribution, then integrating the electric field by parts to obtain the electrostatic potential. Thus

$$V_2'(\vec{z},0) = \frac{q}{4\pi\epsilon_o}\left\{\sum_{\vec{l}} \frac{\{1 - \Omega(|\vec{x}(\vec{l})-\vec{z}|/\eta)\}}{|\vec{x}(\vec{l}) - \vec{z}|} - \frac{\pi\eta^2}{v_a}\right\} \qquad 2.7.11$$

where the boundary condition (2.7.3) has again been imposed. $\Omega(x)$ is the error function given by

$$\Omega(x) = \frac{2}{\sqrt{\pi}}\int_0^x dt\, e^{-t^2} \qquad 2.7.12$$

Adding (2.7.10) and (2.7.11), we find that the total potential of the neutralized Bravais lattice is

$$V'(\vec{z},0) = \frac{q}{4\pi\epsilon_o}\left\{\frac{4\pi}{v_a}\sum_{\vec{h}}{}' \frac{e^{-\eta^2|\vec{y}(\vec{h})|^2/4}}{|\vec{y}(\vec{h})|^2} e^{i\vec{y}(\vec{h})\cdot\vec{z}} + \right.$$

$$\left. \sum_{\vec{l}} \frac{\{1 - \Omega(|\vec{x}(\vec{l})-\vec{z}|/\eta)\}}{|\vec{x}(\vec{l}) - \vec{z}|} - \frac{\pi\eta^2}{v_a}\right\} \qquad 2.7.13$$

The self-potential at a vacant lattice site is

$$V'^{0}(0,0) = \frac{q}{4\pi\epsilon_o}\left\{ \frac{4\pi}{v_a} \sum_{\vec{h}}{}' \frac{e^{-\eta^2 |\vec{y}(\vec{h})|^2/4}}{|\vec{y}(\vec{h})|^2} + \sum_{\vec{l}}{}' \frac{\{1 - \Omega(|x(1)|/\eta)\}}{|\vec{x}(\vec{l})|} \right.$$

$$\left. - \frac{\pi\eta^2}{v_a} - \frac{2\eta}{\sqrt{\pi}} \right\} \qquad 2.7.14$$

The ' on the sum over $\vec{l}$ indicates the exclusion of the term associated with $\vec{l} = 0$ and the $2\eta/\sqrt{\pi}$ term is the potential at the center of a Gaussian charge distribution due to the charge distribution.

The the electrostatic potential $V'(\vec{z})$ due to the infinite crystal and the self-potential V'^{k} of a k-type ion in the infinite crystal are 2.7.15

$$V'(\vec{z}) = \frac{e}{4\pi\epsilon_o}\left\{ \frac{4\pi}{v_a} \sum_{\vec{h}}{}' \frac{S(\vec{h})\, e^{-\eta^2 |\vec{y}(\vec{h})|^2/4}}{|\vec{y}(\vec{h})|^2} e^{i\vec{y}(\vec{h})\cdot\vec{z}} + \sum_{\vec{l}} \sum_{k}^{b} s^k \frac{\{1 - \Omega[|\vec{x}(\vec{l}) + \vec{x}^k - \vec{z}|/\eta]\}}{|\vec{x}(\vec{l}) + \vec{x}^k - \vec{z}|} \right\}$$

where

$$S(\vec{h}) = \sum_{k}^{b} s^k\, e^{-i\vec{x}^k \cdot \vec{y}(\vec{h})} \qquad 2.7.16$$

is a structure amplitude and

$$V'^{k} = \frac{e}{4\pi\epsilon_o}\left\{ \frac{4\pi}{v_a} \sum_{\vec{h}}{}' \frac{S(\vec{h})\, e^{-\eta^2 |\vec{y}(\vec{h})|^2/4}}{|\vec{y}(\vec{h})|^2} e^{i\vec{y}(\vec{h})\cdot\vec{x}^k} - \frac{2s^k}{\sqrt{\pi}\eta} \right.$$

$$\left. + \sum_{\vec{l}}{}' \sum_{k'}^{b} s^{k'} \frac{\{1 - \Omega[|\vec{x}(\vec{l}) + \vec{x}^k - \vec{x}^{k'}|/\eta]\}}{|\vec{x}(\vec{l}) + \vec{x}^k - \vec{x}^{k'}|} \right\} \qquad 2.7.17$$

Comparing equations (2.7.17) and (2.4.18), we see that Tosi's result is equivalent to Ewald's result if we set $\eta = 1/R$ and $\vec{x}^k = 0$.

H. Summary

Each of the methods described in this chapter has attempted to evaluate the electrostatic potential of an infinite crystal. The main problem that the authors had to overcome was the conditional convergence of the infinite sum.

The methods of Madelung and Evjen relied on special ordering of the sums to obtain the accepted values for the electrostatic potential. The first does not have a wide range of applicability and the second method is prone to errors as Evjen's result for CsCl shows.

Three of the methods, Ewald's, Born's, and H&M's, relied on the introduction of a vanishingly small exponential term (either explicitly as with Ewald or implicitly as with H&M) to insure absolute convergence of the Coulomb sum.

The last author, Tosi, used a different boundary condition to obtain results which are equivalent to Ewald's.

All the above methods will give the accepted value for the electrostatic potential if used correctly. We will not give any further discussion of Madelung's or Born's methods since we introduced them for historical reasons.

In Chapter IV , we will show under what circumstances Evjen's method may be used. In addition, we will show that the methods relying on the introduction of a vanishing exponential (Ewald and H&M) do, in fact, give the accepted values for the electrostatic potential of an infinite crystal. In both Chapters III and IV we are able to compare

our results with those of Tosi.

There has been no rigorous discussion of the relationship between the accepted value for the electrostatic potential of the infinite crystal and the actual value of the physically relevant, finite crystal. In the following chapters, we will show how the two quantities are related and give meaning to the accepted value of the infinite crystal.

CHAPTER III

THE ELECTROSTATIC POTENTIAL OF A FINITE CRYSTAL

A. Introduction

We have found that a general formula can be derived for the electrostatic potential within a finite crystal of point charges with arbitrary symmetry. In a finite crystal, (see definition in Section 1.3), the lattice spacing is assumed to be uniform throughout the crystal. In a real finite crystal this is not the case since the crystal structure is asymmetrical at the surface. This causes the equilibrium conditions to have different forms near the surface and hence the lattice spacing to change near the surface. However, we are not interested, at this time, in equilibrium conditions. Thus we will evaluate the electrostatic potential of a finite crystal in which the ions near the surface have the same lattice spacing as those in the bulk of the sample. The resulting expression can be used to calculate numbers associated with the electrostatic potential as readily as any other method known to the author. In contrast to the infinite crystal case, there are no difficulties with physical interpretation, since the sum for the electrostatic potential, eq (1.3.6), contains a finite number of terms and hence this potential is a unique function for each crystal.

The electrostatic potential at a point P with position vector $\vec{z}$ (see fig. 1.3) in a finite crystal of point ions is

$$V(\vec{z}) = \frac{1}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \sum_{k}^{r} \frac{q^k}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 3.1.1$$

(see eq (1.3.6)) where k denotes the type of ion, q^k is the charge of this ion, $\vec{l}$ labels a Bravais lattice site,

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k \qquad \text{(see eq (1.3.5))} \qquad 3.1.2$$

is the position of the k-type ion in the $\vec{l}$-th charge repetition unit (c.r.u.), $\vec{x}^k$ is the position of the k-type ion in the c.r.u. relative to the ion which occupies a Bravais lattice site (it is independent of the lattice index $\vec{l}$), $\vec{x}(\vec{l})$ is the position vector of the $\vec{l}$-th lattice site, the sum over $\vec{l}$ is over all lattice sites within some finite region V[*1] and the sum over k is over all the ions in the c.r.u. The ' on the sum over $\vec{l}$ indicates that, if $\vec{z}$ is an ion site, say $\vec{x}(\vec{l}',\vec{k}')$, then $\vec{l} = \vec{l}'$ is to be omitted from the sum when $k = k'$. As eq (3.1.1) is written, we first sum over all the ions in a c.r.u., then sum over the Bravais lattice sites within V. For a finite sum, the order of summation is not important. We could equally well sum over the contribution due to each type of ion, then sum over the different types of ions. We note that, for an infinite sum, this option is not open to us. The sum over k and the sum over $\vec{l}$ are not interchangeable since the sum over $\vec{l}$ diverges if taken first.

Since we are considering finite sums, the potential at point P due to one type of ion, which we will call the partial potential,

*1 We note that the region V has some degree of arbitrariness at this point in the thesis since we may change the surface of V without changing the number of lattice points within the region.

$$V(\vec{z},k) \overset{\text{defn}}{=} \frac{q^k}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l},k) - \vec{z}|} \qquad 3.1.3$$

is finite. Thus

$$V(\vec{z}) = \sum_{k}^{r} V(\vec{z},k) \qquad 3.1.4$$

Substituting (3.1.2) into (3.1.3), the partial potential may be rewritten as

$$V(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} \qquad 3.1.5$$

where

$$\vec{z}^k = \vec{z} - \vec{x}^k \qquad 3.1.6$$

The technique we will use is to evaluate each $V(\vec{z},k)$ separately, then substitute into (3.1.4) to obtain $V(\vec{z})$. This procedure is not possible using the methods discussed in Chapter II since in those cases either each $V(\vec{z},k)$ is infinite as in Madelung's or Evjen's methods or a different quantity as in Ewald's method. In order to perform a similar procedure for the infinite crystal, one has to assume a uniform background of charge of opposite sign to the ions occupying the lattice sites as Tosi has done (see Section 2.7). The quantity Tosi calculates is related to, but not equal to $V(\vec{z},k)$.

An added advantage of this procedure is that we are able to ignore consideration of unit cell structures and crystal symmetries of the total crystal and consider only the symmetry of each Bravais lattice associated with each type of ion. We will refer to the Bravais lattice with an ion in the c.r.u. as the sub-lattice of that ion. This is also

possible using Tosi's method. This eliminates the inconsistancies such as those arising in CsCl using Evjen's method as discussed in Section 2.3.

In Section B, we introduce the mathematical relation on which our method is based. In Section C, we use this relation to derive a general expression for the partial potential of a simple cubic lattice. The generalization to other types of lattices is straightforward. We will give the results for an orthorhombic Bravais lattice in Section D without proving them. The partial potential is found to consist of two parts - one which is periodic in $\vec{z}$ with the period of the lattice and one which is non-periodic in $\vec{z}$ and depends on the shape of the finite array. We call these parts respectively, the intrinsic and extrinsic partial potentials. In Section D, we give explicit expressions for the extrinsic partial potential for an array in the shape of an ellipsoid and the intrinsic partial potentials associated with cubic and orthorhombic Bravais lattices. In Section E, we give a general discussion of the evaluation of the electrostatic potential of a finite crystal using the method developed in Section C.

B. General Theory

Consider the integral

$$I(\vec{x}) = \frac{1}{a^3} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} f(\vec{x}+\vec{y}) \qquad 3.2.1$$

This is the integration of an arbitrary function $f(\vec{x})$, thoughout a cube of side a centered at $\vec{x}$. Thus $I(\vec{x})$ is the average value of $f(\vec{x})$ in the cubic region of side a centered at $\vec{x}$. We may expand the integrand in a single Taylor's series in $\vec{y}$ about $\vec{x}$, provided $f(\vec{x})$ has no singularities* in the region we are considering*1.

The Taylor series expansion of $f(\vec{x}+\vec{y})$ in $\vec{y}$ about $\vec{x}$ is

$$f(\vec{x}+\vec{y}) = \sum_{m=0}^{\infty} \frac{y_1^m}{m!} \frac{\partial^m}{\partial x_1^m} \sum_{n=0}^{\infty} \frac{y_2^n}{n!} \frac{\partial^n}{\partial x_2^n} \sum_{p=0}^{\infty} \frac{y_3^p}{p!} \frac{\partial^p}{\partial x_3^p} f(\vec{x}) \qquad 3.2.2$$

Substituting (3.2.2) into (3.2.1), $I(\vec{x})$ may be written in the form

$$I(\vec{x}) = \frac{1}{a^3} \sum_{m=0}^{\infty} \frac{1}{m!} \frac{\partial^m}{\partial x_1^m} \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial^n}{\partial x_2^n} \sum_{p=0}^{\infty} \frac{1}{p!} \frac{\partial^p}{\partial x_3^p} f(\vec{x}) \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_1 y_1^m \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_2 y_2^n \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_3 y_3^p \qquad 3.2.3$$

Performing the integrations, we see that the terms associated with m, n, p odd vanish. Therefore we may write $I(\vec{x})$ as

---

*1 If $f(\vec{x})$ has a singularity at some point, say $\vec{x}_o$, then $f(\vec{x}+\vec{y})$ has two different expansions - one for $|\vec{y}| > |\vec{x}_o|$ and another for $|\vec{y}| < |\vec{x}_o|$. Provided $|\vec{x}-\vec{x}_o| > \frac{1}{2}\sqrt{3}a$, then the singularity is not within the region of integration of (3.2.1). In this case, only one expansion is sufficient in the integration region. This is the case of interest here.

$$I(\vec{x}) = \hat{\Gamma}(\vec{x}) f(\vec{x}) \qquad 3.2.4$$

where

$$\hat{\Gamma}(\vec{x}) = \sum_{m=0}^{\infty} \frac{(\frac{1}{2}a)^{2m}}{(2m+1)!} \frac{\partial^{2m}}{\partial x_1^{2m}} \sum_{n=0}^{\infty} \frac{(\frac{1}{2}a)^{2n}}{(2n+1)!} \frac{\partial^{2n}}{\partial x_2^{2n}} \sum_{p=0}^{\infty} \frac{(\frac{1}{2}a)^{2p}}{(2p+1)!} \frac{\partial^{2p}}{\partial x_3^{2p}} \qquad 3.2.5$$

is a differential operator of $\vec{x}$. From (3.2.1) and (3.2.4), we see that $\hat{\Gamma}(\vec{x})$ has the property that

$$\hat{\Gamma}(\vec{x}) f(\vec{x}) = \frac{1}{a^3} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} f(\vec{x}+\vec{y}) \qquad 3.2.6$$

Rearranging terms on the right of (3.2.5), we may write the differential form of $\hat{\Gamma}(\vec{x})$ as

$$\hat{\Gamma}(\vec{x}) = \sum_{p=0}^{\infty} \hat{D}_{2p} \qquad 3.2.7$$

where $\hat{D}_{2p}$ is a differential operator which contains derivatives of only order 2p, given by

$$\hat{D}_{2p} = (\tfrac{1}{2}a)^{2p} \sum_{m=0}^{p} \sum_{n=0}^{p-m} \frac{1}{[2(p-m-n)+1]!(2m+1)!(2n+1)!} \frac{\partial^{2p}}{\partial x_1^{2(p-m-n)} \partial x_2^{2m} \partial x_3^{2n}} \qquad 3.2.8$$

For the special case of the Coulomb potential, $f(\vec{x}) = 1/|\vec{x}|$, the identity (3.2.6) takes the form

$$\hat{\Gamma}(\vec{x}) \frac{1}{|\vec{x}|} = \frac{1}{a^3} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} \frac{d\vec{y}}{|\vec{y}-\vec{x}|} \qquad 3.2.9$$

Eq (3.2.9) is valid only for values of $|\vec{x}| > \frac{1}{2}\sqrt{3}a$ since $f(\vec{x})$ has a singularity at $\vec{x}_o = 0$ and the discussion in the footnote of the preceding page applies.

C. Evaluation of the Partial Potential $V(\vec{z},k)$

The partial potential at a point P, with position vector $\vec{z}$, due to a finite, simple cubic array of similar point charges of type k is

$$V(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} \quad \text{(see eq (3.1.5)} \qquad 3.3.1$$

where, as before, we have used (see fig 3.2, P. 69)

$$\vec{z}^k = \vec{z} - \vec{x}^k \qquad \text{(see eq (3.1.6))} \qquad 3.3.2$$

and

$$\vec{x}(\vec{l}) = (l_1\hat{e}_1 + l_2\hat{e}_2 + l_3\hat{e}_3)a \qquad \text{(see eq (1.2.1))} \qquad 3.3.3$$

a is the lattice parameter of the simple cubic lattice.

We split the sum over $\vec{l}\in V$ into two parts - one over a region V_n ($\vec{l}\in V_n$) and the other over the rest ($\vec{l}\notin V_n$). V_n is a cube of side (2n+1)a centered at $\vec{x}_z$ - the lattice site of the k = 0 ion which is nearest the point P. This volume is defined by associating a cube of side a (with center at a lattice site*1) with each of the lattice sites within a cube of side 2na. The result is a cubic region of side (2n+1)a. Thus

$$V(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o}\left[\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} + \sum_{\vec{l}\in V_n} \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|}\right] \qquad 3.3.4$$

---

*1 The cube of side a centered about a lattice point $\vec{l}$ will be referred to as the basic cube of the lattice site.

At this point n is an arbitrary, non-negative integer.

For convenience in writing, we will set the second term in (3.3.4) equal to $v'(\vec{z})$. It is a function of $\vec{z}$ and is parameterized by three quantities $\vec{x}_z$, V, V_n which will not be written explicitly. Thus

$$v'(\vec{z}) \overset{\text{defn}}{=} \sum_{1 \notin V_n} \frac{1}{|\vec{x}(\vec{1}) - \vec{z}^k|} \qquad 3.3.5$$

We will now use the theory developed in Section B to evaluate $v'(\vec{z})$. From eq (3.2.9), we can write

$$\hat{\Pi}(\vec{x}(\vec{1})) \frac{1}{|\vec{x}(\vec{1})-\vec{z}^k|} = \frac{1}{a^3} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} \frac{d\vec{y}}{|\vec{x}(\vec{1})+\vec{y}-\vec{z}^k|} \qquad 3.3.6$$

Since the function $1/|\vec{x}(\vec{1})-\vec{z}^k|$ has a singularity at $\vec{z}^k = \vec{x}(\vec{1})$, the identity (3.3.6) is valid only for

$$|\vec{x}(\vec{1}) - \vec{z}^k| > \tfrac{1}{2}\sqrt{3}a \qquad 3.3.7$$

From the geometry of the lattice, we note that the $\vec{z}^k$ and $\vec{x}(\vec{1})$ appearing in the definition (3.3.5) of $v'(\vec{z})$, satisfy the inequality

$$|\vec{x}(\vec{1}) - \vec{z}^k| > (n-\tfrac{1}{2})a \qquad 3.3.8^{*2}$$

---

*2 According to our definition of V_n, (i.e. that its center be $\vec{x}_z$), $\vec{z}$ (not $\vec{z}^k$), may range throughout the basic cube at the center of V_n. Depending on the problem, the vectors $\vec{x}^k$ may also range throughout a cube of side a. This means that the vectors $\vec{z}^k$ may range within a cube of side 2a. Thus

$$|\vec{x}(\vec{1}) - \vec{z}^k| \geq |\vec{x}(1)-\vec{x}_z|_{\min} - |\vec{z}^k - \vec{x}_z|_{\max}$$

$$\geq (n+1)a - \tfrac{1}{2}2\sqrt{2}a$$

$$> (n-\tfrac{1}{2})a$$

Therefore, if we restrict n to be greater than or equal to two, the inequality (3.3.7) is automatically satisfied for all $\vec{l} \in V_n$ (see fig 3.1).

We will define a quantity $v''(\vec{z})$ as the sum of

$$\hat{\Gamma}(\vec{x}(\vec{l})) \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|}$$

over all the lattice points $\vec{x}(\vec{l})$ which have $\vec{l} \notin V_n$. i.e.

$$v''(\vec{z}) \overset{\text{defn}}{=} \sum_{\vec{l} \notin V_n} \hat{\Gamma}(\vec{x}(\vec{l})) \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} \qquad 3.3.9$$

Due to the nature of the function on which $\hat{\Gamma}(\vec{x}(\vec{l}))$ operates, it may be regarded as either an operator of $\vec{x}(\vec{l})$ or of $-\vec{z}$. We choose $\hat{\Gamma}$ to be an operator of $-\vec{z}$, so that it commutes with the sum over $\vec{l}$. We note that from the definition of $\hat{\Gamma}$, (eq (3.2.5)), that it is an even operator. i.e.

$$\hat{\Gamma}(-\vec{z}) = \hat{\Gamma}(\vec{z}) \qquad 3.3.10$$

Thus

$$\begin{aligned} v''(\vec{z}) &= \sum_{\vec{l} \notin V_n} \hat{\Gamma}(\vec{z}) \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} \\ &= \hat{\Gamma}(\vec{z}) \sum_{\vec{l} \in V_n} \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|} \\ &= \hat{\Gamma}(\vec{z}) v'(\vec{z}) \qquad 3.3.11 \end{aligned}$$

We will first find an explicit expression for $v''(\vec{z})$, then solve the differential equation (3.3.11) for $v'(\vec{z})$.

Using (3.3.6), $v''(\vec{z})$ may be rewritten as

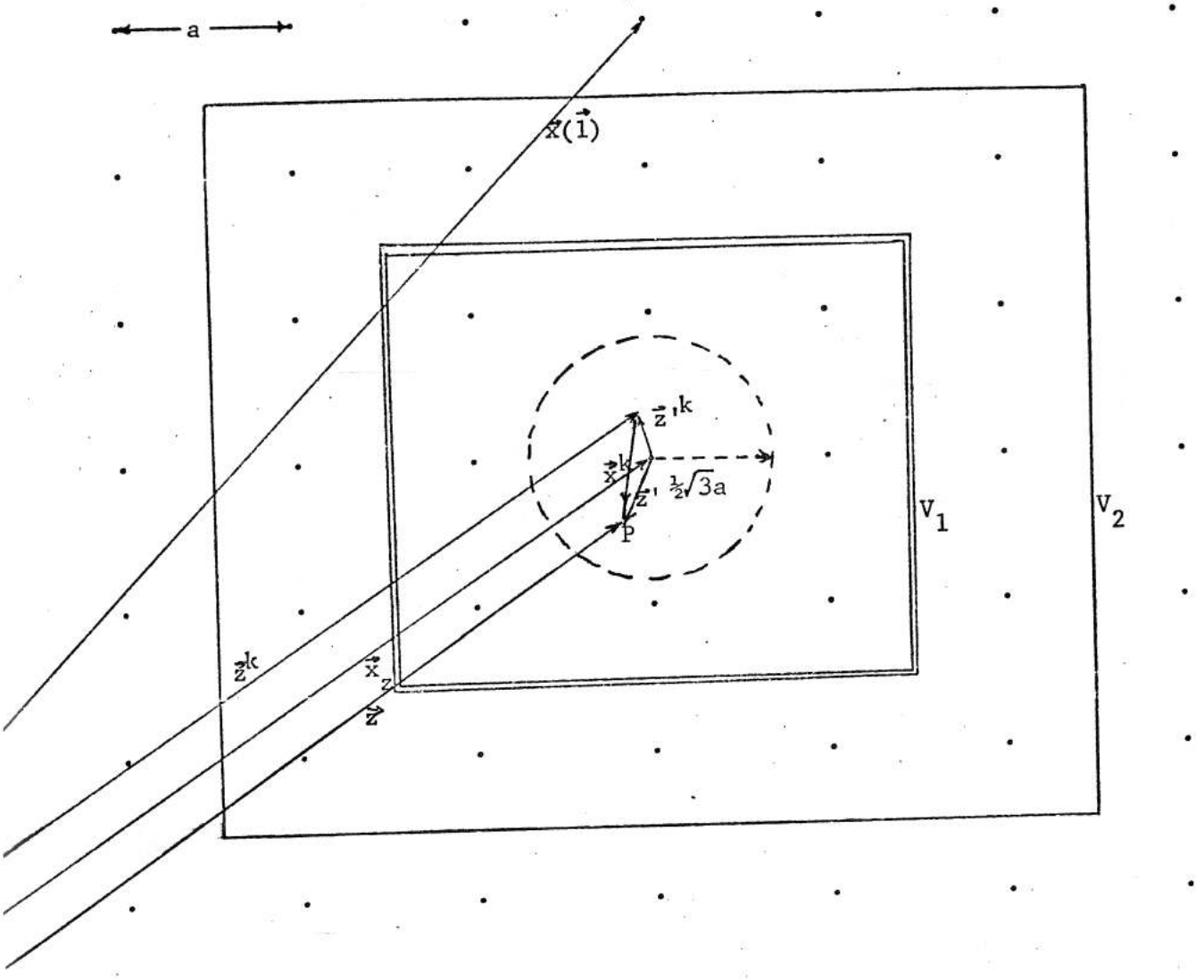

Figure 3.1

The Region V_n

The points within the sphere have $|\vec{x}(\vec{l})-\vec{z}^{l,k}|<\frac{1}{2}\sqrt{3}a$ and thus the relation (3.3.7) is not valid for lattice points in this region.

The cubic region enclosed by the double line (V_1) must be excluded since most of the basic cubes of the lattice points within this region enclose parts of the sphere where (3.3.7) is not satisfied.

The cubic region enclosed by the single line (V_2) is chosen to be excluded for convenience.

See Figure 3.2 for an expanded diagram of the vectors related to $\vec{z}$.

$$v''(\vec{x}) = \frac{N}{V} \sum_{\vec{l} \notin V_n} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} \frac{d\vec{y}}{|\vec{x}(\vec{l})+\vec{y}-\vec{z}^k|} \qquad 3.3.12$$

where $N/V = a^{-3}$. We may now uniquely define V as follows:

'V is the volume of the array of charges defined by associating a basic cube with each lattice site of the k=0 ion in the crystal.'*3

N is the number of occupied lattice sites in the array.

Introducing the transformation $\vec{y} = \vec{y}' - \vec{x}(\vec{l})$, the integral on the right of (3.3.12) may be written as

$$\iiint_{\vec{x}(\vec{l})-\frac{1}{2}a}^{\vec{x}(\vec{l})+\frac{1}{2}a} \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|}$$

While the integrals in (3.3.12) are of different functions over the same region, after the transformation, they are integrals of the same function over different regions. We may now combine the sum and integrals to obtain an integral over one region

$$v''(\vec{z}) = \frac{N}{V} \iiint_{V'} \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|} \qquad 3.3.13$$

where we have dropped the prime on the $\vec{y}$'s. V' is the region defined as the region V from which the region V_n is excluded.

Although the integrand is singular, the volume element dominates

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*3 If the volume built up from the basic cubes does not have a smooth surface, as for example in the case of an ellipsoid, then we will use V to denote the volume which is constructed using basic cubes and V_s to denote the smooth volume which best approximates V in both size and shape.

so that an integration over the region of the singularity is finite (see Appendix 1). Hence we may add and subtract the integral over the region V_n to the R.H.S. of (3.3.13) to obtain

$$v''(z) = \frac{N}{V}\left\{\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|} - \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|}\right\} \qquad 3.3.14$$

At this point it is convenient to set

$$\vec{z}^k = \vec{x}_z + \vec{z}'^k \qquad 3.3.15$$

in the second integral in (3.3.14) (see fig 3.2). We introduce the prime to indicate that $\vec{z}'^k$ has a different origin from $\vec{z}^k$ although it refers to the same point in space. The origin of $\vec{z}'^k$ is the center of V_n and the origin of $\vec{z}^k$ will be chosen to be the center of V.

Introducing the transformation $\vec{y} = \vec{y}' + \vec{x}_z$ into the second integral of (3.3.14), we find that it does not depend on $\vec{x}_z$. i.e.

$$v''(\vec{z}) = \frac{N}{V}\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|} - \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^k|} \qquad 3.3.16$$

Since the second integral does not depend on $\vec{x}_z$, we may consider it as being a periodic function of $\vec{z}$ with the period of the lattice.

We have succeeded in our aim of finding an explicit expression for the L.H.S. of (3.3.11). We now need to solve the differential equation (3.3.11) to find $v'(\vec{z})$, which is the quantity which actually appears in the partial potential (see eqs (3.3.4) and (3.3.5)).

As stated earlier, $v'(\vec{z})$ is a function of $\vec{z}$ with three parameters $\vec{x}_z$, V, V_n. We will now reduce the problem to two independent differential equations where the unknown functions are functions of one variable and are parameterized by only one quantity.

From the definition of $v'(\vec{z})$, eq (3.3.5), we may write it as

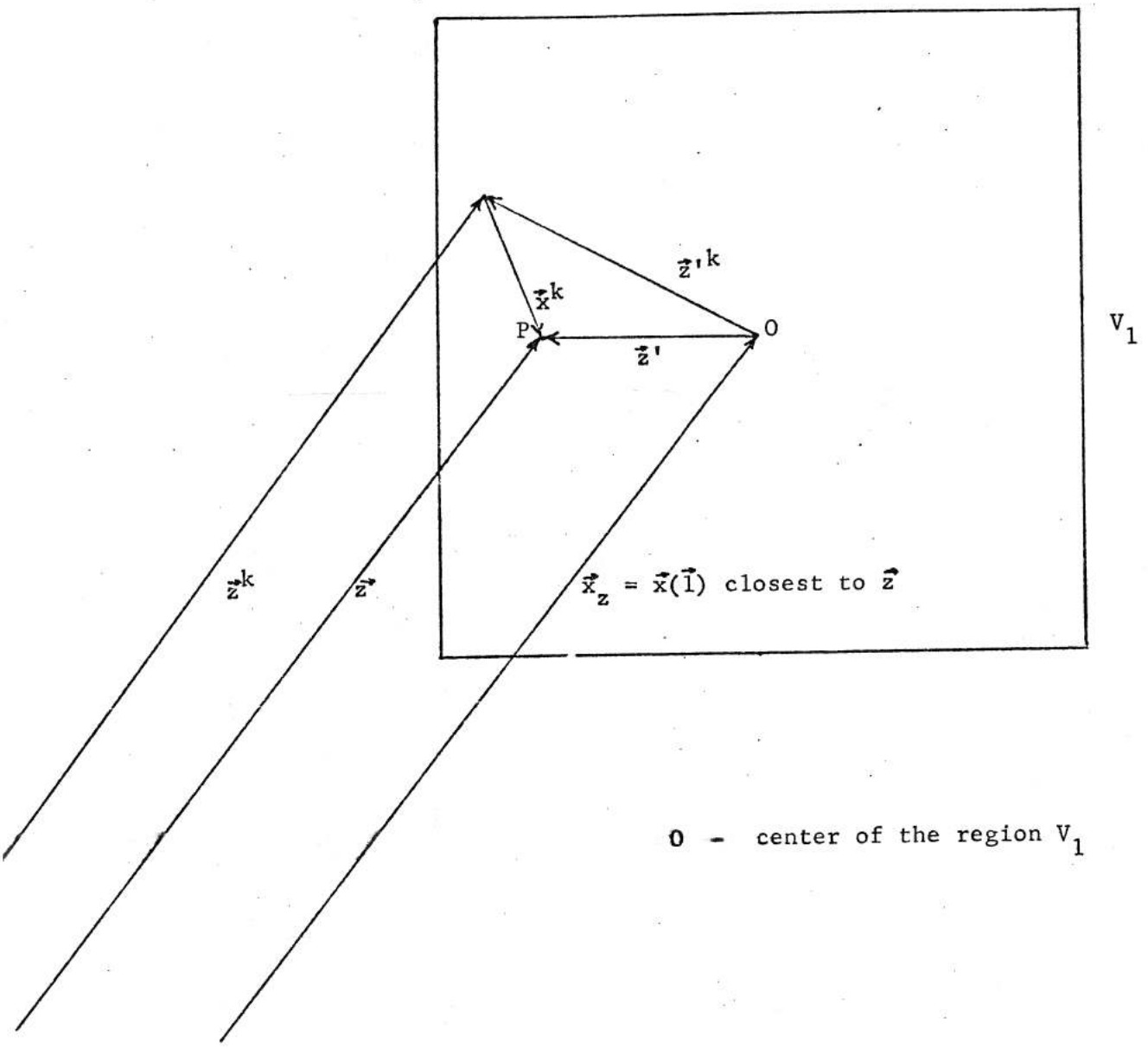

Figure 3.2

Vectors Related to $\vec{z}$

To avoid confusion between the various vectors used in this chapter, we have given all the vectors related to the position vector $\vec{z}$ in the above figure.

$$v'(\vec{z}) = \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^k|} - \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^k|} \qquad 3.3.17$$

Shifting the limits of summation of the second term, as we did to obtain eq (3.3.12), by setting $\vec{x}(\vec{l}) = \vec{x}(\vec{l}') + \vec{x}_z$, the second term may be rewritten as

$$\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^k|} = \sum_{\vec{l}'\in V_n}{}' \frac{1}{|\vec{x}(\vec{l}')-\vec{z}'^k|} \qquad 3.3.18$$

where the origin of summation is now the center of the region V_n. Thus

$$v'(\vec{z}) = \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^k|} - \sum_{\vec{l}'\in V_n}{}' \frac{1}{|\vec{x}(\vec{l}')-\vec{z}'^k|} \qquad 3.3.19$$

Let us now consider the two general sums

$$\phi(\vec{z},V) \overset{\text{defn}}{=} \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}|} \qquad \vec{z}\in V \qquad 3.3.20$$

and

$$\phi'(\vec{z}',V_n) = \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'|} \qquad \vec{z}'\in V_n \qquad 3.3.20a$$

$$= \phi(\vec{z}',V_n)$$

since the sum is of the same form as in eq (3.3.20), only with different parameters. In terms of these functions, $v'(\vec{z})$ may be written as

$$v'(\vec{z}) = \phi(\vec{z}^k,V) - \phi(\vec{z}'^k,V_n) \qquad 3.3.20b$$

Although $\phi(\vec{z},V)$ and $\phi(\vec{z}',V_n)$ are functions of different parameters, the two functions may have terms which are exactly the same. These terms will have to be independent of V and V_n since these quantities are unrelated. However, the position vectors of the functions, as they

are used in eq (3.3.20b), are assumed to be related as follows

$$\vec{z}' = \vec{z} - \vec{x}_z \qquad \text{(see eq (3.3.15))}$$

Thus the common terms could be functions of $\vec{z}$ or $\vec{z}'$; provided they are periodic (with period of the lattice spacing). Thus we assume $\phi(\vec{z},V)$ and $\phi(\vec{z}',V_n)$ may be written in the form

$$\phi(\vec{z},V) = \frac{N}{V} f(\vec{z},V) + g(\vec{z}) \qquad 3.3.21$$

and

$$\phi(\vec{z}',V_n) = \frac{N}{V} f(\vec{z}',V_n) + g(\vec{z}') \qquad 3.3.21a$$

where

$$g(\vec{z}) = g(\vec{z}'+\vec{x}_z)$$
$$= g(\vec{z}') \qquad 3.3.21b$$

due to the assumption of periodicity. $g(\vec{z}')$ is independent of the three parameters V, V_n, and $\vec{x}_z$. It contains all the terms which are the same in $\phi(\vec{z},V)$ and $\phi(\vec{z}',V_n)$, except for the constant part of these functions. This constant is shared between f and g. We need this restriction since we find later (see eq (3.3.46)) that f has a constant term. We choose to write the functions in these forms so that when we take the difference between them to get $v'(\vec{z})$, eq (3.3.20b), all the common terms (except possibly a constant) are explicitly cancelled.

Although the sum on the L.H.S. of eq (3.3.20a) is defined for $\vec{z}' \subset V_n$, due to the way in which $\phi(\vec{z}',V_n)$ is used (in eq (3.3.20b), only the values for $\vec{z}'$ within a limited region at the center of V_n are of interest to us. This limited region is a cube of side 2a. This happens because the position vector we are interested in (i.e. that appears as

the argument in eq (3.3.20b) is $\vec{z}'^{k}$ not $\vec{z}'$. Although $\vec{z}'$ lies only within the basic cube at the center of V_n, $\vec{z}'^{k}$ ranges over a cube of side 2a (see footnote *2 of eq (3.3.8)).

We note that $\emptyset(\vec{z}^{k},V)$ is proportional to the partial potential of the region V. We will assign physical meanings to f and g at the end of this section.

We will first solve for the f's using $v'(\vec{z})$, then solve for g.

Substituting (3.3.21) and (3.3.21a) into eq (3.3.20b), we obtain

$$v'(\vec{z}) = \frac{N}{V}\left[f(\vec{z}^{k},V) - f(\vec{z}'^{k},V_n)\right]. \qquad 3.3.22$$

Operating on (3.3.22) with $\hat{\Pi}$, we have

$$\hat{\Pi}\, v'(\vec{z}) = \frac{N}{V}\left[\hat{\Pi} f(\vec{z}^{k},V) - \hat{\Pi} f(\vec{z}'^{k},V_n)\right] \qquad 3.3.23$$

From eq (3.3.7), with the aid of (3.3.11), we have

$$\hat{\Pi}\, v'(\vec{z}) = \frac{N}{V}\left[\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}^{k}|} - \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^{k}|}\right] \qquad 3.3.24$$

Thus

$$\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}^{k}|} - \hat{\Pi} f(\vec{z}^{k},V) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^{k}|} - \hat{\Pi} f(\vec{z}'^{k},V_n) = C \qquad 3.3.25$$

where C is a constant since $\vec{z}^{k}$, $\vec{z}'^{k}$ and V, V_n are independent. We may set C = 0 since in our definitions of $f(\vec{z}^{k},V)$ and $f(\vec{z}'^{k},V_n)$, we allowed

a constant term to appear either in f or in g. We would choose this constant to be part of g.

Hence the functions $f(\vec{z}^k,V)$ and $f(\vec{z}'^k,V_n)$ are solutions of the differential equations

$$\hat{\Gamma} f(\vec{z}^k,V) = \iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}^k|} \qquad 3.3.26$$

and

$$\hat{\Gamma} f(\vec{z}'^k,V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^k|} \qquad 3.3.27$$

Since eqs (3.3.26) and (3.3.27) are of the same form, we will only discuss eq (3.3.26) and assume all statements are the same for eq (3.3.27) with $\vec{z} = \vec{z}'$ and $V = V_n$.

Unfortunately, eq (3.3.26) is not sufficient to uniquely determine f, since as with all differential equations, the solution of (3.3.26) is not unique. We may add any solution $\tilde{f}$ of the homogeneous equation

$$\hat{\Gamma} \tilde{f} = 0 \qquad 3.3.28$$

to f and still satisfy (3.3.26). Thus $f + \tilde{f}$ is also a solution of (3.3.26). We must remember that we are trying to find a different representation for $v'(\vec{z})$. Thus $f(\vec{z}^k,V)$ is a well defined function. Since f must satisfy equation (3.3.20), we impose the following boundary conditions on f:

1. f must not contain a solution of (3.3.28) which is not a function of V, and

2. f must have the same V dependence as the L.H.S. of (3.3.20).

These boundary conditions are sufficient to uniquely define $f(\vec{z}^k,V)$

Although we will not use $\tilde{f}$ explicitly, we need to know some of its' properties for later calculations. In addition to satisfying (3.3.28), the solutions $\tilde{f}$ must also satisfy Laplace's equation. From the definition of $v'(\vec{z})$, we see that it satisfies Laplace's equation. i.e.

$$\nabla^2 v'(\vec{z}) = 0 \qquad 3.3.29$$

Thus

$$\nabla^2 \frac{N}{V}\left\{f(\vec{z},V) - f(\vec{z}',V_n) + \tilde{f}(\vec{z},V) + \tilde{f}(\vec{z}',V_n)\right\} = 0 \qquad 3.3.30$$

From (3.3.26), we have that

$$\hat{\Pi}\nabla^2 f(\vec{z},V) = \nabla^2\left\{\iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|}\right.$$

$$= -4\pi \qquad 3.3.31$$

Hence

$$\nabla^2 f(\vec{z},V) = -4\pi \qquad 3.3.32$$

Similarily

$$\nabla^2 f(\vec{z}',V_n) = -4\pi \qquad 3.3.33$$

Thus, eq (3.3.30) reduces to

$$\nabla^2\left\{\tilde{f}(\vec{z},V) - \tilde{f}(\vec{z}',V_n)\right\} = 0 \qquad 3.3.34$$

Since $\vec{z}$, $\vec{z}'$ and V, V_n are independent variables, (3.3.34) gives

$$\nabla^2\tilde{f}(\vec{z},V) = \nabla^2\tilde{f}(\vec{z}',V_n) = C \qquad 3.3.35$$

where C is an arbitrary constant. Operating on (3.3.35) with $\hat{\Pi}$, we have

$$\hat{\Pi}\,\nabla^2\tilde{f}(\vec{z},V) = \hat{\Pi}\,C \qquad 3.3.36$$

or

$$\nabla^2\,\hat{\Pi}\,\tilde{f}(\vec{z},V) = C \qquad 3.3.37$$

Since $\tilde{f}$ satisfies eq (3.3.28), we must have C = 0.

Returning to eq (3.3.23), we have that the solution of (3.3.11) can be written in the form

$$v'(\vec{z}) = \frac{N}{V}\left[f(\vec{z}^k,V) - f(\vec{z}'^k,V_n)\right] \qquad 3.3.38$$

where $f(\vec{z}^k,V)$ and $f(\vec{z}'^k,V_n)$ are solutions of eqs (3.3.26) and (3.3.27) respectively which satisfy the boundary conditions stated in the discussion following eq (3.3.29).

The problem has now been reduced to solving (3.3.26) or (3.3.27) for a function of one variable with only one explicit parameter. The third parameter, $\vec{x}_z$, appears implicitly through $\vec{z}'^k = \vec{z}^k - \vec{x}_z$. The functions $f(\vec{z}^k,V)$ and $f(\vec{z}'^k,V_n)$ do not have $\vec{x}_z$ as an explict parameter. As we have done in simplifying eq (3.3.11), we will first find an explicit form for the R.H.S. of (3.3.26), then use this result to obtain an explicit form for $f(\vec{z},V)$.

The integrals in eqs (3.3.26) and (3.3.27) will be defined as

$$I(\vec{z},d) = \iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad 3.3.39$$

where $\vec{z}$ is a general variable (i.e. $\vec{z}=\vec{z}^k$ in (3.3.26) and $\vec{z}=\vec{z}'^k$ in eq (3.3.26)) and V is a general volume. The origin of $\vec{z}$ is chosen to be the center of the region of integration and d is a measure of the size of the volume. The choice of d is arbitrary; a convenient one to use might be the cube root of the volume ($d = V^{1/3}$). To find the expansion for $I(\vec{z},d)$ in powers of d, we define the limits of integration in terms of this parameter, then integrate (3.3.39) to obtain the required expansion. In (3.3.27), half the length of a side $d = (n+\frac{1}{2})a = \frac{1}{2}V^{1/3}$, is a convenient parameter to use.

From Jackson[17], the integrand can be expanded in spherical harmonics as follows:

$$\frac{1}{|\vec{y}-\vec{z}|} = \frac{4\pi}{z}\sum_{m=0}^{\infty}\sum_{p=-m}^{m}\frac{(y/z)^m}{(2m+1)}Y_m^p(\theta,\phi)Y_m^{p*}(\theta',\phi') \qquad y<z$$

$$= \frac{4\pi}{y}\sum_{m=0}^{\infty}\sum_{p=-m}^{m}\frac{(z/y)^m}{(2m+1)}Y_m^p(\theta,\phi)Y_m^{p*}(\theta',\phi') \qquad y>z \qquad 3.3.40$$

where (z,θ,ϕ) and (y,θ',ϕ') are respectively the spherical coordinates of $\vec{z}$ and $\vec{y}$. Substituting (3.3.40) into (3.3.39), we may perform the integration to obtain

$$I(\vec{z},d) = d^2\sum_{m=0}^{\infty}(z/d)^{2m}\sum_{p=-m}^{m}\alpha_{mp}Y_{2m}^{2p}(\theta,\phi) - \frac{2\pi z^2}{3} \qquad 3.3.41$$

where

$$\alpha_{mp} = \frac{4\pi}{(4m+1)}\iint_{4\pi}d\Omega\, Y_{2m}^{2p*}(\theta',\phi')\left\{-\frac{\eta^{2(m-1)}}{2(m-1)}(1-\delta_{m,1}) + \delta_{m,1}\ln(\eta)\right\} \qquad 3.3.42$$

(see Appendix I*). η is the equation of the bounding surface (for example, in the case of an ellipsoid with semi-axes b_1, b_2, b_3, $\eta^2 = (d/y)^2\left[(y_1/b_1)^2+(y_2/b_2)^2+(y_3/b_3)^2\right]$ with d being proportional to the cube root of the volume i.e. $d = (\pi b_1 b_2 b_3)^{1/3}$). The odd powers of z/d and odd spherical harmonics vanished due to the symmetry properties of the integral. Equations (3.3.41) and (3.3.42) are valid no matter what kind of bounding surface V has. However for practical calculations, the surface of V needs to be smooth. For a slab, which is a shape that can be built up of cubes, the bounding surfaces are planes and hence no smoothing problems arise. However, for an array which closely approximates an ellipsoidal shape, the surface of V is not smooth - it differs

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from the smooth surface of a perfect ellipsoid because of the cube stacking which led to V. For macroscopic sized specimens, we approximate the rough surface by a smooth ellipsoidal surface V_s say; the difference between the rough surface and smooth surface contributes a constant to the total potential. This point will be discussed in greater detail in Section D.

From (3.3.41), we see that $I(\vec{z},d)$ is a sum of terms such as $z^{2m}Y_{2m}^{2p}$, which is a solution of Laplace's equation, plus a term proportional to z^2.

We wish to find a solution of the differential equation (3.3.26)

$$\hat{\Gamma} f(\vec{z},V) = I(\vec{z},d) \qquad 3.3.42$$

To obtain some insight into the nature of $\hat{\Gamma}(\vec{z})$, we will now discuss some of its properties.

$\hat{\Gamma}(\vec{z})$ does not operate on d, therefore $f(\vec{z},V)$ will have the same type of power series in d as $I(\vec{z},d)$ has (except for the dependence of the part of f which is a solution of the homogeneous eq (3.3.28)).

We note that

$$\hat{\Gamma}(\vec{z})z^2 = z^2 + \tfrac{1}{4}a^2 \qquad 3.3.43$$

and hence that

$$\hat{\Gamma}(\vec{z})(z^2 - \tfrac{1}{4}a^2) = z^2 \qquad 3.3.44$$

The function $z^{2m}Y_{2m}^{2p}$ is a polynomial of degree 2m in z_1, z_2, z_3 which contains terms only of order 2m. We recall that $\hat{\Gamma}$ can be written as in eq (3.2.7). Thus when we act on $z^{2m}Y_{2m}^{2p}$ with $\hat{D}_{2t}$, which is a differential operator which has only derivatives of order 2t, then we obtain another polynomial which is of order 2(m-t). This polynomial is also a solution of Laplace's equation. Thus we may write the

polynomials as a sum of spherical harmonics of order 2(m-t) as follows

$$\hat{D}_{2t} z^{2m} Y_{2m}^{2p} = \sum_{s=-(m-t)}^{m-t} \epsilon_s^{tmp} \, z^{2(m-t)} Y_{2(m-t)}^{2s} \qquad t \leq m \qquad 3.3.45$$

$$= 0 \qquad t > m$$

where the ϵ_s^{tmp} are constants.

Thus $\hat{\Gamma}(\vec{z})$ acting on a spherical harmonic will always decrease in steps of two, or leave unchanged, the order of the harmonic. The maximum order of $z^{2m} Y_{2m}^{2p}$, associated with each power of (1/d), that may occur in $f(\vec{z},V)$ is the power of (1/d) plus 2, as in $I(\vec{z},d)$. Therefore we allow, as the coefficient of each power of (1/d) in $f(\vec{z},d)$, a sum of all orders of $z^{2m} Y_{2m}^{2p}$ up to the order of (1/d) plus 2. Odd powers of 1/d will not occur in $f(\vec{z},V)$ because $\hat{\Gamma}$ would operate on an odd power to give the same odd power. No odd powers occur in $I(\vec{z},d)$, so there must be no odd powers in $f(\vec{z},V)$.

Thus, from these comments and eq (3.3.44), we choose a solution $f(\vec{z},V)$ of the form

$$f(\vec{z},V) = d^2 \sum_{m=0}^{\infty} d^{-2m} \sum_{p=0}^{m} \sum_{s=-p}^{p} \beta_{ps}^{m} z^{2p} Y_{2p}^{2s}(\theta,\emptyset) - \frac{2\pi}{3}(z^2 - \tfrac{1}{4}a^2) \qquad 3.3.46$$

The β_{ps}^{m} are unknown constants which we have to find in terms of the α_{mp}'s which appear in $I(\vec{z},d)$. Operating (3.2.7) on (3.3.46) with the aid of (3.3.45), we equate the result to $I(\vec{z},d)$ to obtain

$$\beta_{ns}^{m} = \alpha_{ms} a^{2m} \qquad n = m$$

$$0 = \sum_{p=n}^{m} \sum_{s=-p}^{p} \beta_{ps}^{m} \sum_{t=-n}^{n} \epsilon_t^{p-n,ms} \qquad n = 0,1,\ldots,m-1 \qquad 3.3.47$$

where we have used the fact that the coefficients of each term $d^{2m} z^{2p} Y_{2p}^{2s}$ must be the same on both sides of the equation. These

equations can now be solved uniquely for the β^m_{ps}. This procedure is carried out explicitly for special cases in Section D.

We now need to check that this solution satisfies the boundary conditions on page 73. We see immediately that the first boundary condition is trivially satisfied. We will show that the second boundary condition is also satisfied for the simplest case of $V = V_n$ (i.e. $d = (n+\frac{1}{2})a$ in (3.3.46)). The same argument can be generalized to more complex V. We introduce

$$\phi(\vec{z},V_n) = \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}|} \qquad 3.3.48$$

Instead of comparing the n dependence of $\phi(\vec{z},V_n)$ and $f(\vec{z},V_n)$, we will compare the n dependence of the quantities

$$\Delta f(\vec{z},V_n) = f(\vec{z},V_n) - f(\vec{z},V_{n-1}) \qquad 3.3.49$$

and

$$\Delta\phi(\vec{z},V_n) = \phi(\vec{z},V_n) - \phi(\vec{z},V_{n-1}) \qquad 3.3.50$$

Clearly if Δf and $\Delta\phi$ have the same n dependence then f and ϕ will also have the same n dependence since f and ϕ can be obtained from Δf and $\Delta\phi$ by summing over n. From eq (3.3.46), we have

$$\Delta f(\vec{z},V_n) = \sum_{m=0}^{\infty} a^{-2(m-1)} \left\{(n+\tfrac{1}{2})^{-2(m-1)} - (n-\tfrac{1}{2})^{-2(m-1)}\right\} \sum_{p=0}^{m} \sum_{s=-p}^{p} \beta^m_{ps} z^{2p} Y_{2p}^{2s} \qquad 3.3.51$$

Therefore the n dependence of $\Delta f(\vec{z},V_n)$ is given by

$$(n+\tfrac{1}{2})^{-2(m-1)} - (n-\tfrac{1}{2})^{-2(m-1)} = -\left\{(n+\tfrac{1}{2})^{2(m-1)} - (n-\tfrac{1}{2})^{2(m-1)}\right\}/(n^2-\tfrac{1}{4})^{2(m-1)}$$

$$= -\frac{1}{n^{2m-1}}\left[\frac{(1+1/2n)^{2(m-1)} - (1-1/2n)^{2(m-1)}}{n(1-1/4n^2)^{2(m-1)}}\right] \qquad 3.3.52$$

Expanding the term in square brackets on the R.H.S. of (3.3.52) in a power series in $1/n^2$ (the odd powers cancel), we obtain

$$(n+\tfrac{1}{2})^{-2(m-1)} - (n-\tfrac{1}{2})^{-2(m-1)} = \frac{1}{n^{2m-1}} \sum_{r=0}^{\infty} C_r^m \, n^{-2r} \qquad 3.3.53$$

where the C_r^m are constants. Thus

$$\Delta f(\vec{z},V_n) = \sum_{m=0}^{\infty} \frac{a^{-2(m-1)}}{n^{2m-1}} \sum_{r=0}^{\infty} C_r^m n^{-2r} \sum_{p=0}^{m} \sum_{s=-2p}^{p} \beta_{ps}^m z^{2p} Y_{2p}^{2s}(\theta,\phi) \qquad 3.3.54$$

Rearranging the orders of summation, we may write (3.3.54) as

$$\Delta f(\vec{z},V_n) = \sum_{p=0}^{\infty} \sum_{s=-p}^{p} z^{2p} Y_{2p}^{2s} \sum_{m=p}^{\infty} \sum_{r=0}^{\infty} a^{-2(m-1)} C_r^m \beta_{ps}^m n^{1-2(r+m)}$$

$$= \sum_{p=0}^{\infty} \sum_{s=-p}^{p} z^{2p} Y_{2p}^{2s} \sum_{m=p}^{\infty} \beta'^{m}_{ps} n^{1-2m} \qquad 3.3.55$$

where we have combined the sum over r and the sum over m into one sum over m with new coefficients β'^{m}_{ps}.

We will now determine the n dependence of $\Delta\phi(\vec{z},V_n)$. From the definition of ϕ, eq (3.3.48), we may write $\Delta\phi$ as

$$\Delta\phi(\vec{z},V_n) = \sum_{\vec{1}\in V_n}{}' \frac{1}{|\vec{x}(\vec{1})-\vec{z}|} - \sum_{\vec{1}\in V_{n-1}}{}' \frac{1}{|\vec{x}(\vec{1})-\vec{z}|}$$

$$= \sum_{\vec{1}\in S_n} \frac{1}{|\vec{x}(\vec{1})-\vec{z}|} \qquad 3.3.56$$

where S_n is the set of points next to the surface of V_n. i.e. within the region $V_n - V_{n-1}$.

We may expand $1/|\vec{x}(\vec{1})-\vec{z}|$ in a Taylor's series in $\vec{z}$, using eq (3.3.40) to obtain

$$\Delta\phi(\vec{z},V_n) = \sum_{\vec{l}\in S_n} \sum_{m=0}^{\infty} \sum_{p=-m}^{m} \frac{4\pi}{(2m+1)} \frac{z^m}{|\vec{x}(\vec{l})|^{m+1}} Y_m^p(\theta,\phi) Y_m^{p*}(\theta',\phi')$$

$$= \sum_{m=0}^{\infty} \sum_{p=-m}^{m} z^m Y_m^p(\theta,\phi) \sum_{\vec{l}\in S_n} \frac{4\pi}{(2m+1)} \frac{|\vec{x}(\vec{l})|^m Y_m^{p*}(\theta',\phi')}{|\vec{x}(\vec{l})|^{2m+1}} \qquad 3.3.57$$

Using the property of $\Delta\phi(\vec{z},V_n)$ that it is invariant under the operations of inversion and reflection, we may rewrite $\Delta\phi(\vec{z},V_n)$ as

$$\Delta\phi(\vec{z},V_n) = \sum_{m=0}^{\infty} \sum_{p=-m}^{m} z^{2m} Y_{2m}^{2p}(\theta,\phi) \sum_{\vec{l}\in S_n} \frac{4\pi}{(4m+1)} \frac{|\vec{x}(\vec{l})|^{2m} Y_{2m}^{2p*}(\theta',\phi')}{|\vec{x}(\vec{l})|^{4m+1}} \qquad 3.3.58$$

The coefficient

$$\beta_{mp}(S_n) = \sum_{\vec{l}\in S_n} \frac{4\pi}{(4m+1)} \frac{|\vec{x}(\vec{l})|^{2m} Y_{2m}^{2p*}(\theta',\phi')}{|\vec{x}(\vec{l})|^{4m+1}} \qquad 3.3.59$$

is an odd function of n. Each of the terms may be written in the form

$$f(\vec{x}/n)n^{-2m-1}$$

where $f(\vec{z})$ is an even function of $\vec{z}$. As functions of n, each term is of the form

$$f(1+l_1/n, 1+l_2/n, 1+l_3/n)n^{-2m-1}$$

where $|l_i| < n$. However due to the inversion symmetry, only terms of the form

$$f(1+\vec{l}/n) + f(1-\vec{l}/n)$$

etc. have to be considered. This polynomial is an even function of n, i.e.

$$f(1+\vec{l}/n) + f(1-\vec{l}/n) = \sum_{r=0}^{\infty} C_r(\vec{l})n^{-2r} \qquad 3.3.60$$

Thus

$$\beta_{mp}(S_n) = n^{-2m-1} \sum_{r=0}^{\infty} n^{-2r} \sum_{\vec{l} \in S_n} C_r(\vec{l})$$

$$= n^{-2m-1} \sum_{r=0}^{\infty} n^{-2r} \left[n^{-2(r+1)} \sum_{s=0}^{r} C_{rs}^{mp} n^{-2s} \right]$$

$$= n^{-2m-1} \sum_{r=0}^{\infty} C'^{mp}_{r} n^{-2(r-1)}$$

$$= \sum_{r=m}^{\infty} C_{mp}^{r} n^{1-2r} \qquad 3.3.61$$

where C_{mp}^{rs}, C'^{mp}_{r}, and C_{mp}^{r} are constants whose exact nature is not important to us. Substituting (3.3.61) into (3.3.58), we have

$$\phi(\vec{z}, V_n) = \sum_{m=0}^{\infty} \sum_{p=-m}^{m} z^{2m} Y_{2m}^{2p}(\theta, \phi) \sum_{r=m}^{\infty} C_{mp}^{r} n^{1-2r} \qquad 3.3.62$$

which is of the same form as (3.3.55).

We have shown, eq (3.3.47), that there is only one non-trivial solution of

$$\hat{\Gamma} f(\vec{z}, V_n) = I(\vec{z}, (n+\tfrac{1}{2})a) \qquad \text{(see eq (3.3.27))} \qquad 3.3.63$$

which can be written in the form (3.3.46), with the β_{mp}^{s} found in terms of the α_{mp}'s through eqs (3.3.47).

If the coefficients C_{mp}^{s} differ from the β'^{s}_{mp}, then this would mean that there are two possible solutions to eqs (3.3.47). This is obviously not true and hence

$$\beta'^{s}_{mp} = C_{mp}^{s} \qquad 3.3.64$$

Thus $f(\vec{z}, V_n)$ has the same V_n dependence as $\phi(\vec{z}, V_n)$ as required by the second boundary condition.

Therefore the required solution of (3.3.11) is

$$v'(\vec{z}) = \frac{N}{V}\left[f(\vec{z}^{k},V) - f(\vec{z}'^{k},V_n)\right] \qquad 3.3.65$$

where $f(\vec{z}^{k},V)$ and $f(\vec{z}'^{k},V_n)$ can be written in a power series (3.3.46) with the coefficients β^{m}_{ps} obtained from (3.3.47) in terms of the α_{mp}.

Returning to eqs (3.3.20) and (3.3.21), we may solve (3.3.21) for $g(\vec{z}'^{k})$ to obtain

$$g(\vec{z}'^{k}) = \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^{k}|} - \frac{N}{V} f(\vec{z}'^{k},V_n) \qquad 3.3.66$$

Substituting (3.3.66) into (3.3.21), it becomes

$$\sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^{k}|} = \frac{N}{V} f(\vec{z}^{k},V) + \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^{k}|} - \frac{N}{V} f(\vec{z}'^{k},V_n) \qquad 3.3.67$$

Therefore the partial potential may be written in the form

$$V(\vec{z},k) = \frac{q^{k}}{4\pi\epsilon_o}\left\{\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^{k}|} - \frac{N}{V} f(\vec{z}'^{k},V_n)\right\} + \frac{q^{k}}{4\pi\epsilon_o}\frac{N}{V} f(\vec{z}^{k},V) \qquad 3.3.68$$

Eq (3.3.68) lends itself to the definition of two new quantities: $V_i(\vec{z}',k)$ - the intrinsic partial potential and $V_e(\vec{z},k)$ - the extrinsic partial potential. These quantities are defined by

$$V_i(\vec{z}',k) \overset{\text{defn}}{=} \frac{q^{k}}{4\pi\epsilon_o}\left\{\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^{k}|} - \frac{N}{V} f(\vec{z}'^{k},V_n)\right\} \qquad 3.3.69$$

and

$$V_e(\vec{z},k) \overset{\text{defn}}{=} \frac{q^{k}}{4\pi\epsilon_o}\frac{N}{V} f(\vec{z}^{k},V) \qquad 3.3.70$$

$V_i(\vec{z}',k)$ is independent of $\vec{x}_z$. It depends only on $\vec{z}'$, the relative position of the point P with respect to the nearest k=0 lattice point, and on the lattice parameter a. Thus we may consider $V_i(\vec{z}',k)$ as a

periodic function of $\vec{z}$. It is independent of the shape and size of the microscopic region V_n by definition. An intrinsic Madelung constant will be defined using this quantity.

When considering the electrostatic potential or electrostatic energy, the additional term arising from $V_e(\vec{z},k)$ must be considered since it does not always vanish. Unlike V_i, V_e is characteristic of the sample under consideration. In addition to the lattice parameter a, it depends on the position vector $\vec{z}$ non-periodically, and on the shape of the sample, (see eq (3.4.18)).

Writing (3.3.68) in terms of the intrinsic and extrinsic partial potentials, it becomes

$$V(\vec{z},k) = V_i(\vec{z}',k) + V_e(\vec{z},k) \qquad 3.3.71$$

We have therefore succeeded in our objective of finding a usable expression for the partial potential of a finite array of point charges.

D. Sample Calculations

To give a better understanding of the steps involved in calculating the extrinsic and intrinsic partial potentials, we will give detailed calculations for three different problems - the extrinsic partial potential of an ellipsoid, and the intrinsic partial potentials of sub-lattices with cubic and orthorhombic symmetries.

(i) The extrinsic partial potential of an ellipsoid

As stated earlier, our calculations are valid for volumes V which may be build up from basic cubes of side a. Thus the region of integration we should consider is an ellipsoid with a microscopically rough (~a) surface. Letting the volume of the perfect ellipsoid which best approximates V in both size and shape be V_s, then the difference between the two volumes is a microscopically thin shell $V - V_s$. The integral, eq (3.3.39), may thus be written as

$$I(\vec{z},d) = I(\vec{z},d\,) + I'(\vec{z},V-V_s) \qquad 3.4.1$$

where $I'(\vec{z},V-V_s)$ is the integral over the microscopically thin shell and d_s is the parameter associated with V_s. Eq (3.4.1) may be rewritten as

$$I'(\vec{z},V-V_s) = I(\vec{z},d) - I(\vec{z},d_s)$$

$$= \iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|} - \iiint_{V_s} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad 3.4.2$$

If the point of interest is sufficiently far from the surface, then the shell appears of uniform thickness, say $a' \sim a$, and (3.4.2) may be approximated by the surface integral

$$I'(\vec{z}, V-V_s) = a' \iint_{V_s} \frac{dS}{|\vec{y}-\vec{z}|}$$

$$= I_s \qquad 3.4.3$$

where I_s is a constant independent of $\vec{z}$ (Ramsey (1956)[18]) which is of no particular interest to us.

From the standard gravitational theory of ellipsoids (Ramsey), we have

$$I(\vec{z}, d_s) = L_0 - 2\pi(L_1 z_1^2 + L_2 z_2^2 + L_3 z_3^2) \qquad 3.4.4$$

where we have chosen the origin to be at the center of the ellipsoid and the coordinate axes are parallel to the principle axes. The constants L_i (i=0,1,2,3) are given by

$$L_0 = 2\pi b_1 b_2 b_3 \int_0^\infty D(v)\,dv \qquad 3.4.5$$

and

$$L_i = b_1 b_2 b_3 \int_0^\infty \frac{D(v)\,dv}{(b_i^2+v)} \qquad i = 1,2,3 \qquad 3.4.6$$

where b_1, b_2, b_3 are the semi-axes of the ellipsoid and

$$D(v) = \left\{(b_1^2+v)(b_2^2+v)(b_3^2+v)\right\}^{-\frac{1}{2}} \qquad 3.4.7$$

The L_i (i=1,2,3) are the principal values of the so-called depolarization tensor.

In terms of our previous notation (see eq (3.3.41))

$$L_0 = \alpha_{00} d_s^2 \qquad 3.4.8$$

$$L_1 = \frac{1}{3} - \frac{1}{4\pi}\sqrt{\frac{15}{2\pi}}\alpha_{11} + \frac{1}{4\pi}\sqrt{\frac{5}{4\pi}}\alpha_{10} \qquad 3.4.9$$

$$L_2 = \frac{1}{3} + \frac{1}{4\pi}\sqrt{\frac{15}{2\pi}}\alpha_{11} \qquad 3.4.10$$

$$L_3 = \frac{1}{3} - \frac{1}{4\pi}\sqrt{\frac{5}{4\pi}}\,\alpha_{10} \qquad 3.4.11$$

where $d_s = (\pi b_1 b_2 b_3)^{1/3}$.

We now want to solve the differential equation

$$\hat{\Gamma}(\vec{z})f(\vec{z},V_s) = I(\vec{z},d_s)$$
$$= L_0 - 2\pi(L_1 z_1^2 + L_2 z_2^2 + L_3 z_3^2) \qquad 3.4.12$$

Since $I(\vec{z},d_s)$ is second order in z_i, $f(\vec{z},V_s)$ must also be only second order in z_i (see the discussion preceeding eq (3.3.46)). Thus eq (3.3.46) may be written in the simple form

$$f(\vec{z},V_s) = L_0 - 2\pi\left\{L_1(z_1^2+\gamma_{20}^1) + L_2(z_2^2+\gamma_{20}^2) + L_3(z_3^2+\gamma_{20}^3)\right\} \qquad 3.4.13$$

Now

$$\hat{\Gamma}(\vec{z})f(\vec{z},V_s) = L_0 - 2\pi\left\{L_1(z_1^2+\tfrac{1}{4}a+\gamma_{20}^1) + L_2(z_2^2+\tfrac{1}{4}a+\gamma_{20}^2) + L_3(z_3^2+\tfrac{1}{4}a+\gamma_{20}^3)\right\} \qquad 3.4.14$$

Equating eqs (3.4.14) and (3.4.4), we find

$$\gamma_{20}^i = -\tfrac{1}{4}a^2 \qquad i = 1,2,3 \qquad 3.4.15$$

Hence

$$f(\vec{z},V_s) = L_0 + \frac{\pi a^2}{6} - 2\pi(L_1 z_1^2 + L_2 z_2^2 + L_3 z_3^2) \qquad 3.4.16$$

where we have used the property of the L_i that

$$L_1 + L_2 + L_3 = 1 \qquad 3.4.17$$

Therefore the extrinsic partial potential associated with an ellipsoidal cubic array is

$$V_e(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o}\frac{N}{V}\left\{L_0 + I_s + \frac{\pi a^2}{6} - 2\pi(L_1 z_1^2 + L_2 z_2^2 + L_3 z_3^2)\right\} \qquad 3.4.18$$

where we have included the correction term I_s. This expression for $V_e(\vec{z},k)$ is valid only for points far from the surface due to the assumption in the calculation of I_s.

(ii) The intrinsic partial potential for a cubic sub-lattice

This is the next simplest problem, since the function $I(\vec{z},d)$ and hence $f(z,V)$ possess the full symmetry of a cube (i.e. possess m3m symmetry). Therefore, instead of the general equation (3.3.41), we may use the symmetry relations to obtain the simpler expression

$$I(\vec{z},d) = d^2 \sum_{m=0}^{\infty} (z/d)^{2m} \sum_{p=0}^{m(6)} \alpha_m^p S_m^p - \frac{2\pi z^2}{3} \qquad 3.4.19$$

where

$$d = (n+\tfrac{1}{2})a \qquad 3.4.20$$

and m(6) is the integral number of times six divides m. The S_m^p are symmetric combinations of $z^{2m} Y_{2m}^{2p}$ which are invariant under the operations of m3m. The m(6) arise because, although there is only one such combination for $m \leq 5$, when $m \geq 6$ there are two or more symmetric combinations (2 for $6 \leq m \leq 11$, 3 for $12 \leq m \leq 17$ etc). There is no second order combination which is invariant under m3m symmetry operations and hence $S_1^0 = 0$. The coefficients α_m^p appearing in eq (3.4.19) are given by (see (3.3.42))

$$\alpha_1^0 = 0$$

$$\alpha_m^0 = \sqrt{\frac{4m+1}{4\pi}}\, \alpha_{m0} \qquad 3.4.21$$

$$= -\frac{1}{2(m-1)} \iint_{4\pi} d\Omega\, P_{2m}(\cos\theta')\, \eta^{2(m-1)} \qquad m=0,2,3,4,5,6$$

The coefficients α_m^p $(p \neq 0)$ are difficult to evaluate. However we need only α_6^1 which was found by an analytic continuation of the ϵ_t^{mpr} (see Table 3.4). Since we are only interested in the S_m^p up to m = 6,

we will introduce the new polynomials

$$S_{2m} = S_m^0 \qquad m = 0,1,2,3,4,5 \qquad 3.4.22$$

$$S_{12} = S_6^0 + (\alpha_6^1/\alpha_6^0) S_6^1 \qquad 3.4.23$$

Explicit expressions for the above 6 polynomials is given in Table 3.1. The coefficients of the six polynomials in eq (3.4.19) are given in Table 3.2. The expression for η for a cube which is needed in eq (3.4.21) is given in Table 3.3.

The first 6 of the $\hat{D}_{2m}$ operators are given in Table 3.4. If we operate $\hat{D}_{2m}$ on S_{2p}, then we obtain an S_{2t} of equal or of lower order. i.e.

$$\tilde{D}_{2m} S_{2p} = \epsilon^{mp} S_{2(p-m)} \qquad m \leq p$$
$$= 0 \qquad m > p \qquad 3.4.24$$

The values for ϵ^{mp} are given in Table 3.5. Since $S_2 = 0$, we have immediately that

$$\hat{D}_{2m} S_{2(m+1)} = 0 \quad \text{(or hence } \epsilon^{m,m+2} = 0 \text{ for all m)} \qquad 3.4.25$$

and since the S_{2p} are solutions of Laplace's equation

$$\hat{D}_2 S_{2m} = 0 \quad \text{(or hence } \epsilon^{2,m} = 0 \text{ for all m)} \qquad 3.4.26$$

Since $I(\vec{z},d)$ has the simpler form given by (3.4.19), eq (3.4.46) also can be written in the simpler form

$$f(\vec{z},V_n) = d^2 \sum_{m=0}^{\infty} d^{-2m} \sum_{p=0}^{m} \sum_{t=0}^{p(6)} \beta_{pt}^m S_p^t - \frac{2\pi}{3}(z^2 - \tfrac{1}{4}a^2) \qquad 3.4.27$$

Considering only the terms up to m = 6, and ignoring the remainder of the terms, the explicit expression for $f(\vec{z},V_n)$ is

$$f(\vec{z},V_n) = \beta_0^0 d^2 + 0d^0 + d^{-2}(\beta_2^2 S_4 + \beta_2^0) + d^{-4}(\beta_3^3 S_6 + \beta_3^0) \qquad 3.4.28$$
$$+ d^{-6}(\beta_4^4 S_8 + \beta_4^2 S_4 + \beta_4^0) + d^{-8}(\beta_5^5 S_{10} + \beta_5^3 S_6 + \beta_5^2 S_4 + \beta_5^0)$$
$$+ d^{-10}(\beta_6^6 S_{12} + \beta_6^4 S_8 + \beta_6^3 S_6 + \beta_6^2 S_4 + \beta_6^0) + \frac{2\pi}{3}(z^2 - \tfrac{1}{4}a^2)$$

where we have set

$$\beta_m^p = \beta_{m0}^p \qquad 3.4.29$$

and used S_m rather than S_m^p.

Operating on $f(\vec{z},V_n)$ with $\hat{\Gamma}$ gives

$$\hat{\Gamma}(\vec{z})f(\vec{z},V_n) = \beta_0^0 d^2 + d^{-2}\{\beta_2^2(S_4+\epsilon^{22}) + \beta_2^0\} + d^{-4}\{\beta_3^3(S_6+\epsilon^{33}) + \beta_3^0\}$$
$$+ d^{-6}\{\beta_4^4(S_8+\epsilon^{24}S_4+\epsilon^{44}) + \beta_4^2(S_4+\epsilon^{22}) + \beta_4^0\}$$
$$+ d^{-8}\{\beta_5^5(S_{10}+\epsilon^{25}S_6+\epsilon^{35}S_4+\epsilon^{55}) + \beta_5^3(S_6+\epsilon^{33}) + \beta_5^2(S_2+\epsilon^{22}) + \beta_5^0\}$$
$$+ d^{-10}\{\beta_6^6(S_{12}+\epsilon^{26}S_8+\epsilon^{36}S_6+\epsilon^{46}S_4+\epsilon^{66}) + \beta_6^4(S_8+\epsilon^{24}S_4+\epsilon^{44}) + \beta_6^3(S_6+\epsilon^{33})$$
$$+ \beta_6^2(S_4+\epsilon^{22}) + \beta_6^0\} + \frac{2\pi z^2}{3} \qquad 3.4.30$$

Equating the coefficients of the different powers of d and the different orders of S_m in eqs (3.4.30) and (3.4.19), we find

$$\beta_0^0 = \alpha_0 \quad \beta_2^2 = \alpha_2 \quad \beta_2^0 = -\epsilon^{22}\alpha_2 \quad \beta_3^3 = \alpha_3 \quad \beta_3^0 = -\epsilon^{33}\alpha_3$$
$$\beta_4^4 = \alpha_4 \quad \beta_4^2 = -\epsilon^{24}\alpha_4 \quad \beta_4^0 = (-\epsilon^{44}+\epsilon^{22}\epsilon^{24})\alpha_4 \qquad 3.4.31$$
$$\beta_5^5 = \alpha_5 \quad \beta_5^3 = -\epsilon^{25}\alpha_5 \quad \beta_5^2 = -\epsilon^{35}\alpha_5 \quad \beta_5^0 = (-\epsilon^{55}+\epsilon^{33}\epsilon^{25}+\epsilon^{22}\epsilon^{35})\alpha_5$$
$$\beta_6^6 = \alpha_6 \quad \beta_6^4 = -\epsilon^{26}\alpha_6 \quad \beta_6^3 = -\epsilon^{36}\alpha_6 \quad \beta_6^2 = (-\epsilon^{46}+\epsilon^{24}\epsilon^{26})\alpha_6$$
$$\beta_6^0 = (-\epsilon^{66}+\epsilon^{44}\epsilon^{26}+\epsilon^{33}\epsilon^{36}+\epsilon^{22}\epsilon^{46}-\epsilon^{22}\epsilon^{24}\epsilon^{26})\alpha_6$$

where we have set

$$\alpha_m = \alpha_m^0 \qquad 3.4.32$$

The numerical values of the β_m^p are given in Table 6.3. Substituting these values into (3.4.29), we obtain

$$f(\vec{z},V_n) = a^2\Big\{ \alpha_0(n+\tfrac{1}{2})^2 + \alpha_2(n+\tfrac{1}{2})^{-2}(S_4a^{-4}+\frac{1}{40}) + \alpha_3(n+\tfrac{1}{2})^{-4}(S_6a^{-6}-\frac{1}{84})$$
$$+ \alpha_4(n+\tfrac{1}{2})^{-6}(S_8a^{-8}+\frac{7}{6}S_4a^{-4}+\frac{13}{480}) + \alpha_5(n+\tfrac{1}{2})^{-8}(S_{10}a^{-10}+\frac{21}{10}S_6a^{-6}-S_4a^{-4}-\frac{23}{440}$$
$$+ \alpha_6(n+\tfrac{1}{2})^{-10}(S_{12}a^{-12}+12S_8a^{-8}+5S_6a^{-6}+13S_4a^{-4}+\frac{2611}{1265}) + \frac{2\pi}{3}(z^2a^{-2}-\tfrac{1}{4})\Big\} \qquad 3.4.33$$

Substituting (3.4.33) into eq (3.3.68), the explicit expression for the intrinsic partial potential at point $\vec{z}'$ associated with a cubic lattice with lattice constant a is

$$V_i(\vec{z}',k) = \frac{q^k}{4\pi\epsilon_0 a}\Big\{ \sum_{l_1,l_2,l_3=-n}^{n}{}' \frac{a}{\{(l_1a-z_1'^k)^2+(l_2a-z_2'^k)^2+(l_3a-z_3'^k)^2\}^{\frac{1}{2}}}$$
$$- \alpha_0(n+\tfrac{1}{2})^2 - \alpha_2(n+\tfrac{1}{2})^{-2}(S_4a^{-4}+\frac{1}{40}) - \alpha_3(n+\tfrac{1}{2})^{-4}(S_6a^{-6}-\frac{1}{84})$$
$$- \alpha_4(n+\tfrac{1}{2})^{-6}(S_8a^{-8}+\frac{7}{6}S_4a^{-4}+\frac{13}{480}) - \alpha_5(n+\tfrac{1}{2})^{-8}(S_{10}a^{-10}+\frac{21}{10}S_6a^{-6}-S_4a^{-4}-\frac{23}{440})$$
$$- \alpha_6(n+\tfrac{1}{2})^{-10}(S_{12}a^{-12}+12S_8a^{-8}+5S_6a^{-6}+13S_4a^{-4}+\frac{2611}{1265}) + \frac{2\pi}{3}(|\vec{z}'^k|^2a^{-2}-\tfrac{1}{4})\Big\} \qquad 3.4.34$$

where the S_m are understood to be functions of $\vec{z}'^k$. Although $V_i(\vec{z}',k)$ may appear to be a function of n, the n dependence of the sum over $\vec{l}$ is exactly canceled by the n dependence of the series (at least up to

$(n+\frac{1}{2})^{-10}$ which is the order to which (3.4.34) is valid).

We note that

$$\iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} = \alpha_0 (n+\tfrac{1}{2})^2 a^2 + \frac{2\pi z^2}{3} + O([n+\tfrac{1}{2}]^{-2}) \qquad 3.4.35$$

(See eq (3.4.19)).

Therefore we may write $V_i(\vec{z}',k)$ in the form

$$V_i(\vec{z}',k) = \frac{q^k}{4\pi\epsilon_o}\left\{ \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^k|} - \frac{1}{a^3}\iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^k|} + \frac{\pi}{6a} + O([n+\tfrac{1}{2}]^{-2}) \right\} \qquad 3.4.36$$

Taking the limit $V_n \to \infty$, of eq (3.4.36), we have

$$\lim_{V_n\to\infty} V_i(\vec{z}',k) = \frac{q^k}{4\pi\epsilon_o}\left[\lim_{V_n\to\infty} \left\{ \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^k|} - \frac{1}{a^3}\iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'^k|} \right\} + \frac{\alpha}{6a} \right] \qquad 3.4.37$$

Comparing (3.4.37) with (2.7.4), we see that the intrinsic partial potential is the quantity which Tosi evaluated, i.e. the electrostatic potential due to a neutralized Bravais lattice.

$$S_0 = 1$$

$$S_4 = z_1^4 + z_2^4 + z_3^4 - 3(z_1^2 z_2^2 + z_2^2 z_3^2 + z_3^2 z_1^2)$$

$$S_6 = z_1^6 + z_2^6 + z_3^6 - \frac{15}{2}\left[z_1^4(z_2^2+z_3^2) + z_2^4(z_3^2+z_1^2) + z_3^4(z_1^2+z_2^2)\right] + 90 z_1^2 z_2^2 z_3^2$$

$$S_8 = z_1^8 + z_2^8 + z_3^8 - 14\left[z_1^6(z_2^2+z_3^2) + z_2^6(z_3^2+z_1^2) + z_3^6(z_1^2+z_2^2)\right] + 35(z_1^4 z_2^4 + z_2^4 z_3^4 + z_3^4 z$$

$$S_{10} = z_1^{10} + z_2^{10} + z_3^{10} - \frac{45}{2}\left[z_1^8(z_2^2+z_3^2) + z_2^8(z_3^2+z_1^2) + z_3^8(z_1^2+z_2^2)\right] + 504 z_1^2 z_2^2 z_3^2 (z_1^4 + z_2^4 + z_3^4$$
$$- 630 z_1^2 z_2^2 z_3^2 (z_1^2 z_2^2 + z_2^2 z_3^2 + z_3^2 z_1^2) + 21\left[z_1^6(z_2^4+z_3^4) + z_2^6(z_3^4+z_1^4) + z_3^6(z_1^4+z_2^4)\right]$$

$$S_{12} = z_1^{12} + z_2^{12} + z_3^{12} - 33\left[z_1^{10}(z_2^2+z_3^2) + z_2^{10}(z_3^2+z_1^2) + z_3^{10}(z_1^2+z_2^2)\right]$$
$$+ \frac{945}{2}\left[z_1^8(z_2^4+z_3^4) + z_2^8(z_3^4+z_1^4) + z_3^8(z_1^4+z_2^4)\right] - 1350 z_1^2 z_2^2 z_3^2 (z_1^6 + z_2^6 + z$$
$$+ 3150 z_1^2 z_2^2 z_3^2\left[z_1^4(z_2^2+z_3^2) + z_2^4(z_3^2+z_1^2) + z_3^4(z_1^2+z_2^2)\right] - 15750\, z_1^4 z_2^4 z_3^4$$
$$- 1092(z_1^6 z_2^6 + z_2^6 z_3^6 + z_3^6 z_1^6)$$

Table 3.1

Symmetric Combinations of Spherical Harmonics

m	α_m
0	$+ 9.520309455918213$
2	$-\frac{4\sqrt{3}}{27}$
3	$-\frac{\sqrt{3}}{486}$
4	$\frac{17\sqrt{3}}{5103}$
5	$\frac{13\sqrt{3}}{314928}$
6	$\frac{49728559\sqrt{3}}{11.2^{18}.3^{11}}$

Table 3.2

Coefficients α_m, of $S_{2m}/[(n+\frac{1}{2})a]^{2m-2}$, which appear in the expansion of $\iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}|}$ for V_n a cube

ϕ limits	θ limits	$\eta(\theta,\phi)$
$-\frac{\pi}{4}, \frac{\pi}{4}$	$0, \tan^{-1}\left[\frac{1}{\cos\phi}\right]$	$\cos\theta$
	$\tan^{-1}\left[\frac{1}{\cos\phi}\right], \pi - \tan^{-1}\left[\frac{1}{\cos\phi}\right]$	$\sin\theta\cos\phi$
	$\pi - \tan^{-1}\left[\frac{1}{\cos\phi}\right], \pi$	$-\cos\theta$
$\frac{\pi}{4}, \frac{3\pi}{4}$	$0, \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}\pi)}\right]$	$\cos\theta$
	$\tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}\pi)}\right], \pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}\pi)}\right]$	$\sin\theta\cos(\phi-\frac{1}{2}\pi)$
	$\pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}\pi)}\right], \pi$	$-\cos\theta$
$\frac{3\pi}{4}, \frac{5\pi}{4}$	$0, \tan^{-1}\left[\frac{1}{\cos(\phi-\pi)}\right]$	$\cos\theta$
	$\tan^{-1}\left[\frac{1}{\cos(\phi-\pi)}\right], \pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\pi)}\right]$	$\sin\theta\cos(\phi-\pi)$
	$\pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\pi)}\right], \pi$	$-\cos\theta$
$\frac{5\pi}{4}, \frac{7\pi}{4}$	$0, \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}3\pi)}\right]$	$\cos\theta$
	$\tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}3\pi)}\right], \pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}3\pi)}\right]$	$\sin\theta\cos(\phi-\frac{1}{2}3\pi)$
	$\pi - \tan^{-1}\left[\frac{1}{\cos(\phi-\frac{1}{2}3\pi)}\right], \pi$	$-\cos\theta$

Table 3.3

The Angular Dependence of η for a Cube

m	$\hat{D}_{2m}$
0	1
1	$\frac{a^2}{2^2 3!}\nabla^2$
2	$\frac{a^4}{2^4}\left[\frac{1}{5!}\left(\frac{\partial^4}{\partial z_1^4}+\frac{\partial^4}{\partial z_2^4}+\frac{\partial^4}{\partial z_3^4}\right)+\frac{1}{(3!)^2}\left(\frac{\partial^4}{\partial z_1^2\partial z_2^2}+\frac{\partial^4}{\partial z_2^2\partial z_3^2}+\frac{\partial^4}{\partial z_3^2\partial z_1^2}\right)\right]$
3	$\frac{a^6}{2^6}\left[\frac{1}{7!}\left(\frac{\partial^6}{\partial z_1^6}+\frac{\partial^6}{\partial z_2^6}+\frac{\partial^6}{\partial z_3^6}\right)+\frac{1}{5!3!}\left\{\frac{\partial^4}{\partial z_1^4}\left(\frac{\partial^2}{\partial z_2^2}+\frac{\partial^2}{\partial z_3^2}\right)+\frac{\partial^4}{\partial z_2^4}\left(\frac{\partial^2}{\partial z_3^2}+\frac{\partial^2}{\partial z_1^2}\right)+\frac{\partial^4}{\partial z_3^4}\left(\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right)\right.\right.$ $\left.\left.+\frac{1}{(3!)^3}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\right]$
4	$\frac{a^8}{2^8}\left[\frac{1}{9!}\left(\frac{\partial^8}{\partial z_1^8}+\frac{\partial^8}{\partial z_2^8}+\frac{\partial^8}{\partial z_3^8}\right)+\frac{1}{7!3!}\left\{\frac{\partial^6}{\partial z_1^6}\left(\frac{\partial^2}{\partial z_2^2}+\frac{\partial^2}{\partial z_3^2}\right)+\frac{\partial^6}{\partial z_2^6}\left(\frac{\partial^2}{\partial z_3^2}+\frac{\partial^2}{\partial z_1^2}\right)+\frac{\partial^6}{\partial z_3^6}\left(\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right)\right.\right.$ $\left.\left.+\frac{1}{5!(3!)^2}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\nabla^2+\frac{1}{(5!)^2}\left(\frac{\partial^8}{\partial z_1^4\partial z_2^4}+\frac{\partial^8}{\partial z_2^4\partial z_3^4}+\frac{\partial^8}{\partial z_3^4\partial z_1^4}\right)\right]$

(continued)

Table 3.4

Explicit Expressions for the First Six $\hat{D}_{2m}$'s

Table 3.4 cont.

m	$\hat{D}_{2m}$

5 $$\frac{a^{10}}{2^{10}}\Bigg[\frac{1}{11!}\left(\frac{\partial^{10}}{\partial z_1^{10}}+\frac{\partial^{10}}{\partial z_2^{10}}+\frac{\partial^{10}}{\partial z_3^{10}}\right)+\frac{1}{7!(3!)^2}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\left(\frac{\partial^4}{\partial z_1^4}+\frac{\partial^4}{\partial z_2^4}+\frac{\partial^4}{\partial z_3^4}\right)$$
$$+\frac{1}{9!3!}\left\{\frac{\partial^8}{\partial z_1^8}\left(\frac{\partial^2}{\partial z_2^2}+\frac{\partial^2}{\partial z_3^2}\right)+\frac{\partial^8}{\partial z_2^8}\left(\frac{\partial^2}{\partial z_3^2}+\frac{\partial^2}{\partial z_1^2}\right)+\frac{\partial^8}{\partial z_3^8}\left(\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right)\right\}$$
$$+\frac{1}{7!5!}\left\{\frac{\partial^6}{\partial z_1^6}\left(\frac{\partial^4}{\partial z_2^4}+\frac{\partial^4}{\partial z_3^4}\right)+\frac{\partial^6}{\partial z_2^6}\left(\frac{\partial^4}{\partial z_3^4}+\frac{\partial^4}{\partial z_1^4}\right)+\frac{\partial^6}{\partial z_3^6}\left(\frac{\partial^4}{\partial z_1^4}+\frac{\partial^4}{\partial z_2^4}\right)\right\}$$
$$+\frac{1}{(5!)^2 3!}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\left(\frac{\partial^4}{\partial z_1^2\partial z_2^2}+\frac{\partial^4}{\partial z_2^2\partial z_3^2}+\frac{\partial^4}{\partial z_3^2 z_1^2}\right)\Bigg]$$

6 $$\frac{a^{12}}{2^{12}}\Bigg[\frac{1}{13!}\left(\frac{\partial^{12}}{\partial z_1^{12}}+\frac{\partial^{12}}{\partial z_2^{12}}+\frac{\partial^{12}}{\partial z_3^{12}}\right)+\frac{1}{9!(3!)^2}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\left(\frac{\partial^6}{\partial z_1^6}+\frac{\partial^6}{\partial z_2^6}+\frac{\partial^6}{\partial z_3^6}\right)$$
$$+\frac{1}{11!3!}\left\{\frac{\partial^{10}}{\partial z_1^{10}}\left(\frac{\partial^2}{\partial z_2^2}+\frac{\partial^2}{\partial z_3^2}\right)+\frac{\partial^{10}}{\partial z_2^{10}}\left(\frac{\partial^2}{\partial z_3^2}+\frac{\partial^2}{\partial z_1^2}\right)+\frac{\partial^{10}}{\partial z_3^{10}}\left(\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right)\right\}$$
$$+\frac{1}{9!5!}\left\{\frac{\partial^8}{\partial z_1^8}\left(\frac{\partial^4}{\partial z_2^4}+\frac{\partial^4}{\partial z_3^4}\right)+\frac{\partial^8}{\partial z_2^8}\left(\frac{\partial^4}{\partial z_3^4}+\frac{\partial^4}{\partial z_1^4}\right)+\frac{\partial^8}{\partial z_3^8}\left(\frac{\partial^4}{\partial z_1^4}+\frac{\partial^4}{\partial z_2^4}\right)\right\}+\frac{1}{(5!)^3}\frac{\partial^{12}}{\partial z_1^4\partial z_2^4\partial z_3^4}$$
$$+\frac{1}{7!5!3!}\frac{\partial^6}{\partial z_1^2\partial z_2^2\partial z_3^2}\left\{\frac{\partial^4}{\partial z_1^4}\left(\frac{\partial^2}{\partial z_2^2}+\frac{\partial^2}{\partial z_3^2}\right)+\frac{\partial^4}{\partial z_2^4}\left(\frac{\partial^2}{\partial z_3^2}+\frac{\partial^2}{\partial z_1^2}\right)+\frac{\partial^4}{\partial z_3^4}\left(\frac{\partial^2}{\partial z_1^2}+\frac{\partial^2}{\partial z_2^2}\right)\right\}$$
$$+\frac{1}{(7!)^2}\left(\frac{\partial^{12}}{\partial z_1^6\partial z_2^6}+\frac{\partial^{12}}{\partial z_2^6\partial z_3^6}+\frac{\partial^{12}}{\partial z_3^6\partial z_1^6}\right)\Bigg]$$

1	0	0	0	0	0	0
1	$\frac{1}{4}a^2$	0	0	0	0	0
1	0	$-\frac{1}{40}a^4$	0	0	0	0
1	0	0	$\frac{1}{84}a^6$	0	0	0
1	0	$-\frac{7}{6}a^4$	0	$\frac{1}{480}a^8$	0	0
1	0	$-\frac{21}{16}a^4$	$1a^6$	0	$-\frac{1}{440}a^{10}$	0
1	0	$-12a^4$	$5a^6$	$1a^8$	0	$-\frac{1}{364}a^{12}$

Diagonal Components

$$\frac{2}{2},\ \frac{6}{4.3.2},\ -\frac{3}{6.5.4},\ \frac{4}{8.7.6},\ \frac{3/2}{10.9.8},\ -\frac{3}{12.11.10},\ -\frac{6}{14.13.12}$$

Table 3.5

Components of the ϵ_0^{mp0} Matric

The ϵ_0^{m60} components were obtained by analytic continuation of the diagonal component series by assuming it could be written with a denominator in the same sequence as the other denominators as indicated.

1	$-\frac{1}{4}a^2$	$\frac{1}{40}a^4$	$-\frac{1}{84}a^6$	$\frac{13}{480}a^8$	$-\frac{23}{440}a^{10}$	$\frac{2611}{1265}a^{12}$
0	1	0	0	0	0	0
0	0	1	0	$\frac{7}{6}a^4$	$-1a^6$	$13a^8$
0	0	0	1	0	$\frac{21}{10}a^4$	$5a^6$
0	0	0	0	1	0	$12a^4$
0	0	0	0	0	1	0
0	0	0	0	0	0	1

Table 3.6

The β_m^p/α_m Matrix for a Cubic Lattice

(iii) The intrinsic partial potential for an orthorhombic sub-lattice

To show how the method described in Section C is generalized to more complex sub-lattices, we will evaluate the intrinsic partial potential for an orthorhombic sub-lattice with lattice parameters (a_1,a_2,a_3). The integral in eq (2.2.1) is now over a box of sides (a_1,a_2,a_3) rather than over a cube of side a. The method described in Section C proceeds step by step for the orthorhombic case as it does for the cubic case.

We were only able to evaluate the coefficients α_{mp}, eq (3.3.42) up to m = 2. The α_{m0} are easily evaluated for $m > 2$ but symmetry operations are not sufficient to determine the α_{mp} $(p \neq 0)$ as was true for the cubic case.

As in Section C, we find that an expression for the integral over a box with sides $(2n+1)(a_1,a_2,a_3)$ is needed (cf volume V_n - a cube of side $(2n+1)a$). We may write $I(\vec{z},d)$, (keeping only terms up to m=2), as

$$I(\vec{z},d) = \alpha_{00}d + \alpha_{20}z^2Y_{20} + \alpha_{22}z^2(Y_{22}+Y_{2,-2}) + d^{-2}\Big\{\alpha_{40}z^4Y_{40} + \alpha_{42}z^4(Y_{42}+Y_{4,-2}) + \alpha_{44}z^4(Y_{44}+Y_{4,-4})\Big\} + \frac{2\pi z^2}{3} \qquad 3.4.37$$

where

$$d = (n+\tfrac{1}{2})a \qquad 3.4.38$$

with

$$a = (a_1^2 + a_2^2 + a_2^2)^{\frac{1}{2}} \qquad 3.4.39$$

The operator $\hat{\Gamma}(\vec{z})$, up to the fourth order, is (cf Table 3.4)

$$\hat{\Gamma}(\vec{z}) = 1 + \frac{1}{24}\left(a_1^2\frac{\partial^2}{\partial z_1^2} + a_2^2\frac{\partial^2}{\partial z_2^2} + a_3^2\frac{\partial^2}{\partial z_3^2}\right) + \frac{1}{16}\left[\frac{1}{5!}\left(a_1^4\frac{\partial^4}{\partial z_1^4} + a_2^4\frac{\partial^4}{\partial z_2^4} + a_3^4\frac{\partial^4}{\partial z_3^4}\right)\right.$$

$$\left. + \frac{1}{(3!)^2}\left(a_1^2a_2^2\frac{\partial^4}{\partial z_1^2\partial z_2^2} + a_2^2a_3^2\frac{\partial^4}{\partial z_2^2\partial z_3^2} + a_3^2a_1^2\frac{\partial^4}{\partial z_3^2\partial z_1^2}\right)\right] \qquad 3.4.40$$

Instead of writing $I(\vec{z},d)$ in the form (3.4.37), it is more convenient to write it as

$$I(\vec{z},d) = \alpha_{00}d^2 + \alpha_{20}P_{20}(\vec{z}) + \alpha_{22}P_{22}(\vec{z}) + d^{-2}\{\alpha_{40}P_{40}(\vec{z}) + \alpha_{42}P_{42}(\vec{z})$$

$$+ \alpha_{44}P_{44}(\vec{z})\} + \frac{2\pi z^2}{3} \qquad 3.4.41$$

where the $P_{rs}(\vec{z})$ are polynomials of order m in the components of $\vec{z}$. The relevant $P_{rs}(\vec{z})$ up to m = 4 are given in Table 3.7. The α_{m0} are determined from (3.3.42) using the η given in Table 3.8. The α_{mp} ($p\neq 0$) were found using the symmetry properties of the integral. (It is invariant under the combined operation $a_1 \to a_2$, $a_2 \to a_3$, $a_3 \to a_1$; $z_1 \to z_2$, $z_2 \to z_3$, $z_3 \to z_1$ etc). The values for the $\alpha_{2m,2p}$ are given in Table 3.9. The ϵ_t^{mps} for the operator $\hat{\Gamma}$ and polynomials P_{rs} are given in Table 3.10.

The form of the solution $f(\vec{z},V)$ is

$$f(\vec{z},V) = \beta_{00}^0 d^2 + \beta_{20}^2 P_{20} + \beta_{22}^2 P_{22} + \beta_{00}^2 + d^{-2}(\beta_{40}^4 P_{40} + \beta_{42}^4 P_{42} + \beta_{44}^4 P_{44} +$$

$$+ \beta_{20}^4 P_{20} + \beta_{22}^4 P_{22} + \beta_{00}^4) + \frac{2\pi(z^2 - a^2)}{3} \qquad 3.4.42$$

Thus, operating on $f(\vec{z},V)$ with $\hat{\Gamma}$, gives us

$$\hat{\Gamma}(\vec{z})f(\vec{z},V) = \beta_{00}^{0}d^{2} + \beta_{20}^{2}(P_{20}+\epsilon_{0}^{220}) + \beta_{22}^{2}(P_{22}+\epsilon_{0}^{222}) + \beta_{00}^{2}$$

$$+ d^{-2}\{\beta_{40}^{4}(P_{40}+\epsilon_{0}^{240}P_{20}+\epsilon_{2}^{240}P_{22}+\epsilon_{0}^{440}) + \beta_{42}^{4}(P_{42}+\epsilon_{0}^{242}P_{20}+\epsilon_{2}^{242}P_{22}+\epsilon_{0}^{4}$$

$$+\beta_{44}^{4}(P_{44}+\epsilon_{0}^{244}P_{20}+\epsilon_{2}^{244}P_{22}+\epsilon_{0}^{444}) + \beta_{20}^{4}(P_{20}+\epsilon_{0}^{220})$$

$$+\beta_{22}^{4}(P_{22}+\epsilon_{0}^{222})+\beta_{00}^{4}\} + \frac{2\pi z^{2}}{3} \qquad 3.4.43$$

Comparing (3.4.37) and (3.4.43), and equating the coefficients of the terms with equal powers of $\vec{z}$ and the same polynomial P_{rs}, we have

$$\beta_{00}^{0} = \alpha_{00} \quad \beta_{20}^{2} = \alpha_{20} \quad \beta_{22}^{2} = \alpha_{22} \quad \beta_{00}^{2} = -(\alpha_{20}\epsilon_{0}^{220}+\alpha_{22}\epsilon_{0}^{222})$$

$$\beta_{40}^{4} = \alpha_{40} \quad \beta_{42}^{4} = \alpha_{42} \quad \beta_{44}^{4} = \alpha_{44}$$

$$\beta_{20}^{4} = -(\epsilon_{0}^{240}\alpha_{40} +\epsilon_{0}^{242}\alpha_{42} + \epsilon_{0}^{244}\alpha_{44}) \qquad 3.4.44$$

$$\beta_{22}^{4} = -(\epsilon_{2}^{240}\alpha_{40} +\epsilon_{2}^{242}\alpha_{42} + \epsilon_{2}^{244}\alpha_{44})$$

$$\beta_{00}^{4} = -(\epsilon_{0}^{440}\alpha_{40}+ \epsilon_{0}^{442}\alpha_{42} + \epsilon_{0}^{444}\alpha_{44} + \epsilon_{0}^{220}\beta_{20}^{4} + \epsilon_{0}^{222}\beta_{22}^{4})$$

Thus the intrinsic partial potential associated with an orthorhombic lattice with lattice parameters (a_1,a_2,a_3) is

$$V_i(\vec{z}',0)= \frac{q^0}{4\pi\epsilon_o}\left[\sum_{l_1,l_2,l_3=-n}^{n\ '} \frac{1}{\{(l_1a_1-z_1')^2+(l_2a_2-z_2')^2+(l_3a_3-z_3')^2\}^{\frac{1}{2}}} \right.$$

$$- \frac{1}{a_1a_2a_3}\left\{\alpha_{00}\{(n+\tfrac{1}{2})a\}^2 + \alpha_{20}P_{20} + \alpha_{22}P_{22} - \beta_{00}^{2} + \frac{1}{\{(n+\tfrac{1}{2})a\}^2}(\alpha_{40}P_{40}\right.$$

$$\left.\left.+\alpha_{42}P_{42}+ \alpha_{44}P_{44}+ \beta_{20}^{4}P_{20}+ \beta_{22}^{4}P_{22}+ \beta_{00}^{4})\right\} + \frac{2\pi}{3}(z'^{2} - \frac{a^2}{12}) + O\{[(n+\tfrac{1}{2})a]^{-4}\}\right]$$

3.4.45

$$P = 1$$

$$P_{20} = z_3^2 - \tfrac{1}{2}(z_1^2 + z_2^2)$$

$$P_{22} = \tfrac{1}{2}(z_1^2 - z_2^2)$$

$$P_{40} = z_3^4 + \frac{3}{64}(z_1^4 + z_2^4) - 3z_3^2(z_1^2 + z_2^2) + z_1^2 z_2^2$$

$$P_{42} = -\left\{z_1^4 - z_2^4 - 6z_3^2(z_1^2 - z_2^2)\right\}$$

$$P_{44} = z_1^4 + z_2^4 - 6z_1^2 z_2^2$$

Table 3.7

The Polynomials $P_{2m,2p}$ for m = 0,1,2

ϕ limits	θ limits	$\eta(\theta,\phi)/d$
$-\phi_1, \phi_1$	$0, \tan^{-1}\left[\frac{b/c}{\cos\phi}\right]$	$\cos\theta/c$
	$\tan^{-1}\left[\frac{b/c}{\cos\phi}\right], \pi - \tan^{-1}\left[\frac{b/c}{\cos\phi}\right]$	$\sin\theta\cos\phi/b$
	$\pi - \tan^{-1}\left[\frac{b/c}{\cos\phi}\right], \pi$	$-\cos\theta/c$
$\phi_1, \pi - \phi_1$	$0, \tan^{-1}\left[\frac{b/c}{\cos(\phi-\frac{1}{2}\pi)}\right]$	$\cos\theta/c$
	$\tan^{-1}\left[\frac{b/c}{\cos(\phi-\frac{1}{2}\pi)}\right], \pi - \tan^{-1}\left[\frac{b/c}{\cos(\phi-\frac{1}{2}\ )}\right]$	$\sin\theta\cos(\phi-\frac{1}{2}\pi)/a$
	$\pi - \tan^{-1}\left[\frac{b/c}{\cos(\phi-\frac{1}{2}\pi)}\right], \pi$	$-\cos\theta/c$
$\pi - \phi_1, \pi + \phi_1$	$0, \pi$	$\eta(\theta,\phi-\pi)/d$
$\pi + \phi_1, 2\pi - \phi_1$	$0, \pi$	$\eta(\theta,\phi-\pi)/d$

$$\phi_1 = \tan^{-1}(a/b)$$

Table 3.8

$\eta(\theta,\phi)$ for a Box with Sides 2(a,b,c)

m	p	α_{mp}
0	0	$4\left[bc\ln\left\{\frac{(a^2+b^2+c^2)^{\frac{1}{2}}+a}{(a^2+b^2+c^2)^{\frac{1}{2}}-a}\right\} + ca\ln\left\{\frac{(a^2+b^2+c^2)^{\frac{1}{2}}+b}{(a^2+b^2+c^2)^{\frac{1}{2}}-b}\right\} + ab\ln\left\{\frac{(a^2+b^2+c^2)^{\frac{1}{2}}+c}{(a^2+b^2+c^2)^{\frac{1}{2}}-c}\right\}\right.$ $\left. - a^2\tan^{-1}\left\{\frac{bc}{a(a^2+b^2+c^2)^{\frac{1}{2}}}\right\} - b^2\tan^{-1}\left\{\frac{ca}{b(a^2+b^2+c^2)^{\frac{1}{2}}}\right\} - c^2\tan^{-1}\left\{\frac{ab}{c(a^2+b^2+c^2)^{\frac{1}{2}}}\right\}\right]$
1	0	$4\left[-\frac{1}{2}\pi + 3\tan^{-1}\left\{\frac{ab}{c(a^2+b^2+c^2)^{\frac{1}{2}}}\right\} + \frac{3abc}{(a^2+b^2+c^2)^{\frac{1}{2}}}\left\{\frac{\ln(c/a)}{(a^2+c^2)} + \frac{\ln(c/b)}{(b^2+c^2)}\right\}\right]$
1	1	$2\left[\alpha_{20}(b,c,a) + \frac{1}{2}\alpha_{20}(a,b,c)\right]$
2	0	$\frac{abc}{12(a^2+b^2+c^2)} - \frac{c^2}{12}\left\{3\left(\frac{1}{(a^2+c^2)} + \frac{1}{(b^2+c^2)}\right) + 2\left(\frac{a^2}{(a^2+c^2)^2} + \frac{b^2}{(b^2+c^2)^2}\right)\right\}$
2	1	$-\frac{1}{2}\left[\alpha_{40}(b,c,a) - \alpha_{40}(c,a,b)\right]$
2	2	$\frac{1}{2}\left[\alpha_{40}(b,c,a) + \alpha_{40}(c,a,b) - \frac{3}{4}\alpha_{40}(a,b,c)\right]$

Table 3.9

The Coefficients α_{mp} for a Box of Sides 2(a,b,c)

$$\epsilon_t^{0pm} = \delta_{mt}$$

$$\epsilon_t^{22m} = \begin{pmatrix} v_2^0 & 0 \\ 0 & v_2^2 \end{pmatrix}$$

$$\epsilon_t^{24m} = \begin{pmatrix} 6v_2^0 & 3v_2^2 & 0 \\ 12v_2^2 & 12v_2^2 & 0 \\ 0 & 0 & 24v_2^2 \end{pmatrix} \qquad \epsilon_t^{44m} = \begin{pmatrix} v_4^0 & 0 & 0 \\ 0 & v_4^2 & 0 \\ 0 & 0 & v_4^4 \end{pmatrix}$$

$$v_2^0 = \frac{1}{24}\left[2a_3^2 - (a_1^2 + a_2^2)\right] \qquad v_2^2 = \frac{1}{24}(a_1^2 - a_2^2)$$

$$v_4^0 = \frac{1}{16}\left[\frac{1}{5}a_3^4 + \frac{3}{40}(a_1^4 + a_2^4) - \frac{1}{3}a_3^2(a_1^2 + a_2^2) + \frac{1}{12}a_1^2a_2^2\right]$$

$$v_4^2 = -\frac{1}{16}\left[\frac{1}{5}(a_1^4 - a_2^4) - \frac{2}{3}a_3^2(a_1^2 - a_2^2)\right]$$

$$v_4^4 = \frac{1}{16}\left[\frac{1}{5}(a_1^4 + a_2^4) - \frac{2}{3}a_1^2a_2^2\right]$$

Table 3.10

Values of ϵ_t^{lmp} for an Orthorhomic Lattice with Lattice Parameters (a_1, a_2, a_3)

E. The Finite Crystal

We stated earlier (Section 1.3) that the definition of a finite crystal for our purposes is:

'A crystal which is constructed by associating a neutral charge repetition unit (c.r.u.) with each lattice point within a finite region V of a Bravais lattice.'

The electrostatic potential $V(\vec{z})$ of a finite ionic crystal

$$V(\vec{z}) = \frac{1}{4\pi\epsilon_o} \sum_{k}^{r} \sum_{\vec{1}\in V}{}' \frac{q^k}{|\vec{x}(\vec{1})+\vec{x}^k-\vec{z}|} \qquad 3.5.1$$

where $\vec{z}$ is the position vector of the point of interest, $\vec{x}^k$ the position vector of the k-th ion in the c.r.u. and $\vec{x}(\vec{1})$ is a lattice vector.

Using the results of Section C, eq (3.3.71), we may write (3.5.1) as

$$V(\vec{z}) = \sum_{k}^{r} V(\vec{z},k)$$

$$= \sum_{k}^{r} V_i(\vec{z}',k) + \sum_{k}^{r} V_e(\vec{z},k) \qquad 3.5.2$$

Thus we may define an intrinsic electrostatic potential $V_i(\vec{z}')$ and an extrinsic electrostatic potential $V_e(\vec{z})$ as follows:

$$V_i(\vec{z}') \overset{\text{defn}}{=} \sum_{k}^{r} V_i(\vec{z}',k) \qquad 3.5.3$$

and

$$V_e(\vec{z}) \overset{\text{defn}}{=} \sum_{k}^{r} V_e(\vec{z},k) \qquad 3.5.4$$

We will now show that, although $V_i(\vec{z}')$ was derived using the c.r.u.,

we may use any c.b.u. in the sum over k.

In our calculations in Section C, we chose the center of V_n to be at $\vec{x}_z$ to aid later calculations. We may equally well have chosen the center of V_n to be some other lattice point, $\vec{x}(\vec{l})$ say. The only change in the analysis is the minimum value which n may have (see eq (3.3.8)). We see immediately that this change of origin does not change $V_i(\vec{z}',k)$ since it changes neither $V(\vec{z},k)$ nor $V_e(\vec{z},k)$ (see eq (3.3.71)). Thus

$$V_i(\vec{z}',k) = \frac{q^k}{4\pi\epsilon_o}\left\{\sum_{\vec{l}'\in V_n}{}' \frac{1}{\left|\vec{x}(\vec{l}')-\vec{z}'^{\,k}+\{\vec{x}(\vec{l})-\vec{x}_z\}\right|} - \frac{N}{V}f(\vec{z}'^{\,k}+\vec{x}_z-\vec{x}(\vec{l}),V_n)\right\} \qquad 3.5.5$$

All we have effectively done is to give the point P a new position vector $\vec{z}^k - \vec{x}(\vec{l})$ rather than $\vec{z}'^{\,k} = \vec{z}^k - \vec{x}_z$. Thus we may write

$$V_i(\vec{z}',k) = \frac{q^k}{4\pi\epsilon_o}\frac{1}{n_L}\sum_{\vec{l}\in L}\left\{\sum_{\vec{l}'\in V_n}{}' \frac{1}{\left|\vec{x}(\vec{l}')-\vec{z}'^{\,k}+\{\vec{x}(\vec{l})-\vec{x}_z\}\right|} - \frac{N}{V}f(\vec{z}'^{\,k}+\vec{x}_z-\vec{x}(\vec{l}),V_n)\right\} \qquad 3.5.6$$

where L is a set of one or more lattice points near $\vec{x}_z$ and n_L is the number of lattice points in this set. Thus

$$V_i(\vec{z}') = \frac{1}{4\pi\epsilon_o}\sum_{k}^{r}\sum_{\vec{l}\in L}\frac{q^k}{n_L}\left\{\sum_{\vec{l}'\in V_n}{}' \frac{1}{\left|\vec{x}(\vec{l}')-\vec{z}'^{\,k}+\{\vec{x}(\vec{l})-\vec{x}_z\}\right|} - \frac{N}{V}f(\vec{z}'^{\,k}-\vec{x}(\vec{l})+\vec{x}_z,V_n)\right\} \qquad 3.5.7$$

The sum over $\vec{l}$ and the sum over k may now be combined to give a new sum over k. i.e.

$$\sum_{k}^{r}\sum_{\vec{l}\in L}\frac{q^k}{n_L}\{\quad\} = \sum_{k}^{b} q'^{k}\{\quad\} \qquad 3.5.8$$

where q'^{k} may be fractions of the ionic charge q^k and the sum is now over a c.b.u. rather than over a c.r.u.

Thus

$$V_i(\vec{z}) = \frac{1}{4\pi\epsilon_o} \sum_k^b q^k \left\{ \sum_{\vec{l}' \in V_n}' \frac{1}{|\vec{x}(\vec{l}') - \vec{z}'^k|} - \frac{Nf(\vec{z}'^k, V_n)}{V} \right\} \quad 3.5.9$$

where the $\vec{x}^k$ implicit in eq (3.5.9) are those of the c.b.u. Therefore the $\vec{x}^k$ in eqs (3.5.3) and (3.5.9) may be different if the c.r.u. and c.b.u. which are used are different.

To obtain a better understanding of how eqs (3.5.3) and (3.5.9) are used, we will let the finite crystal be a line of alternating point charges (see fig 3.3.a). Using this crystal, we will discuss how the intrinsic and extrinsic electrostatic potentials are evaluated.

In fig 3.3.a, the crystal is considered to be a superposition of two sub-lattices, each with lattice spacing a, one shifted with respect to the other by an amount ½a, i.e. there are two ions in the c.r.u. with $x^0 = 0$ and $x^1 = \frac{1}{2}a$. To evaluate the electrostatic potential as a function of the position near the ion site C (which is vacant), we proceed as follows.

The point A is the center of the region V and hence will be the origin which is used in the evaluation of the extrinsic partial potentials associated with each sub-lattice. We let the distance from A to P be z, then the distance used, when considering the k=1 sub-lattice, is $z - x^1 = z - \frac{1}{2}a$. We note that this is just the distance from B (the center of the region V^1) to the point P. The origin A remains

---

*1 The region V is defined by the k=0 sub-lattice. When we are considering a k≠0 sub-lattice, we will refer to the region defined by associating a basic cube with each k=1 ion site as V^k. The regions V^k which belong to the same c.r.u. will have the same volume.

unchanged as the point P moves along the line. A_1 and A_2 represent the origins, relative to which the point P is measured, which are used in the evaluation of the intrinsic partial potentials. Conceptually, we may consider the origin as being fixed at A with $V_i(z)$ being a periodic function of z. However, to use the formulae of Sections 3.4.ii and 3.4.iii, we must express each of the intrinsic partial potentials as a function of the distance from the nearest k=0 sub-lattice point. Thus the distances used in the evaluation of the intrinsic partial potentials are as follows:

Point	Nearest k=0 Lattice Site	x_z	Position Vector z'^k
P_1	A_1	2a	$(z'^0)_1 = z_1 - x_z$ $= z_1 - 2a$ $(z'^1)_1 = (z'^0)_1 - x^1$ $= z_1 - 5a/2$
P_2	A_2	3a	$(z'^0)_2 = z_2 - x_z$ $= z_2 - 3a$ $(z'^1)_2 = (z'^0)_2 - x^1$ $= z_2 - 7a/2$

In fig. 3.3.c, we have shown how the same finite array, as discussed above may be constructed using four sub-lattices with lattice spacing 2a. The volumes V^k vary for the different sub-lattices. i.e.

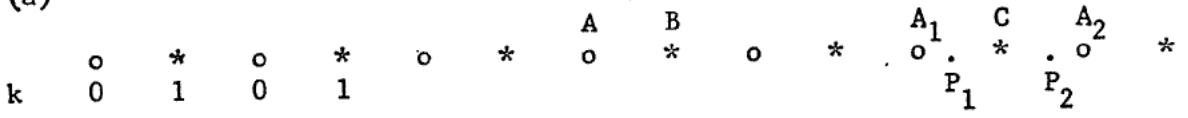
$$V^0 = V^1 = 4(2a); \quad V^2 = V^3 = 3(2a)$$

Thus for this case the crystal is constructed using two c.r.u.'s. The

values of the intrinsic and extrinsic electrostatic potentials at any point remain unchanged.

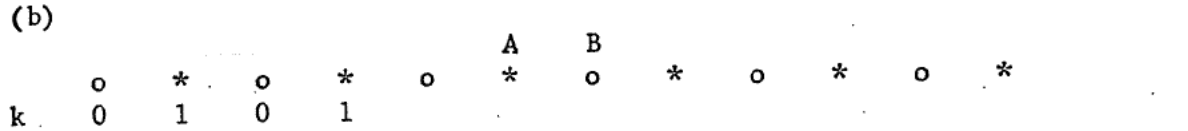
Returning to eqs (3.5.4) and (3.5.9), we may associate a dipole moment with both the c.r.u. and c.b.u. The extrinsic electrostatic potential depends on the choice of the c.r.u. and hence on the dipole moment of the c.r.u. In contrast, the intrinsic electrostatic potential does not depend on the c.b.u. and hence does not depend on the dipole moment of the c.b.u.

(a)



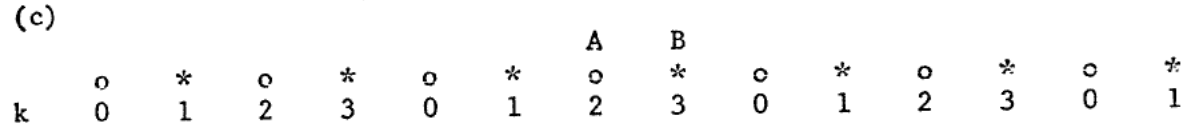
A finite crystal in which the centers of the regions V^k (A and B) are lattice sites of the sub-lattices which define V^k.

(b)



A finite crystal in which the centers of the regions V^k are not at lattice sites of the sub-lattices which define V^k.

(c)



A finite crystal which may be considered to be built of four sub-lattices instead of two as in (a).

o - ion of charge q

* - ion of charge -q

A - center of region V^0

B - center of region V^1

Figure 3.2

Finite Crystals

CHAPTER IV

THE INTRINSIC ELECTROSTATIC POTENTIAL

A. Introduction

We have seen in Chapter III that the electrostatic potential, $V(\vec{z})$, may be written as a sum of two types of terms - intrinsic and extrinsic. This chapter will be devoted to the discussion of the quantities which are derived from the intrinsic partial potential.

The intrinsic electrostatic potential was defined in Section 3.5 as

$$V_i(\vec{z}) = \sum_k^b V_i(\vec{z},k) \qquad \text{(see eq (3.5.2))}$$

$$= \frac{1}{4\pi\epsilon_o} \sum_k^b q^k \left\{ \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}+\vec{x}^k|} - \frac{Nf(\vec{z}-\vec{x}^k, V_n)}{V} \right\} \qquad 4.1.1$$

where we have substituted for $V_i(\vec{z},k)$ using eq (3.3.69). In addition we define an intrinsic electrostatic energy per c.b.u. as

$$U_i \overset{\text{defn}}{=} \tfrac{1}{2} \sum_{k'}^b q^{k'} V_i(\vec{x}^{k'})$$

$$= \frac{1}{8\pi\epsilon_o} \sum_{k,k'}^b q^k q^{k'} \left\{ \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{x}^{k'}|} - \frac{Nf(\vec{x}^{k'}-\vec{x}^k, V_n)}{V} \right\} \qquad 4.1.2$$

We have dropped the ' on $\vec{z}$' since in this chapter there is only one origin, the center of V_n, which we need to consider (not two origins, the center of V_n and the center of V, as in Chapter III).

In Section B, we will discuss the properties of the intrinsic electrostatic potential, eq (4.1.1), and in Section C we will define an intrinsic Madelung constant which is associated with eq (4.1.2). In Section D, we will give the numerical results for NaCl, CsCl, ZnS, and $BaTiO_3$. In Section E, we will compare the intrinsic electrostatic potential with the quantity evaluated by Evjen and in Section F, we will prove that the intrinsic electrostatic potential is equivalent to the quantity evaluated by Ewald, H&M, etc, whose methods are based, either explicitly or implicitly, on the introduction of a vanishing exponential.

B. The Intrinsic Electrostatic Potential

We have defined the intrinsic electrostatic potential of a finite array of point charges as

$$V_i(\vec{z}) = \sum_k^b \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{z}|} - \frac{N}{V} f(\vec{z}-\vec{x}^k, V_n) \right\} \quad 4.2.1$$

The first property of $V_i(\vec{z})$ which we will investigate is its average value over the basic cube associated with the center of V_n. To do this, we will first evaluate the average value of the intrinsic partial potential, $V_i(\vec{z},k)$, over the basic cube. i.e.

$$V_i^{av}(k) = \frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} V_i(\vec{y},k) \quad 4.2.2$$

Thus

$$V_i^{av}(k) = \frac{q^k}{4\pi\epsilon_o} \left\{ \frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{y}|} - \frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} \frac{N}{V} f(\vec{y}-\vec{x}^k, V_n) \right\} \quad 4.2.3$$

In the second term we may use the relation

$$\frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} dy f(\vec{y}-\vec{x}^k) = \hat{\Gamma} f(-\vec{x}^k) \qquad \text{(see eq (3.2.6))} \quad 4.2.4$$

since $f(\vec{z})$ has no singularities within the region of integration. Thus

$$\frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} f(\vec{y}-\vec{x}^k, V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{x}^k|} \qquad \text{(see eq (3.3.21))} \quad 4.2.5$$

For the first term in eq (4.2.3), we proceed as for the derivation of eq (3.3.13) by introducing the transformation $\vec{y} = \vec{x}(\vec{l}) - \vec{y}'$. Then

$$\iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y} \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{y}|} = \sum_{\vec{l}\in V_n}' \iiint_{\vec{x}(\vec{l})-\frac{1}{2}a}^{\vec{x}(\vec{l})+\frac{1}{2}a} \frac{d\vec{y}}{|\vec{y}-\vec{x}^k|} \quad 4.2.6$$

combining the integrals over the different regions into a single integral, eq (4.2.6) may be written as

$$\int_{-\frac{1}{2}a}^{\frac{1}{2}a}\int\int d\vec{y} \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{y}|} = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{x}^k|} \qquad 4.2.7$$

Hence

$$V_i^{av}(k) = \frac{q^k}{4\pi\epsilon_o}\left\{\frac{N}{V}\iiint_{V_n}\frac{d\vec{y}}{|\vec{y}-\vec{x}^k|} - \frac{N}{V}\iiint_{V_n}\frac{d\vec{y}}{|\vec{y}-\vec{x}^k|}\right\}$$

$$= 0 \qquad \text{for all } k \qquad 4.2.8$$

Thus the intrinsic partial potential has the same average value, namely zero, as the electrostatic potential of the neutralized Bravais lattice which Tosi evaluated (see eq (2.7.3)). This result was expected since we showed in Section 3.4 that, for the case of cubic symmetry, the intrinsic partial potential was of the same form as the electrostatic potential of a neutralized cubic Bravais lattice.

The average value of the intrinsic electrostatic potential is

$$V_i^{av} = \sum_k^b V_i^{av}(k)$$

$$= 0 \qquad 4.2.9$$

We will now investigate how the intrinsic electrostatic potential is related to the electrostatic potential of an infinite crystal as defined by eq (1.3.9). The intrinsic electrostatic potential may be written as the difference between two terms as follows

$$V_i(\vec{z}) = V_i'(\vec{z},V_n) - V_i''(\vec{z},V_n) \qquad \text{(see eq (4.2.1))} \qquad 4.2.10$$

where

$$V_i(\vec{z},V_n) = \frac{1}{4\pi\epsilon_o}\sum_k^b q^k \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{z}|} \qquad 4.2.11$$

and

$$V_i''(\vec{z},V_n) = \frac{N}{4\pi\epsilon_o V} \sum_k^b q^k f(\vec{z}-\vec{x}^k,V_n) \qquad 4.2.12$$

From the second boundary condition that $f(\vec{z},V_n)$ must satisfy (see page 73), $V_i'(\vec{z},V_n)$ has the same V_n dependence as $V_i''(\vec{z},V_n)$. They also have the same c.b.u. dependence since $V_i(\vec{z})$ is independent of the c.b.u.*0 In eq (4.2.1), V_n is any arbitrary region which may be constructed using cubes (in Chapter III we chose V_n to be a cube for convenience). Letting $V_n \to \infty$, we find that $V_i'(\vec{z},V_n)$ becomes the electrostatic potential of an infinite crystal. i.e.

$$\lim_{V_n\to\infty} V_i'(\vec{z},V_n) = \frac{1}{4\pi\epsilon_o} \lim_{V_n\to\infty} \sum_k^b q^k \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^k-\vec{z}|}$$

$$= V^\infty(\vec{z}) \qquad \text{(see eq (1.3.9))} \qquad 4.2.13$$

If the L.H.S. of (4.2.13) depends on the shape of V_n or on the c.b.u., then $V^\infty(z)$ may be referred to as conditionally convergent. (See Section 1.5). Since V_i' and V_i'' have the same V_n and c.b.u. dependence, by examining the V_n or c.b.u. dependence of V_i'' we examine the V_n or c.b.u. dependence of V_i' at the same time. i.e. if $\lim_{V_n\to\infty} V_i''$ depends on V_n or on the c.b.u., then this is also true for $\lim_{V_n\to\infty} V_i'$ and hence $V^\infty(z)$ would be conditionally convergent; similarily if $\lim_{V_n\to\infty} V_i''$ is a constant, independent of both V_n and c.b.u., then $V^\infty(\vec{z})$ would be represented by an absolutely convergent series.

Using the results from Section 3.3.ii, we have that for V_n a cube

$$f(\vec{z},V_n) = \alpha_{00}[(n+\tfrac{1}{2})a]^2 - \frac{2\pi}{3}(z^2-\tfrac{1}{4}a^2) + O(n^{-2}) \qquad 4.2.14$$

(See eq (3.4.33)).

*0 See proof at the beginning of Section 3.5.

Therefore

$$V_i''(\vec{z},V_n) = \frac{N}{4\pi\epsilon_o V}\sum_k^b q^k f(\vec{z}-\vec{x}^k,V_n)$$

$$= \frac{N}{4\pi\epsilon_o V}\left[\sum_k^b q^k\left\{\chi_{00}\left[(n+\tfrac{1}{2})a\right]^2 + \frac{a^2}{6}\right\} - \frac{2\pi}{3}\sum_k^b q^k|\vec{z}-\vec{x}|^2 + O(n^{-2})\right] \qquad 4.2.15$$

The first term vanishes due to charge neutrality. The second term may be written as

$$-\frac{2\pi}{3}\sum_k^b q^k(z_i-x_i^k)(z_i-x_i^k) = -\frac{2\pi N}{3V}\sum_k^b q^k(z_i z_i - 2x_i^k z_i + x_i^k x_i^k)$$

$$= \frac{4\pi}{3}(z_i p_i - p_{ii}) \qquad 4.2.16^{*1}$$

where

$$p_i = \frac{N}{V}\sum_k^b q^k x_i^k \qquad 4.2.17$$

is the dipole moment of the c.b.u. per unit volume, and

$$p_{ij} = \tfrac{1}{2}\frac{N}{V}\sum_k^b q^k x_i^k x_j^k \qquad 4.2.18$$

is the quadrupole moment of the c.b.u. per unit volume.

These moments are associated only with the position vectors $\vec{x}^k$ of ions in the c.b.u. They are not to be confused with the moments of the whole crystal which has to derived using the c.r.u. (see discussion in Section 3.5).

Hence

$$V_i''(\vec{z},V_n) = \frac{1}{3\epsilon_o}\left\{(z_i p_i - p_{ii}) + O(n^{-2})\right\} \qquad 4.2.19$$

---

*1 We will be using the Einstein repeated index summation convention for summing over coordinate subscripts.

If we take the limit $V_n \to \infty$, where V_n is a cube, then

$$\lim_{V_n \to \infty} V_i''(\vec{z},V_n) = \frac{1}{3\epsilon_o}(z_i p_i - p_{ii}) \qquad 4.2.20$$

The V_n dependence is implicit in the factor 1/3 and the combination of $\vec{z}$, $\vec{p}$, and p_{ij}. If we had chosen a different shape (a box say with sides $(n_1,n_2,n_3)a$), then from eq (3.4.42)

$$f(\vec{z},V_d) = \alpha_{00}d^2 + \alpha_{10}P_{20} + \alpha_{11}P_{22} + O(d^{-2}) - \frac{2\pi}{3}(z^2 - \tfrac{1}{4}a^2) \qquad 4.2.21$$

where $d = (n_1 n_2 n_3)^{\frac{1}{3}}a$ and the α_{00}, α_{10}, α_{11} are non-zero constants given by eq (3.3.42). This gives rise to a different combination of $z_i p_j$ and p_{ij} than the one given in eq (4.2.20). This result holds for arbitrary shapes since $f(\vec{z},V_n)$ always is the sum of a quadratic term in $\vec{z}$ which is independent of n and of other terms depending on n which vanish when the limit $V_n \to \infty$ or vanish due to charge neutrality.

Therefore the R.H.S. of (4.2.20) will be independent of V_n if and only if

$$1.\ p_i = 0 \qquad i=1,2,3 \qquad 4.2.22$$

$$2.\ p_{ii} = 0 \qquad i,j=1,2,3 \qquad 4.2.23$$

When (4.2.22) and (4.2.23) hold

$$\begin{aligned} V_i(\vec{z}) &= \lim_{V_n \to \infty} V_i'(\vec{z},V_n) - \lim_{V_n \to \infty} V_i''(\vec{z},V_n) \\ &= \lim_{V_n \to \infty} V_i'(\vec{z},V_n) \\ &= V^{\infty}(\vec{z}) \end{aligned} \qquad 4.2.24$$

Thus the series (1.3.9) representing $V^{\infty}(\vec{z})$ is absolutely convergent and is equivalent to the intrinsic electrostatic potential when the c.b.u. of the infinite crystal has vanishing dipole and quadrupole

moments.

We note that, since $V^{\infty}(\vec{z})$ is a function of p_i and p_{ij}, it is always c.b.u. conditionally convergent. However, when the c.b.u. satisfies the criteria (4.2.22) and (4.2.23), then $V^{\infty}(\vec{z})$ is not shape conditionally convergent. This means that the infinite lattice electrostatic potential is a function of the choice of c.b.u. and if this choice of c.b.u. possesses a non-vanishing dipole or quadrupole moment, then the $\vec{l}$ summation is also conditionally convergent.

C. The Madelung Constant

We will now define an intrinsic Madelung constant which is derived using the intrinsic partial potentials. In Section A, we defined the intrinsic electrostatic energy per c.b.u., U_i, by

$$U_i = \tfrac{1}{2}\sum_{k'}^{b} q^{k'} V_i(\vec{x}^{k'}) \qquad \text{(see eq (4.1.2))}$$

$$= \frac{1}{8\pi\epsilon_o} \sum_{k',k}^{b} q^{k'} q^{k} \left[\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^{k}-\vec{x}^{k'}|} - \frac{Nf(\vec{x}^{k'}-\vec{x}^{k},V_n)}{\overline{V}} \right] \qquad 4.3.1$$

The intrinsic Madelung constant, α_i, is defined by

$$\alpha_i \overset{\text{defn}}{=} -4\pi\epsilon_o b U_i/(me)^2 \qquad 4.3.2$$

where b is an appropriate scaling distance, e is the electronic charge, and m is the greatest common factor of q^k/e with k ranging over the c.b.u. (if q^k is not a multiple of e then m = 1). Thus

$$\alpha_i = -b \left\{ \sum_{k',k}^{b} \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^{k}-\vec{x}^{k'}|} - \frac{Nf(\vec{x}^{k'}-\vec{x}^{k},V_n)}{\overline{V}} \right\}/(me)^2 \qquad 4.3.3$$

Since U_i is made up of a linear combination of V_i, U_i and hence α_i are independent of the choice of V_n or c.b.u.

As we did for the intrinsic electrostatic potential, we will write α_i as the difference of two terms. i.e.

$$\alpha_i = \alpha_i'(V_n) - \alpha_i''(V_n) \qquad 4.3.4$$

where

$$\alpha_i'(V_n) = -\tfrac{1}{2} b \left\{ \sum_{k',k}^{b} q^{k'} q^{k} \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^{k}-\vec{x}^{k'}|} \right\}/(me)^2 \qquad 4.3.5$$

and

$$\alpha_i''(V_n) = -\tfrac{1}{2}b \sum_{k',k}^{b} q^{k'} q^{k} f(\vec{x}^{k'} - \vec{x}^{k}, V_n)/(me)^2 \qquad 4.3.6$$

The Madelung constant for an infinite crystal, α^∞, is defined as

$$\alpha^\infty \overset{\text{defn}}{=} -4\pi\epsilon_o b \sum_{k'}^{b} q^{k'} V_i(\vec{x}^{k'})/(me)^2 \qquad 4.3.7$$

Thus

$$\alpha^\infty = \lim_{V_n \to \infty} \alpha_i'(V_n) \qquad 4.3.8$$

Therefore we may investigate the conditional convergence of α^∞ by investigating the V_n and c.b.u. dependence of α_i' which is the same as the V_n and c.b.u. dependence of $\alpha_i''(V_n)$.

$$\alpha_i''(V_n) = -\tfrac{1}{2}b \sum_{k}^{b} q^{k} \left[\frac{N}{V} \sum_{k'}^{b} q^{k'} f(\vec{x}^{k'} - \vec{x}^{k}, V_n) \right]/(me)^2 \qquad 4.3.9$$

We have already evaluated the term in square brackets for V_n a cube (see eq (4.2.19)). Thus

$$\alpha_i''(V_n) = -\frac{2\pi b}{3} \left\{ \sum_{k}^{b} q^{k} (x_i^k p_i - p_{ii}) + O(n^{-2}) \right\}/(me)^2$$

$$= -\frac{2\pi b V}{3N} \left[p_i p_i + O(n^{-2}) \right]/(me)^2 \qquad 4.3.10$$

where the p_{ii} term vanished due to charge neutrality. Hence

$$\lim_{V_n \to \infty} \alpha_i''(V_n) = -\frac{2\pi b V}{3N} p_i p_i/(me)^2 \qquad 4.3.11$$

As in Section B, if V_n was a box say, we would obtain a different combination of $p_i p_j$ on the R.H.S. of (4.3.11). Thus the only way for the R.H.S. of (4.3.11) to be independent of V_n is if $p_i = 0$. Therefore $\lim_{V_n \to \infty} \alpha_i'(V_n)$, and hence α^∞, is represented by an absolutely convergent

series if and only if

$$1.\ p_i = 0 \qquad 4.3.12$$

Taking the limit of α_i as $V_n \to \infty$ (we may do this since α_i is independent of V_n), we have, if the dipole moment of the c.b.u. vanishes,

$$\begin{aligned} \alpha_i &= \lim_{V_n \to \infty} \alpha_i'(V_n) - \lim_{V_n \to \infty} \alpha_i''(V_n) \\ &= \lim_{V_n \to \infty} \alpha_i'(V_n) \\ &= \alpha^{\infty} \end{aligned} \qquad 4.3.13$$

Therefore the infinite series representing the Madelung constant of an infinite crystal is absolutely convergent and equals the intrinsic Madelung constant if the c.b.u. of the infinite crystal has a vanishing dipole moment.

As with $V^{\infty}(\vec{z})$, α^{∞} is always c.b.u. conditionally convergent but when the c.b.u. satisfies (4.3.12), then α^{∞} is not shape conditionally convergent.

In the past it has been common practice to obtain the Madelung constant for a diatomic crystal from the electrostatic potential. This can lead to confusion since the criteria for the absolute convergence of the electrostatic potential and electrostatic energy of an infinite crystal are different. An example of this confusion is the evaluation of the Madelung constant of CsCl using the Evjen method. Evjen used the criterion that $p_i = 0$ which insures the absolute convergence of the electrostatic energy, yet evaluated the electrostatic potential which needs the additional criterion $p_{ij} = 0$ for absolute convergence.

D. Numerics

To show the computational effectiveness of the theory described in Chapter III, we will evaluate the intrinsic electrostatic potential and intrinsic Madelung constants for NaCl, CsCl, ZnS, and $BaTiO_3$. To evaluate these quantities we need to evaluate only five partial potentials.

We define a dimensionless quantity, $\beta^P(\vec{z})$, which we associate with the intrinsic partial potential as follows:

$$V_i(\vec{z},k) = \frac{mes^k}{4\pi\epsilon_o b}\beta^P(\vec{z}) \qquad 4.4.1$$

where e is the electronic charge, b is the scaling distance introduced in Section C, eq (4.3.2) (in this section we will use b = a where a is the lattice parameter), m is the greatest common factor of q^k (all k), and

$$s^k = q^k/e \qquad \text{(see eq (1.3.2))} \qquad 4.4.2$$

Similarily we will define a dimensionless quantity, $\alpha(\vec{z})$, associated with the intrinsic electrostatic potential by

$$\alpha(\vec{z}) = 4\pi\epsilon_o b\, V(\vec{z})/(me) \qquad 4.4.3$$

Thus $\alpha(\vec{z})$ is related to $\beta^P(\vec{z})$ as follows:

$$\alpha(z) = \sum_k^b s^k \beta^P(\vec{z}-\vec{x}^k) \qquad 4.4.4$$

In terms of the $\beta^P(z)$, the intrinsic Madelung constant is just

$$\alpha_i = \sum_{k',k}^b \frac{s^k s^{k'}}{m}\beta^P(\vec{x}^{k'}-\vec{x}^k) \qquad 4.4.5$$

To simplify writing we will set

$$b_1 = \beta^P(0,0,0); \quad b_2 = \beta^P(\tfrac{1}{2},0,0); \quad b_3 = \beta^P(\tfrac{1}{2},\tfrac{1}{2},0); \quad b_4 = \beta^P(\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2});$$
$$b_5 = \beta^P(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{4}) \qquad 4.4.6$$

These partial potentials were evaluated using the formula for $V_i(\vec{z},k)$ given in Section 3.4.ii (see eq (3.4.34)) with n = 7 and all spherical harmonic terms up to the twelfth order. The results are given in Table 4.1. The error in the last significant figure is of the order 3 due to computer error.

The intrinsic self-potentials and intrinsic Madelung constants for NaCl, CsCl, ZnS, and $BaTiO_3$ were evaluated using the results given in Table 4.1. These results plus the accepted values for the Madelung constant of the infinite crystal are given in Table 4.2. The values for $BaTiO_3$ are based on the assumption that

q^k = (valence of the k-th ion)e.

	$\vec{z}$	$\rho^{P}(\vec{z})$	Tosi
b_1	(0,0,0)a	-2.83739737948_5	
b_2	(½,0,0)a	-0.09593230494_5	-0.095932
b_3	(½,½,0)a	-0.58252153154_8	-0.582522
b_4	(½,½,½)a	-0.80193597003_1	-0.801936
b_5	(¼,¼,¼)a	-0.20048399251_1	

Table 4.1

Intrinsic Partial Potentials at Points near a Lattice Site in a Cubic Bravais Lattice

Crystal	Ion Type	$\alpha(\vec{x}^k)$	α_i	α^∞ Accepted Value	α^∞ Evjen[3]
CsCl	Cs	$b_1-b_4 = -2.03536150945_4$	2.03536150945_4	2.03536150942_6^{25}	2.03_4
	Cl	$b_4-b_1 = +2.03536150945_4$			
NaCl	Na	$b_1-b_4+3b_3-3b_2 = -3.49512918926_3$	3.49512918926	$3.4951291892663644_3^{15}$	3.49_6
	Cl	$b_4-b_1+3b_2-3b_3 = +3.49512918926_3$			
ZnS	Zn	$b_1+3b_3-4b_5 = -3.78292610409_5$	3.78292610409	3.7829_3^{14}	3.7_8
	S	$-b_1-3b_3+4b_5 = +3.78292610409_5$			
$BaTiO_3$	Ba	$b_1+2b_4-3b_3 = -2.61936048249_2$	12.3774236978_3	12.37_8^{16}	
	Ti	$b_4+2b_1-3b_2 = -6.18868905866_6$			
	O	$-b_1+2b_2-b_3 = +3.22795440114_1$			

Table 4.2

Intrinsic Electrostatic Self-Potentials and Madelung Constants

E. Comparison with Evjen's Method

Evjen introduced weighting factors w^k (see discussion preceeding eq (2.3.5)), to specify the contribution of an ion's charge to the unit cell he used. Instead of considering weighting factors, we can let the crystal lattice be built up from sub-lattices whose lattice sites are occupied by ions of charge $w^k q$. We then associate a sub-lattice with each of the ions in Evjen's unit cell. Thus our c.b.u. would, in fact, be Evjen's unit cell with the ions actually having fractional charges.

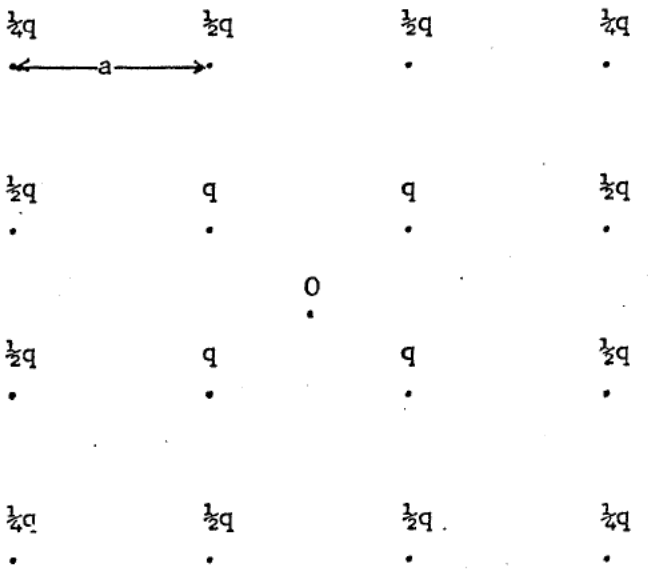
To give a simple example of this procedure, let us consider the set of points in fig. 4.1. This array of charges is the result of taking a sum of nine squares of side a with charge $\frac{1}{4}q$ at each corner. This is the type of sum Evjen considered. What we will do is to consider it as the sum of four sub-lattices (with charge $\frac{1}{4}q$ at each lattice site) with volume $V = (2a)^2$ and centers at $(\pm 1, \pm 1)\frac{1}{2}a$. By inspection of fig. 4.1, we see that these two ways of looking at the sum over the lattice points are equivalent.

The intrinsic electrostatic self-potential at a lattice site whose ions are of type k is (eq (4.1.1) with $\vec{z} = \vec{x}^k$)

$$V_i(\vec{x}^k) = \frac{1}{4\pi\epsilon_o}\left\{\sum_{k'}^{b} q^{k'} \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^{k'}-\vec{x}^k|} - \frac{N}{V}\sum_{k'}^{b} q^{k'} f(\vec{x}^k-\vec{x}^{k'}, V_n)\right\} \qquad 4.5.1$$

where the ' on the sum over $\vec{l}$ indicates that $\vec{l} = 0$ is to be excluded from the sum when $k' = k$.

If we choose our c.b.u. to be Evjen's unit cell, then the first term



O - the origin of our coordinate system

Figure 4.1

A Possible Two-Dimensional Square Array with Fractional Charges

of (4.5.1) is equivalent to the quantity evaluated by Evjen. Thus

$$V_E^{\infty}(\vec{x}^k) = \sum_{k'}^{b} \frac{q^{k'}}{4\pi\epsilon_o} \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})+\vec{x}^{k'}-\vec{x}^k|} \qquad 4.5.2$$

where $V_E^{\infty}(\vec{x}^k)$ is Evjen's self-potential provided V_n is large. Hence

$$V_i(\vec{x}^k) - V_E^{\infty}(\vec{x}^k) = \frac{N}{V} \sum_{k'}^{b} \frac{q^{k'}}{4\pi\epsilon_o} f(\vec{x}^k-\vec{x}^{k'}, V_n)$$

$$= - V_i''(\vec{x}^k; V_n) \qquad 4.5.3$$

where we have introduced the notation of Section B (see eq (4.2.12)). The properties of $V_i''(\vec{x}^k, V_n)$ have already been investigated for V_n a cube, i.e.

$$V_i''(\vec{x}^k, V_n) = \frac{1}{3\epsilon_o} (x_i^k p_i - p_{ii}) + O(n^{-2}) \qquad 4.5.4$$

where

$$p_i = \frac{N}{V} \sum_{k'}^{b} q^{k'} x_i^{k'} \qquad 4.5.5$$

and

$$p_{ij} = \tfrac{1}{2}\frac{N}{V} \sum_{k'}^{b} q^{k'} x_i^{k'} x_j^{k'} \qquad 4.5.6$$

(see eqs (4.2.20), (4.2.22), and (4.2.23)). Therefore for n large

$$V_i(\vec{x}^k) - V_E^{\infty}(\vec{x}^k) = - \frac{1}{3\epsilon_o}(x_i^k p_i - p_{ii}) \qquad 4.5.7$$

We will now evaluate the difference

$$\Delta V = V_i(\vec{x}^k) - V_E^{\infty}(\vec{x}^k) \qquad 4.5.8$$

for the three crystals Evjen considered - NaCl, CsCl, and ZnS.

(1) NaCl

From Table 4.3, we see that the dipole moment density and quadrupole moment densities of Evjen's unit cell for NaCl are

$$p_i = \frac{N}{V} \sum_k^b q^k x_i^k$$

$$= 0 \qquad 4.5.9$$

and

$$p_{ii} = \frac{N}{V} \sum_k^b q^k x_i^k x_i^k$$

$$= \frac{N}{V} (q.0 - \tfrac{1}{2}q.6.\tfrac{1}{4} + \tfrac{1}{4}q.12.\tfrac{1}{2} - \frac{q}{8}.8.\frac{3}{4})a^2$$

$$= 0 \qquad 4.5.10$$

Thus

$$\Delta V = 0 \qquad 4.5.11$$

Therefore Evjen's quantity is equivalent to our intrinsic electrostatic potential for NaCl.

(2) CsCl

For the case of CsCl, we consider two different c.b.u.s (fig 2.4) with the relevant quantities given in Table 4.3.

(i) the ion at the surface of the c.b.u. has opposite charge to the ion at the center of the c.b.u.

$$p_i = 0 \qquad 4.5.12$$

$$p_{ii} = \tfrac{1}{2}\frac{N}{V} (0.q - \frac{q}{8}.8.\frac{3}{4})a^2$$

$$= -\frac{3q}{8a} \qquad 4.5.13$$

Hence

$$\Delta V_E^{(a)} = -\frac{\frac{1}{2}\pi q}{4\pi\epsilon_o a} \qquad 4.5.14$$

(b) the ion at the surface of the c.b.u. has the same charge as the ion at the center of the c.b.u.

$$p_i = 0 \qquad 4.5.15$$

$$p_{ii} = \frac{\frac{1}{2}}{a^3}(0.q - q.8.\frac{3}{4} + \frac{q}{2}.6.1 + \frac{q}{4}.12.2 + \frac{q}{8}.8.3)a^2$$

$$= \frac{3q}{8a} \qquad 4.5.16$$

Hence

$$\Delta V_E^{(b)} = \frac{\frac{1}{2}\pi q}{4\pi\epsilon_o a} \qquad 4.5.17$$

Thus the self-potentials Evjen evaluated for CsCl differ from our intrinsic electrostatic potential. However taking the average of eqs (4.5.14) and (4.5.17), we have

$$\frac{1}{2}(\Delta V_E^{(a)} + \Delta V_E^{(b)}) = 0 \qquad 4.5.18$$

or

$$V_i(\vec{x}^k) = \frac{1}{2}[V_E^{(a)}(\vec{x}^k) + V_E^{(b)}(\vec{x}^k)] \qquad 4.5.19$$

Therefore, the average of the self-potentials, evaluated using the two unit cells of cases (a) and (b), is equivalent to our intrinsic self-potential. Thus the averaging procedure used by Evjen gives the accepted value for the electrostatic self-potential because the averaging eliminates the effect of the quadrupole moment rather than the reason Evjen gave (see discussion following eq (2.3.22)).

(3) ZnS

Again using the data given in Table 4.3 for the unit cell used by Evjen, we have

$$p_i = 0 \qquad 4.5.20$$

$$p_{ii} = \frac{\frac{1}{2}}{a^3}(0.q - q.4.\frac{3}{16} + \frac{q}{4}.12.\frac{1}{2})a^2$$

$$= \frac{3q}{8a} \qquad 4.5.21$$

Hence

$$\Delta V = \frac{\frac{1}{2}\pi q}{4\pi\epsilon_o a} \qquad 4.5.22$$

Therefore Evjen's quantity also differs in the case of ZnS from our intrinsic electrostatic potential.

In order that the quantities Evjen evaluated be equivalent to our intrinsic electrostatic self-potentials, we conclude that the unit cells used in Evjen's method must have the following properties

1. charge neutrality
2. no dipole moment
3. no quadrupole moment

These are just the necessary and sufficient conditions to assure absolute convergence of $V^{\infty}(\vec{z})$ (eq (1.3.9)).

In the next section we prove that the intrinsic electrostatic potential is equivalent to the potential evaluated by Ewald. Since Ewald's results give the accepted values for the electrostatic potential of the infinite crystal, we may conclude that Evjen's results are in error for CsCl and ZnS and that this error is due to Evjen not realizing that the quadrupole moment of the unit cell must vanish for the infinite sum to be absolutely convergent. This is the result of

assuming that the electrostatic potential and electrostatic energy are proportional to each other in diatomic systems. We have shown in Section C that this is not a valid assumption since the two quantities have different properties i.e. the electrostatic potential of an infinite crystal converges absolutely if the dipole and quadrupole moments of the c.b.u. vanish whereas the electrostatic energy of an infinite crystal converges absolutely if only the dipole moment of the c.b.u. vanishes.

Crystal		k	q^k	$\vec{x}^k$
NaCl		0	q	$(0, 0, 0)\frac{1}{2}a$
		1,2,3,4,5,6	$-\frac{1}{2}q$	$(\pm1, 0, 0)\frac{1}{2}a, (0,\pm1, 0)\frac{1}{2}a, (0, 0,\pm1)\frac{1}{2}a$
		7,8,.....,18	$\frac{1}{4}q$	$(\pm1,\pm1, 0)\frac{1}{2}a, (\pm1, 0,\pm1)\frac{1}{2}a, (0,\pm1,\pm1)\frac{1}{2}a$
		19,20,...,26	- q/8	$(\pm1,\pm1,\pm1)\frac{1}{2}a$
CsCl	(a)	0	q	$(0, 0, 0)\frac{1}{2}a$
		1,2,.....,8	- q/8	$(\pm1,\pm1,\pm1)\frac{1}{2}a$
	(b)	0	q	$(0, 0, 0)\frac{1}{2}a$
		1,2,.....,8	- q	$(\pm1,\pm1,\pm1)\frac{1}{2}a$
		9,10,....,14	$\frac{1}{2}q$	$(\pm1, 0, 0)a, (0,\pm1, 0)a, (0, 0,\pm1)a$
		15,16,...,26	$-\frac{1}{4}q$	$(\pm1,\pm1, 0)a, (\pm1, 0,\pm1)a, (0,\pm1,\pm1)a$
		27,28,...,34	q/8	$(\pm1,\pm1,\pm1)a$
ZnS		0	q	$(0, 0, 0)a$
		1,2,3,4	- q	$(1,1,-1)\frac{1}{4}a, (1,-1,1)\frac{1}{4}a, (-1,1,1)\frac{1}{4}a, (-1,-1,-1)\frac{1}{4}$
		5,6,.....,16	$\frac{1}{4}q$	$(\pm1,\pm1, 0)\frac{1}{2}a, (\pm1, 0,\pm1)\frac{1}{2}a, (0,\pm1,\pm1)\frac{1}{2}a$

Table 4.3

Tables of the origins of the sub-lattices (plus the charges of the ions occupying the sub-lattice) with respect to the ion site chosen as the origin. These quantities are obtainable from figs. 2.3, 2.4, and 2.5.

F. Comparison of the Intrinsic Electrostatic Potential with the Electrostatic Potential Evaluated by Harris and Monkhorst

The intrinsic partial potential at a point P with position vector $\vec{z}$ due to a sub-lattice (with charges q^k) shifted by an amount $\vec{x}^k$ with respect to the Bravais lattice sites occupied by the k = 0 ions is

$$V_i(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o}\left\{\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}^k|} - \frac{N}{V} f(\vec{z}^k,V_n)\right\} \qquad 4.6.1$$

where the ' denotes the exclusion of $\vec{l} = 0$ from the sum when $\vec{z}^k = 0$ (i.e. when $\vec{z} = \vec{x}^k$), and

$$\vec{z}^k = \vec{z} - \vec{x}^k \qquad \text{(see eq (3.1.6))} \qquad 4.6.2$$

$f(\vec{z},V_n)$ is a solution of the equation

$$\hat{\Gamma} f(\vec{z},V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad \text{(see eq (3.3.27))} \qquad 4.6.3$$

subject to the boundary conditions given on page 73.

In order to use fourier transforms, we introduce the quantities

$$\lim_{\beta\to 0} e^{-\beta|\vec{x}(\vec{l})-\vec{z}^k|} = 1 \quad \text{and} \quad \lim_{\beta\to 0} e^{-\beta|\vec{y}-\vec{z}|} = 1$$

into respectively, the first term on the R.H.S. of (4.6.1) and into the integrand on the R.H.S. of eq (4.6.3).

Thus the intrinsic partial potential becomes

$$V_i(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o}\left\{\sum_{\vec{l}\in V_n}{}' \lim_{\beta\to 0} \frac{e^{-\beta|\vec{x}(\vec{l})-\vec{z}^k|}}{|\vec{x}(\vec{l})-\vec{z}^k|} - \frac{N}{V} f(\vec{z}^k,V)\right\} \qquad 4.6.4$$

where $f(\vec{z},V_n)$ is now a solution of the equation

$$\hat{\Pi} f(\vec{z},V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \lim_{\beta\to 0} e^{-\beta|\vec{y}-\vec{z}|} \qquad 4.6.5$$

Both the sum and integral are over finite regions, thus the $\lim_{\beta\to 0}$ commutes with both the sum and integral and eq (4.6.4) may be written as

$$V_i(\vec{z},k) = \lim_{\beta\to 0} \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n}{}' \frac{e^{-\beta|\vec{x}(\vec{l})-\vec{z}^k|}}{|\vec{x}(\vec{l})-\vec{z}^k|} - \frac{N}{V} f(\vec{z}^k,V_n,\beta) \right\} \qquad 4.6.6$$

where $f(\vec{z},V_n,\beta)$ is the solution of

$$\hat{\Pi} f(\vec{z},V_n,\beta) = \iiint_{V_n} \frac{d\vec{y}\, e^{-\beta|\vec{y}-\vec{z}|}}{|\vec{y}-\vec{z}|} \qquad 4.6.7$$

subject to appropriately modified boundary conditions.

The term in curly brackets in eq (4.6.5) is independent of V_n. If we had wished we could have derived this quantity using the method of Section 3.3.

Introducing fourier transforms, we may write

$$\frac{e^{-\beta r}}{r} = \frac{1}{2\pi^2} \iiint \frac{d\vec{k}\, e^{-i\vec{k}.\vec{r}}}{(k^2+\beta^2)} \qquad \text{(see eq (2.6.2))} \qquad 4.6.8$$

To simplify writing we will introduce

$$S = \sum_{\vec{l}\in V_n}{}' \frac{e^{-\beta|\vec{x}(\vec{l})-\vec{z}^k|}}{|\vec{x}(\vec{l})-\vec{z}^k|} \qquad 4.6.9$$

Substituting (4.6.8) into (4.6.9), S takes the form

$$S = \frac{1}{2\pi^2} \sum_{\vec{l}\in V_n}{}' \iiint \frac{d\vec{k}\, e^{-i\vec{k}.[\vec{x}(\vec{l})-\vec{z}^k]}}{(k^2+\beta^2)} \qquad 4.6.10$$

The sum over $\vec{l}$ and the integral over $\vec{k}$ commute. Thus

$$S = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \sum_{\vec{l}\in V_n}{}' e^{-i\vec{k}.\vec{x}(\vec{l})} \qquad 4.6.11$$

The sum over $\vec{l}$ may be evaluated to give

$$S = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \left\{ \prod_{j=1}^{3} \sin(n+\tfrac{1}{2})k_j a_j / \sin\tfrac{1}{2}k_j a_j - \delta_{k,k'} \right\} \qquad 4.6.12^{*1}$$

It is now necessary to solve (4.6.7) for $f(\vec{z},V_n,\beta)$ subject to the boundary conditions (appropriately modified) discussed in Chapter III, page 73.

Substituting (4.6.8) into (4.6.7), we have

$$\hat{\Gamma} f(\vec{z},V_n,\beta) = \iiint_{V_n} d\vec{y}\, \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{-i\vec{k}.(\vec{y}-\vec{z})}}{(k^2+\beta^2)} \qquad 4.6.13$$

The integral over V_n commutes with the integral over $\vec{k}$. Thus

$$\hat{\Gamma} f(\vec{z},V_n,\beta) = \frac{1}{2\pi^2}\iiint \frac{dk\, e^{i\vec{k}.\vec{z}}}{(k^2+\beta^2)} \iiint_{V_n} d\vec{y}\, e^{-i\vec{k}.\vec{y}} \qquad 4.6.14$$

The integral over V_n may now be performed in (4.6.14) to give

$$\hat{\Gamma} f(\vec{z},V_n,\beta) = \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}}}{(k^2+\beta^2)} \prod_{j=1}^{3} \sin k_j a_j (n+\tfrac{1}{2})/\tfrac{1}{2}k_j \qquad 4.6.15$$

To find a solution of (4.6.15), we assume $f(\vec{z})$ has a fourier transform $g(\vec{k})$. i.e.

$$f(\vec{z}) = \frac{1}{8\pi^3}\iiint dk g(\vec{k}) e^{i\vec{k}.\vec{z}} \qquad 4.6.16$$

---

*1 The Einstein repeated index summation notation is not being used.

Using the general form of eq (3.2.6), which is valid for all types of Bravais lattices, to write $\hat{\Gamma}$ in an integral form, we have

$$\begin{aligned}\hat{\Gamma}(\vec{r})f(\vec{z}) &= \frac{N}{V}\iiint_{-\frac{1}{2}a_j}^{\frac{1}{2}a_j} d\vec{y}\; f(\vec{z}+\vec{y}) \\ &= \frac{N}{V}\iiint_{-\frac{1}{2}a_j}^{\frac{1}{2}a_j} d\vec{y}\;\frac{1}{8\pi^3}\iiint d\vec{k}\, g(\vec{k})\, e^{i\vec{k}.(\vec{y}+\vec{z})} \\ &= \frac{N}{V}\frac{1}{8\pi^3}\iiint d\vec{k}\, g(\vec{k})\, e^{i\vec{k}.\vec{z}}\iiint_{-\frac{1}{2}a_j}^{a_j} d\vec{y}\, e^{i\vec{k}.\vec{y}} \\ &= \frac{N}{V}\frac{1}{8\pi^3}\iiint d\vec{k}\, g(\vec{k})\, e^{i\vec{k}.\vec{z}}\prod_{j=1}^{3}\sin\tfrac{1}{2}k_j a_j/\tfrac{1}{2}k_j \end{aligned} \qquad 4.6.17$$

Taking the inverse fourier transforms of (4.6.13) and the R.H.S. of (4.6.11), we have

$$\frac{N}{V}g(\vec{k})\prod_{j=1}^{3}\sin\tfrac{1}{2}k_j a_j/\tfrac{1}{2}k_j = \frac{4\pi}{(k^2+\beta^2)}\prod_{j=1}^{3}\sin k_j a_j(n+\tfrac{1}{2})/\tfrac{1}{2}k_j \qquad 4.6.18$$

Thus we may set

$$g(\vec{k}) = \frac{4\pi V}{N(k^2+\beta^2)}\prod_{j=1}^{3}\sin k_j a_j(n+\tfrac{1}{2})/\sin\tfrac{1}{2}k_j a_j \qquad 4.6.19$$

Therefore a solution of (4.6.7) is

$$f(\vec{z},V_n,\beta) = \frac{V}{N}\frac{1}{2\pi^2}\iiint\frac{d\vec{k}\, e^{i\vec{k}.\vec{z}}}{(k^2+\beta^2)}\prod_{j=1}^{3}\sin k_j a_j(n+\tfrac{1}{2})/\sin\tfrac{1}{2}k_j a_j \qquad 4.6.20$$

We see immediately that this has the same form as S and hence satisfies the modified form of the second boundary condition on page 73.

However if we evaluate the R.H.S. of (4.6.20), we find it may be written in the form

$$f(\vec{z},V_n,\beta) = f_1(\vec{z},\beta) + f_2(\vec{z},V_n,\beta) \qquad 4.6.21$$

where $f_1(\vec{z},\beta)$ is a solution of the homogeneous equation (3.3.28) and is given by

$$f_1(\vec{z},\beta) = 4\pi \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \qquad 4.6.22$$

where $\vec{y}(\vec{h})$ is a reciprocal lattice vector (see eq (1.2.4)) and $\vec{h}$ is a triplet of integers (h_1,h_2,h_3). The ' indicates that the term with $\vec{h} = 0$ is to be omitted (it doesn't satisfy the homogeneous equation). We show in Appendix 2 that solutions of this form are not allowed and hence must be deleted from (4.6.22) to obtain the correct solution.

Thus the required solution of (4.6.7) is

$$f(\vec{z},V_n,\beta) = \frac{V}{N}\frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(n+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} - 4\pi \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \qquad 4.6.23$$

Substituting (4.6.12) and (4.6.23) into eq (4.6.6), the partial potential becomes

$$V_i(\vec{z},k) = \lim_{\beta\to 0} \frac{q^k}{4\pi\epsilon_o}\left[\frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin k_j a_j (n+\frac{1}{2})}{\sin\frac{1}{2}k_j a_j} - \delta_{k,k'}\right.$$

$$\left. - \frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin k_j a_j (n+\frac{1}{2})}{\sin\frac{1}{2}k_j a_j} + \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{\vec{y}(\vec{h})^2+\beta^2\}}\right]$$

$$= \lim_{\beta\to 0} \frac{q^k}{4\pi\epsilon_o}\left\{\frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} - \delta_{k',k}\frac{1}{2\pi^2}\iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)}\right\} \qquad 4.6.24$$

The last term on the R.H.S. of (4.6.24) is present only when $\vec{z}$ is an ion site. When $\vec{z}$ is an ion site, say $\vec{z} = \vec{x}^{k'}$, then each of the terms

the above terms diverges. To obtain the correct limit, the regions of summation and integration must be the same before taking the limit of the region going to infinity (see discussion following eq (2.6.13)).

Therefore the intrinsic electrostatic self-potential at a k' ion site is

$$V_i(\vec{x}^{k'}) = \sum_{k}^{b} V(\vec{x}^{k'},k)$$

$$= \frac{q^{k'}}{4\pi\epsilon_o} \lim_{\beta\to 0}\left[\frac{4\pi N}{V}\sum_{\vec{h}}{}' \frac{1}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} - \frac{1}{2\pi^2}\iiint\frac{d\vec{k}}{(k^2+\beta^2)}\right]$$

$$+ \sum_{k}^{b}{}' \frac{q^k}{4\pi\epsilon_o} \lim_{\beta\to 0} \frac{4\pi N}{V}\sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot(\vec{x}^{k'}-\vec{x}^{k})}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \qquad 4.6.25$$

where the ' on the sum over k denotes the exclusion of k = k'.

The $\lim_{\beta\to 0}$ may now be taken to obtain

$$V_i(\vec{x}^{k'}) = \frac{1}{4\pi\epsilon_o}\left\{\frac{4\pi N}{V}\sum_{\vec{h}}{}' \frac{q^{k'}}{|\vec{y}(\vec{h})|^2} - \frac{q^{k'}}{2\pi^2}\lim_{\beta\to 0}\iiint\frac{d\vec{k}}{(k^2+\beta^2)}\right.$$

$$\left. + \sum_{k}^{b}{}' q^k \frac{4\pi N}{V}\sum_{h}{}' \frac{e^{i\vec{y}(\vec{h})\cdot(\vec{x}^{k'}-\vec{x}^{k})}}{|\vec{y}(\vec{h})|^2}\right\} \qquad 4.6.26$$

Comparing eqs (4.6.26) and (2.6.13) (with $\vec{x}^{k'}=0$ in (4.6.26)), we see that they are identical. Therefore the intrinsic electrostatic potential is equivalent to the potential evaluated by H&M, and hence Ewald,[*2] whose methods are based on the introduction of a vanishing exponential.

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*2 See discussion at the beginning of Secion 2.6.

G. Summary

In this chapter we have found that the electrostatic potential of an infinite crystal may be written as an absolutely convergent infinite sum provided the c.b.u. chosen satisfies the criteria[*1]

1. charge neutrality $\sum_{k}^{b} q^{k} = 0$
2. no dipole moment $p_{i} = 0$
3. no quadrupole moment $p_{ij} = 0$

For this case, the electrostatic potential of the infinite crystal is equivalent to the intrinsic electrostatic potential.

Similarily we found that the Madelung constant of an infinite crystal may be written as an absolutely convergent infinite sum, which equals our intrinsic Madelung constant, if the c.b.u. with which the infinite crystal is constructed satisfies the less stringent criteria

1. charge neutrality
2. no dipole moment

To the author's knowledge, the difference between the conditions of absolute convergence of the infinite series representing the electrostatic potential and Madelung constant of the infinite crystal has not received any attention in the literature. As a result, in diatomic crystals, the quantities $\alpha(\vec{x}^{k})$ and α_{i} (see eqs (4.4.4) and (4.4.5)) have been used interchangeably (i.e. they were assumed to be exactly the same quantities) without regard to the difference in convergence criteria necessary to obtain them.

In Section E, we have shown that Evjen evaluated the wrong quantity

in CsCl and ZnS by using unit cells which had non-vanishing quadrupole moments (he used $\alpha(\vec{x}^k)$ and α_i interchangeably).

In Section F, we have shown that the quantity evaluated by Ewald (who introduced a vanishing exponential) is equivalent to our intrinsic electrostatic potential. As our approach is more appropriate to real systems, we consider this equivalence a proof of the validity of Ewald's procedure rather than of ours.

In Section 1.5, we stated that the accepted value of the electrostatic potential of an infinite crystal was the electrostatic potential which was obtained using a c.b.u. which insured that the sum was not shape conditionally convergent or was the quantity defined by the introduction of the vanishing exponential. We have shown that both of these cases give an electrostatic potential equal to the intrinsic electrostatic potential. Therefore the accepted value of the electrostatic potential of an infinite crystal is the intrinsic electrostatic potential.

The next Chapter will be devoted to the discussion of the extrinsic partial potential which has no counterpart in the infinite crystal theories.

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*1 We have shown this explicitly only for cubic crystals. However, the analysis is easily generalized to more complex crystals to give the same results.

CHAPTER V

THE EXTRINSIC ELECTROSTATIC POTENTIAL

A. Introduction

In Chapter 3, we separated the electrostatic potential of a finite crystal into two parts - an extrinsic and an intrinsic part. This chapter will be devoted to a discussion of the extrinsic part. The extrinsic part contains all the effects which are related to having a finite sample.

In Appendix 3, we will show that the intrinsic electrostatic potential is the same for points at the surface as for points in the bulk of the crystal. Thus any deviation from the bulk properties of the crystal (such as surface energy) near the surface is directly related to the extrinsic electrostatic potential.

The surface energy forms only a small part of the total energy of crystals whose thickness $\gtrsim 50$ A^{o}. Thus little work (compared to the amount of work on bulk properties, such as the Madelung constant) has been done on the evaluation of the energy at the surface. Recently surface effects have become more important since experimental research is being done on surface waves and thin crystals where surface effects are significant.

Tosi has considered the electrostatic potential at the surface of a crystal which extends to infinity away from the surface. Huang and Grindlay (H&G)[19] considered the problem of a semi-infinite slab (two surfaces are present). Tosi used a modification of the Ewald method,

whereas H&G summed the contribution due to each plane as one goes from one surface to the other.

In Section B, we will discuss general properties of the extrinsic electrostatic potential for an ellipsoidal specimen. We will show that the extrinsic term may contribute significantly to bulk properties of the sample such as electrostatic energy.

In Section C, we will derive an explicit expression for the extrinsic electrostatic potential for points near the surface of a slab-shaped specimen. Numerical results for the electrostatic contribution to the surface energies for various orientations in NaCl and CsCl will be given in Section D.

B. The Extrinsic Electrostatic Potential

We have shown in Chapter III that the total electrostatic potential, $V(\vec{z})$, due to a finite array of point charges may be written in the form

$$V(\vec{z}) = V_i(\vec{z}') + V_e(\vec{z}) \qquad 5.2.1$$

$V_i(\vec{z}')$ is the intrinsic electrostatic potential (which may be considered to be a periodic function of $\vec{z}$) given by

$$V_i(\vec{z}') = \sum_k^b V_i(\vec{z}',k)$$

$$= \sum_k^b \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'+\vec{x}^k|} - \frac{N}{V} f(\vec{z}'-\vec{x}^k, V_n) \right\} \qquad 5.2.2$$

$V_e(\vec{z})$ is the extrinsic electrostatic potential (which is a non-periodic function of $\vec{z}$) given by

$$V_e(\vec{z}) = \sum_b^r V_e(\vec{z},k)$$

$$= \sum_k^r \frac{q^k}{4\pi\epsilon_o} \frac{N}{V} f(\vec{z}-\vec{x}^k, V) \qquad 5.2.3$$

In Chapter IV, we discussed how $V_i(\vec{z})$ was related to the electrostatic potential of an infinite crystal, $V^\infty(\vec{z})$. The quantity $V_e(\vec{z})$ has no relation to any quantity which is derivable using infinite crystals. Even the conditional convergence of the infinite sums, such as the sum for the Madelung constant, arise due to the second term in eq (5.2.2) not from $V_e(\vec{z})$, although this term appears similar in form.

We will discuss the properties of $V_e(\vec{z})$ for an ellipsoid. From

Section 3.4.i, we have that the extrinsic partial potential for an ellipsoidal specimen is (the coordinate axes are not parallel to the principal axes)

$$V_e(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o}\frac{N}{V}\left\{L_0 + I_s + \frac{\pi a^2}{6} - 2\pi L_{ij}(z_i - x_i^k)(z_j - x_j^k)\right\} \quad 5.2.4$$

(see eq (3.4.18)) where the $\vec{x}^k$ are defined by the c.r.u.

Thus

$$V_e(\vec{z}) = \sum_k^r V_e(\vec{z},k)$$

$$= \frac{N}{4\pi\epsilon_o V}\left\{\sum_k^r q^k(L_0 + I_s + \frac{\pi a^2}{6}) - 2\pi L_{ij}\sum_k^r q^k(z_i - x_i^k)(z_j - x_j^k)\right\}$$

$$= \frac{N}{4\pi\epsilon_o V}\left\{\sum_k^r q^k(L_0 + I_s + \frac{\pi a^2}{6} - 2\pi L_{ij} z_i z_j) - 2\pi L_{ij}\sum_k^r q^k(2z_i x_j^k - x_i^k x_j^k)\right\} \quad 5.2.5$$

$$= \frac{1}{\epsilon_o} L_{ij}(P_i z_j - P_{ij}) \quad 5.2.6.$$

where

$$P_i = \frac{N}{V}\sum_k^r q^k x_i^k \quad 5.2.7$$

and

$$P_{ij} = \tfrac{1}{2}\frac{N}{V}\sum_k^r q^k x_i^k x_j^k \quad 5.2.8$$

are respectively the extrinsic dipole moment density (polarization) and the extrinsic quadrupole moment density. The first term on the R.H.S. of (5.2.5) vanished due to charge neutrality which we have assumed for the c.r.u.

The quantities $\vec{x}^k$ used to define P_i and P_{ij} do not have the same arbitrariness associated with the corresponding terms (p_i and p_{ij}) derived using the c.b.u. which is used in the evaluation of the intrinsic

electrostatic potential (see eqs (4.2.17) and (4.2.18)). These $\vec{x}^k$ are defined by the particular sample (i.e. choice of c.r.u.) we are considering, whereas the $\vec{x}^k$ of the c.b.u. are chosen according to convenience criteria which depend on the crystal structure, not on the particular sample. Thus P_i and P_{ij} are properties of the sample under consideration.

We note that, for some crystals such as CsCl, we have not found it possible to construct a c.r.u. which is neutral and yet has no dipole moment. When discussing c.b.u.'s we did not have to consider this point since c.b.u.'s are allowed to have charges which are fractions of the ionic charge and hence may have both charge neutrality and vanishing dipole moment. The charges used in the c.r.u. have to be the ionic charges. Charges which are fractions of the ionic charge are not allowed in the c.r.u. since they do not exist in real systems. Therefore, if we neglect effects of surface charge such as electrons and ions from outside the crystal which is not part of the crystal, then samples of CsCl will all have dipole moments. This means that the magnitude of $V_e(\vec{z})$ will be large compared to the magnitude of $V_i(\vec{z}')$ due to the linear dependence on $\vec{z}$. However, the physically relevant quantities are the derivatives of the electrostatic potential with respect to $\vec{z}$. For these quantities, the intrinsic terms will be of the same order as the extrinsic terms. From eqs (4.2.19) and (5.2.6), the intrinsic and extrinsic electrostatic potentials are proportional to $|\vec{P}|z$ where $\vec{P}$ is the dipole moment of the c.b.u. or c.r.u. Therefore the derivatives are proportional to $|\vec{P}|$ which is of the same order in both cases. (The $|\vec{P}|$ of the c.b.u. is assumed non-zero to obtain an estimation of the order of the terms involved in the intrinsic electrostatic potential.)

For crystals such as NaCl where it is possible to construct c.r.u.'s which are electrically neutral and have vanishing dipole and quadrupole moments

We may define an extrinsic electrostatic energy associated with the extrinsic electrostatic potential by

$$U_e \overset{\text{defn}}{=} \tfrac{1}{2}\sum_{k'}^{r} q^{k'} V_e(\vec{x}^{k'})$$

$$= \frac{\frac{1}{2}}{\epsilon_o} L_{ij}\left(\sum_{k'}^{r} q^{k'} P_i x_j^{k'} - \sum_{k'}^{r} q^{k'} P_{ij}\right)$$

$$= \frac{V}{2N\epsilon_o} L_{ij} P_i P_j \qquad 5.2.9$$

As we introduced an intrinsic Madelung constant in Section 4.3, we will introduce an extrinsic Madelung constant, α_e, in this section as follows

$$\alpha_e \overset{\text{defn}}{=} 4\pi\epsilon_o a U_e/(me)^2 \qquad 5.2.10$$

(c.f. eq (4.3.2)).

Thus for an ellipsoidal specimen, the extrinsic Madelung constant is

$$\alpha_e = \frac{2\pi V a}{N} L_{ij} P_i P_j \qquad 5.2.11$$

Assuming that the polarization is of the order $\frac{1}{2}e/a^2$ (this is a reasonable approximation for a crystal such as CsCl), then

$$\alpha_e = \tfrac{1}{2}\pi \qquad 5.2.12$$

which is of the same order as the intrinsic Madelung constant.

We must remember that the above discussion only holds for points far from the surface since this assumption was used in deriving eq (3.4.18) (see discussion preceding eq (3.4.3)). The next section will consider the problem of the extrinsic electrostatic potential near the surface of a crystal.

C. The Extrinsic Partial Potential at the Surface of a Slab

In the section, we will consider the extrinsic partial potential of a finite slab since, next to the ellipsoid, it is the simplest problem to solve. In addition, we will show in the next section that these extrinsic terms contribute significantly to the electrostatic potential and electrostatic energy at the surface of a slab even when the dipole and quadrupole moments of the c.r.u. vanish (causing the extrinsic terms to vanish in the bulk of the sample)*1. The extrinsic partial potential contains the total effect of the presence of the surface on the electrostatic potential.

Generalizing eq (3.3.70), the extrinsic partial potential for an orthorhombic array (with lattice parameters a_1, a_2, a_3) is

$$V_e(\vec{z},k) = \frac{q^k}{4\pi\epsilon_o} \frac{N}{V} f(\vec{z}-\vec{x}^k,V) \qquad 5.3.1$$

---

*1 We note that for an ellipsoid, there is no contribution due to the extrinsic term when the dipole and quadrupole moments vanish. Thus a thin slab, in the limit of the edges going to infinity, does not approach an ellipsoid, as is commonly supposed. We think the reason this happens is that the smoothing operation (i.e. the approximating of $I'(\vec{z},V-V_s)$, eq (3.4.2), by a constant I_s) is not valid when considering a point near the surface. Thus the surface of a slab can never truly approach the surface of an ellipsoid although for points far from the surface the approximation does hold.

---

where $\vec{z}$ is the position vector of the point of interest P (with the origin of the coordinate system chosen to be the center of the region V), $\vec{x}^k$ is the amount the k-th sub-lattice is shifted with respect to the k=0 sub-lattice, V is an arbitrary region (which is made up of basic cubes), $\frac{V}{N} = a_1 a_2 a_3$, and $f(\vec{z},V)$ is a solution of

$$\hat{\Gamma} f(\vec{z},V) = \iiint_V \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad 5.3.2$$

subject to the boundary conditions given on page 73. The extrinsic partial potential is defined at points both inside and outside of the region V.

The simplest surface to consider is a plane, i.e. the surface of a slab. Thus we will let V be a slab with sides of length $\{(2m_1+1)a_1, (2m_2+1)a_2, (2m_3+1)a_3\}$ (see fig. 5.1). To solve eq (5.3.2), we proceed as described in Section 4.6. Thus the solution, for $\vec{z}$ within V, is

$$f^i(\vec{z},V) = \lim_{\beta \to 0} \left\{ \frac{1}{2\pi^2} \iiint \frac{d\vec{k}\, e^{i\vec{k}\cdot\vec{z}}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} - \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \right\}_{\vec{z}\in V} \qquad 5.3.3$$

where the i superscript denotes the interior solution.

For $\vec{z}$ exterior to the region V, the solution is

$$f^e(\vec{z},V) = \lim_{\beta \to 0} \frac{1}{2\pi^2} \iiint \frac{dk\, e^{i\vec{k}\cdot\vec{z}}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j}_{\vec{z}\notin V} \qquad 5.3.4^{*2}$$

The limit $\beta \to 0$ has to be taken after the integration over $\vec{k}$ has been performed. It does not commute with the integral. The e superscript

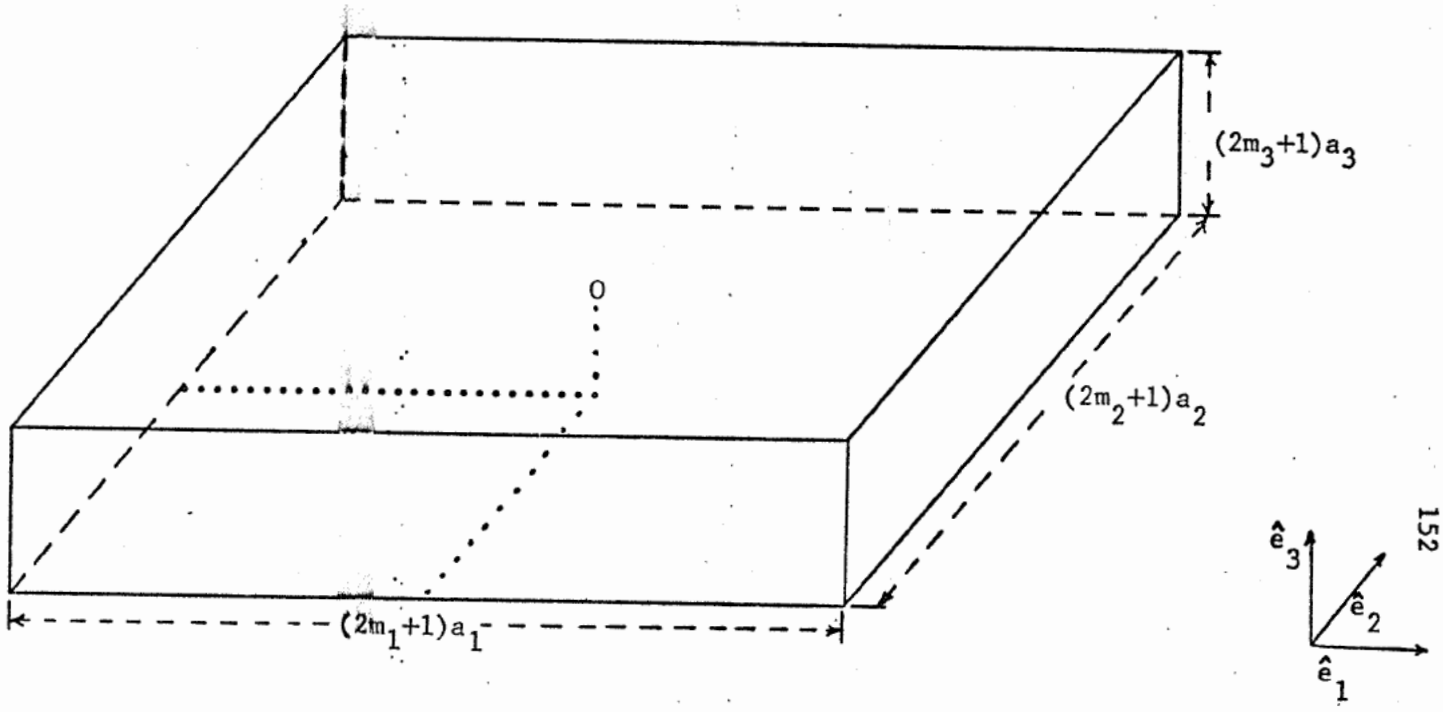

Figure 5.1

A Finite Slab

A finite slab with sides of length $\{(2m_1+1)a_1, (2m_2+1)a_2, (2m_3+1)a_3\}$ and center at 0.

denotes the exterior solution.

There are three cases in which eqs (5.2.3) and (5.2.4) are easily evaluated. They are

(i) $m_j \to \infty \quad j = 1,2,3$

This is the case of an infinite crystal. V_e^e does not exist.

(ii) $m_1, m_2 \to \infty$, m_3 finite

This is the infinite slab case which H&G considered. V_e^e does exist.

(iii) $m_j \to \infty$ $j = 1,2,3$ but also $z_3 = (m_3+\frac{1}{2})a_3 - z_3'$

This insures that the point of interest remains at one of the surfaces while the other surfaces recede to infinity.

This is the case of the semi-infinite crystal. V_e^e does exist.

We will evaluate V_e^i and V_e^e (when it exists) for the first two cases. The third case can be easily derived from the results of the second case.

---

*2 The extrinsic partial potential is not continuous at the surface (i.e. at $|z_j| = (m_j+\frac{1}{2})a_j$)

$$V_e^i(\vec{z},k) \neq V_e^e(\vec{z},k)$$

However the total partial potential

$$V_i(\vec{z},k) + V_e^i(\vec{z},k) = V_e^e(\vec{z},k)$$

is still continuous as expected.

(i) The infinite crystal

Taking the limits $m_p \to \infty$ of eq (5.3.3), we have

$$\lim_{m_p\to\infty} V_e(\vec{z},k) = \frac{Nq^k}{4\pi\epsilon_o V} \lim_{m_p\to\infty} \lim_{\beta\to 0} \left\{ \frac{1}{2\pi^2} \iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} \right.$$

$$\left. - \frac{4\pi V}{N} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \right\} \qquad p = 1,2,3 \qquad 5.3.5$$

To proceed further we have to assume that the $\lim_{m_p\to\infty}$ commutes with the $\lim_{\beta\to 0}$. We are unable to show that this is a valid assumption. Provided this assumption holds, then the limit also commutes with the integration over $\vec{k}$-space. Thus

$$\lim_{m_p\to\infty} V_e(\vec{z},k) = \frac{Nq^k}{4\pi\epsilon_o V} \lim_{\beta\to 0} \left\{ \frac{1}{2\pi^2} \iiint \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \lim_{m_p\to\infty} \left[\frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} \right] \right.$$

$$\left. - \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \right\} \qquad p = 1,2,3 \qquad 5.3.6$$

We may now use the identity

$$\lim_{m\to\infty} \frac{\sin(m+\frac{1}{2})ka}{\sin\frac{1}{2}ka} = \frac{2\pi}{a} \sum_{h} \delta(k-y(h)) \qquad 5.3.7$$

where $y(h)$ is a one-dimensional reciprocal lattice vector, to obtain

$$\lim_{m_p\to\infty} V_e(\vec{z},k) = \frac{Nq^k}{4\pi\epsilon_o V} \lim_{\beta\to 0} \left\{ 4\pi \sum_{\vec{h}} \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} - 4\pi \sum_{h}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{\vec{y}(\vec{h})^2+\beta^2\}} \right\}$$

$$= \lim_{\beta\to 0} Nq^k/V\epsilon_o\beta^2 \qquad 5.3.8$$

which is independent of $\vec{z}$ and goes to ∞ as $\beta\to 0$ as expected. The total electrostatic potential of an infinite array of charge is infinite. We have separated it into two parts - an intrinsic and an extrinsic. The intrinsic remains finite, therefore the extrinsic part must diverge.

(ii) The infinite slab

It is convenient to introduce the quantity $\phi^a(\vec{z},m_3,\beta)$ as follows

$$\lim_{\beta \to 0} \phi^a(\vec{z},m_3,\beta) = \frac{4\pi N \epsilon_o}{Vq^k} \lim_{m_1,m_2 \to \infty} V_e^a(\vec{z},k) \quad a = i,e \qquad 5.3.9$$

Since V_e^e exists in that case, we will evaluate both ϕ^i and ϕ^e for completeness.

(a) ϕ^i

From inspection of eqs (5.3.1) and (5.3.3), we have that

$$\phi^i(\vec{z},m_3,\beta) = \frac{1}{2\pi^2} \lim_{m_1,m_2 \to \infty} \left[\iiint_L \frac{d\vec{k}\, e^{i\vec{k}.\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} - \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \right] \qquad 5.3.10$$

We may immediately take the limits $m_1, m_2 \to \infty$, as we did for the infinite crystal case, to obtain

$$\phi^i(\vec{z},m_3,\beta) = \frac{2Na_3}{V} \sum_{\substack{\vec{h} \\ h_3=0}} e^{i\vec{y}(\vec{h}).\vec{z}^k} \int_{-\infty}^{\infty} \frac{dk_3\, e^{ik_3 z_3^k}}{\{|\vec{y}(\vec{h})|^2+k_3^2+\beta^2\}} \frac{\sin(m_3+\frac{1}{2})k_3 a_3}{\sin\frac{1}{2}k_3 a_3}$$

$$- \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} \qquad 5.3.11$$

We now need the additional identity (found using contour integration)

$$\int_{-\infty}^{\infty} \frac{dk\, e^{ikz}}{(d^2+k^2)} \frac{\sin(m+\frac{1}{2})ka}{\sin\frac{1}{2}ka} = \frac{2\pi}{a} \sum_{h} \frac{e^{iy(h)z}}{\{d^2+y^2(h)\}} - \frac{\pi}{d} e^{-(m+\frac{1}{2})ad} \frac{\cosh dz}{\sinh\frac{1}{2}da} \qquad 5.3.12$$

which is valid for $|z| < (m+\frac{1}{2})a$

Substituting (5.3.12) into (5.3.11), we have

$$\phi^i(\vec{z},m_3,\beta) = \frac{4\pi N}{V}\left\{\sum_{\vec{h}} \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}} - \tfrac{1}{2}a_3 \sum_{\substack{\vec{h}\\ h_3=0}} \frac{e^{-(m+\frac{1}{2})\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}a_3}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}} \frac{\cosh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}z_3^k}{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}\frac{1}{2}a_3}\right.$$

$$\left. - \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}}\right\}$$

$$= \frac{4\pi N}{V}\left\{\beta^{-2} - \tfrac{1}{2}a_3 e^{-(m+\frac{1}{2})a_3} \frac{\cosh\beta z_3^k}{\sinh\beta\frac{1}{2}a_3}\right. \qquad 5.3.13$$

$$\left. - \tfrac{1}{2}a_3 \sum_{\substack{\vec{h}\\ h_3=0}}{}' \frac{e^{-(m+\frac{1}{2})\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}a_3}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}} \frac{\cosh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}z_3^k}{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}\frac{1}{2}a_3}\right\}$$

where the ' indicates the exclusion of $h_1 = h_2 = 0$ from the sum over $\vec{h}$ (we have seperated this term out). Letting β become very small and keeping terms only up to order 0, eq (5.3.13) reduces to

$$\phi^i(\vec{z},m_3,\beta) = \frac{2\pi N}{V}\left\{2(m_3+\tfrac{1}{2})a_3 \frac{}{\beta} - (m_3+\tfrac{1}{2})^2 a_3^2 + (z_3^k)^2 - \frac{a_3^2}{12}\right. \qquad 5.3.14$$

$$\left. - a_3 \sum_{\substack{\vec{h}\\ h_3=0}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} e^{-(m_3+\frac{1}{2})|\vec{y}(\vec{h})|a_3}}{|\vec{y}(\vec{h})|} \frac{\cosh|\vec{y}(\vec{h})|z_3^k}{\sinh|\vec{y}(\vec{h})|\frac{1}{2}a}\right\}$$

We note that this quantity still diverges as $\beta \to 0$, but at a slower rate than the infinite crystal.

We are interested in the value of the extrinsic potential at the surface of the crystal. Thus it is convenient to shift the $\vec{z}$ origin to the surface of V by introducing the transformation

$$z_3 = (m_3+\tfrac{1}{2})a_3 - z_3' \qquad 5.3.15$$

where z_3' is positive (this z_3' is not related to the z_3' associated with

the intrinsic partial potential).

Thus

$$\phi^i(\vec{z}',m_3,\beta) = \frac{2\pi N}{V}\left\{2(m_3+\tfrac{1}{2})a_3^2 + (z_3'^k)^2 - 2z_3'^k(m_3+\tfrac{1}{2}) - \frac{a_3^2}{12}\right. \qquad 5.3.16$$

$$\left. - a_3 \sum_{\substack{\vec{h} \\ h_3=0}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}'^k}}{|\vec{y}(\vec{h})|} e^{-(m_3+\frac{1}{2})|\vec{y}(\vec{h})|a_3} \frac{\cosh|\vec{y}(\vec{h})|\{z_3'^k+(m_3+\frac{1}{2})a_3\}}{\sinh|\vec{y}(\vec{h})|\,\frac{1}{2}a_3}\right\}$$

where

$$\vec{z}'^k = z_1^k\hat{e}_1 + z_2^k\hat{e}_2 + z_3'^k\hat{e}_3 \text{ and } z_3'^k = z_3' + x_3^k \qquad 5.3.17$$

(b) ϕ^e

From inspection of eqs (5.3.1) and (5.3.4), we have

$$\phi^e(\vec{z},m_3,\beta) = \frac{1}{2\pi^2}\lim_{m_1,m_2\to\infty}\iint\frac{d\vec{k}\,e^{i\vec{k}\cdot\vec{z}^k}}{(k^2+\beta^2)}\prod_{j=1}^{3}\frac{\sin(m_j+\frac{1}{2})k_ja_j}{\sin\frac{1}{2}k_ja_j} \qquad 5.3.18$$

Proceeding as for case (a), we take the limits $m_1, m_2 \to \infty$ to obtain

$$\phi^e(\vec{z},m_3,\beta) = \frac{2Na}{V}\sum_{\substack{\vec{h} \\ h_3=0}} e^{i\vec{y}(\vec{h})\cdot\vec{z}^k}\int_{-\infty}^{\infty}\frac{dk_3\,e^{ik_3z_3^k}}{\{|\vec{y}(\vec{h})|^2+\beta^2+k_3^2\}^{\frac{1}{2}}}\cdot\frac{\sin k_3a_3(m_3+\frac{1}{2})}{\sin\frac{1}{2}k_3a_3} \qquad 5.3.19$$

Since $|z_3^k| > (m_3+\frac{1}{2})a$, we have to use the identity

$$\int_{-\infty}^{\infty}\frac{dk\,e^{ikz}}{(d^2+k^2)^{\frac{1}{2}}}\frac{\sin(m+\frac{1}{2})ka}{\sin\frac{1}{2}ka} = \frac{\pi}{d}e^{-dz}\frac{\sinh ad(m+\frac{1}{2})}{\sinh\frac{1}{2}ad} \qquad 5.3.20$$

rather than (5.3.12) which is valid only for $|z| > (m+\frac{1}{2})a$. Thus $\phi^e(\vec{z},m_3,\beta)$ becomes

$$\phi^e(\vec{z},m_3,\beta) = \frac{2\pi Na_3}{V} \sum_{\substack{\vec{h} \\ h_3=0}} \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} e^{-z_3^k\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}} \frac{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}a_3(m_3+\frac{1}{2})}{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}\frac{1}{2}a_3}$$

$$= \frac{2\pi Na_3}{V} \frac{e^{-z_3\beta}}{\beta} \frac{\sinh\beta a_3(m_3+\frac{1}{2})}{\sinh\beta\frac{1}{2}a_3} \qquad 5.3.21$$

$$+ \sum_{\substack{\vec{h} \\ h_3=0}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} e^{-z_3^k\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}}}{\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}} \frac{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}a_3(m_3+\frac{1}{2})}{\sinh\{|\vec{y}(\vec{h})|^2+\beta^2\}^{\frac{1}{2}}\frac{1}{2}a_3}$$

Again expanding in powers of β keeping only terms up to order 0, eq (5.3.21) reduces to

$$\phi^e(\vec{z},m_3,\beta) = \frac{2\pi N}{V}\left\{(m_3+\tfrac{1}{2})a_3\left(\frac{1}{\beta} - z_3^k\right) + a_3 \sum_{\substack{\vec{h} \\ h_3=0}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} e^{-z_3^k|\vec{y}(\vec{h})|}}{|\vec{y}(\vec{h})|} \frac{\sinh|\vec{y}(\vec{h})|a_3(m_3+\frac{1}{2})}{\sinh|\vec{y}(\vec{h})|\frac{1}{2}a_3}\right. \qquad 5.3.22$$

Letting $z_3^k = (m_3+\frac{1}{2})a_3 + z_3'^k$ where $z_3'^k > 0$, (5.3.22) becomes

$$\phi^e(\vec{z}',m_3,\beta) = \frac{4\pi Na_3}{V}\left\{(m_3+\tfrac{1}{2})\left\{\frac{1}{\beta} - z_3'^k - (m_3+\tfrac{1}{2})a_3\right\}\right. \qquad 5.3.23$$

$$+ \tfrac{1}{2} \sum_{\substack{\vec{h} \\ h_3=0}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}'^k} e^{-z_3'^k|\vec{y}(\vec{h})|} e^{-(m_3+\frac{1}{2})a_3|\vec{y}(\vec{h})|}}{|\vec{y}(\vec{h})|} \frac{\sinh|\vec{y}(\vec{h})|a_3(m_3+\frac{1}{2})}{\sinh|\vec{y}(\vec{h})|\frac{1}{2}a_3}$$

We note that at $z_3' = 0$, ϕ^e diverges in the same manner as ϕ^i as $\beta \to 0$.

In addition

$$\vec{z}' = z_1\hat{e}_1 + z_2\hat{e}_2 + z_3'\hat{e}_3 \qquad 5.3.24$$

D. Numerics

In this section, we will evaluate the extrinsic electrostatic potential as a function of the distarce from the surface of NaCl and CsCl slabs. Experimentally, neutral surfaces are the easiest to obtain. Thus, we will consider slabs which have electrically neutral surfaces. The simplest neutral planes to consider are the (100) and (110) planes in NaCl and the (110) plane in CsCl

The lattice arrays associated with each of these orientations are given in fig.s 5.2, 5.3, and 5.4 respectively. In order to use what we have defined as the extrinsic electrostatic potential, we first have to decompose each of these arrays into its sub-lattice components (i.e. determine the c.r.u.).

The simplest decomposition into sub-lattices of each array is as follows:

(1) NaCl (100)

- 8 cubic sub-lattices with lattice parameter a
- $k = 0,1,\ldots,7$

(2) NaCl (110)

- 4 tetragonal sub-lattices with lattice parameters $(1, \frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}})a$
- $k = 0,1,2,3$

(3) CsCl (110)

- 4 tetragonal sub-lattices with lattice parameters $(1,\sqrt{2},\sqrt{2})a$

The $\overset{+}{x}^k$ values for each of the above cases are given in Table 5.1.

For simplicity we will assume each of the sub-lattices has the

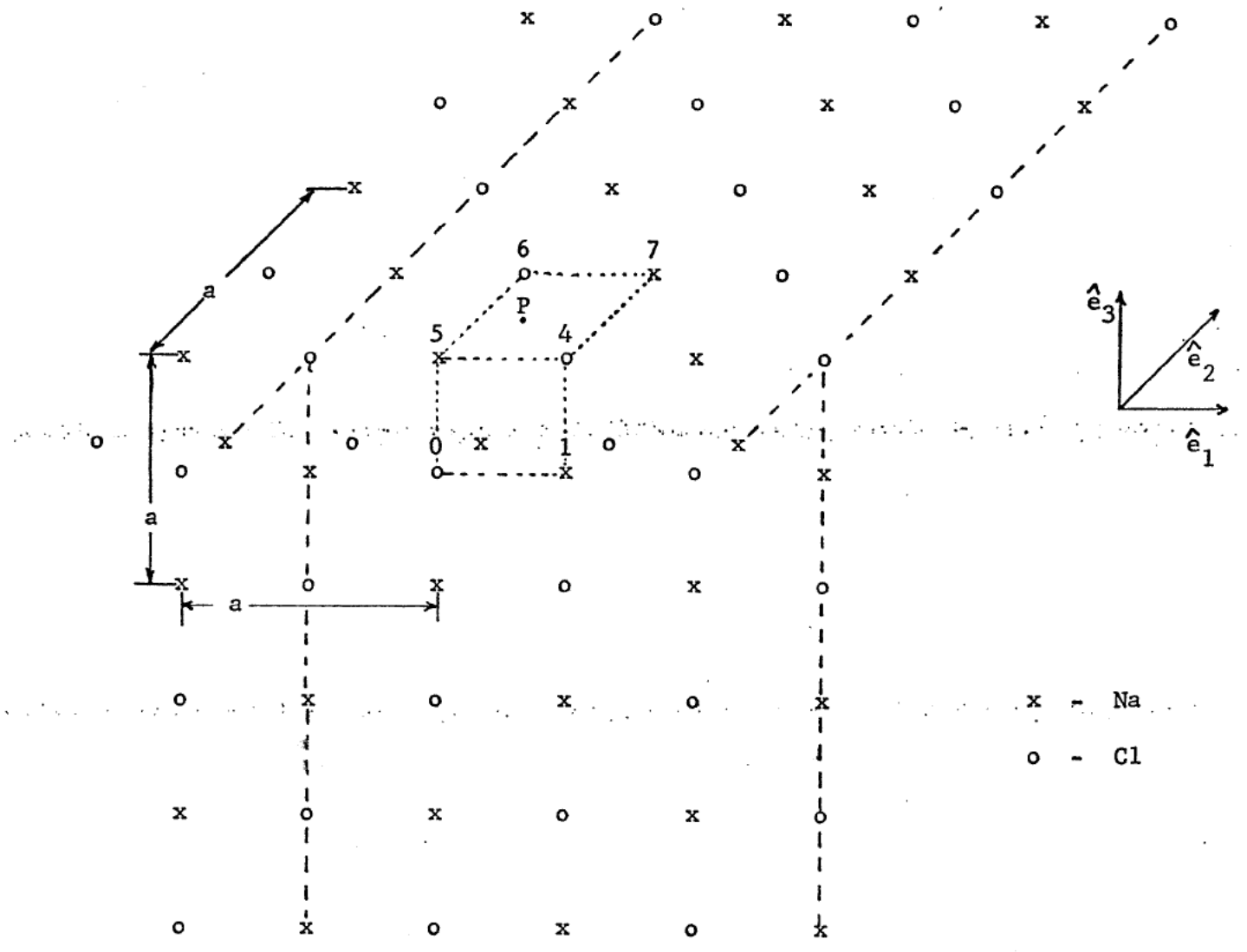

Figure 5.2

A (100) Surface of NaCl

Top and side view of the lattice array of NaCl with a (100) plane at the surface. The numbers labelling the ion sites are the k values assigned to the sub-lattices.

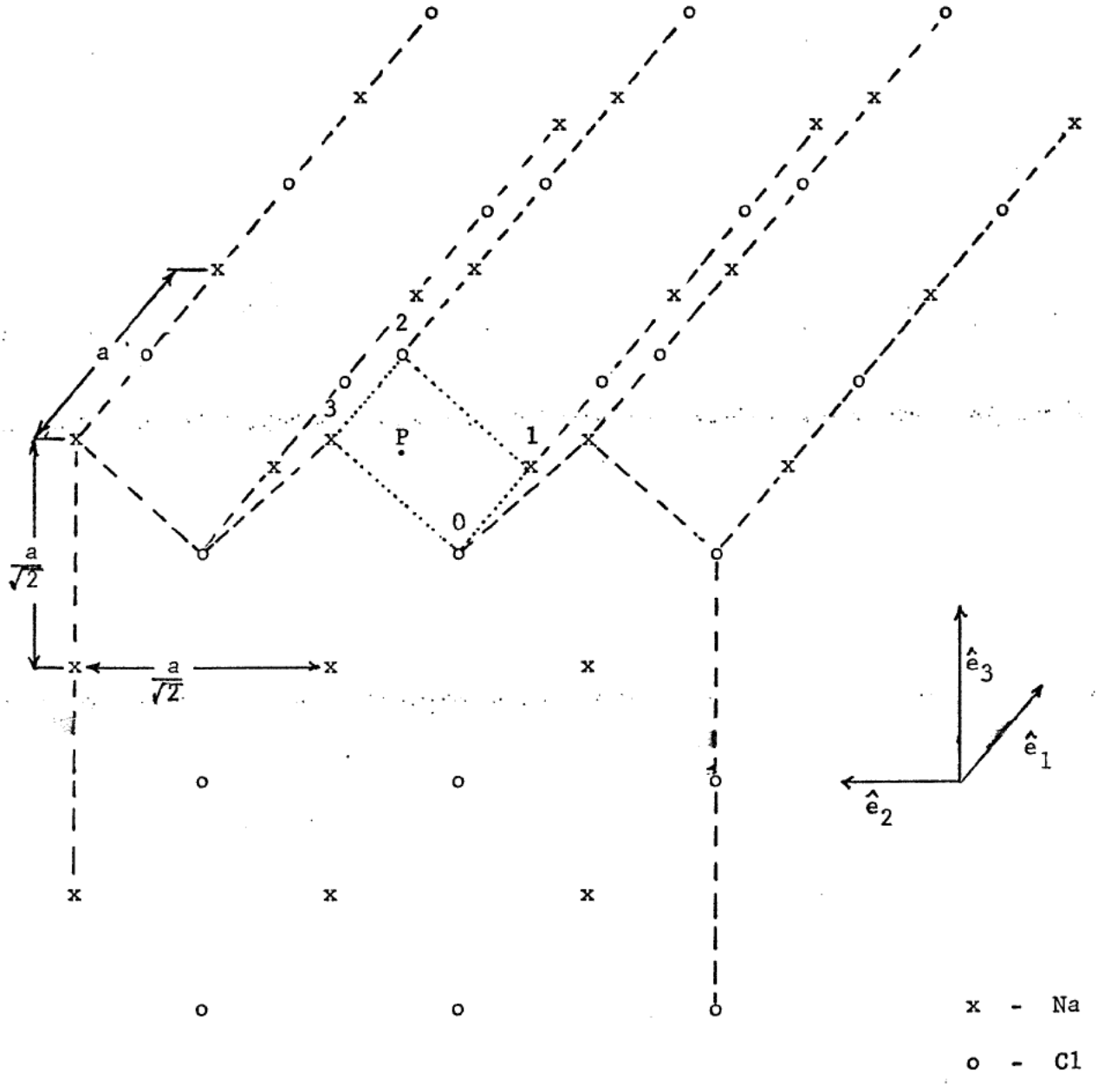

Figure 5.3

A (110) Surface of NaCl

Top and side view of the lattice array of NaCl with a (110) plane at the surface. The numbers labelling the ion sites are the k values assigned to the sub-lattices.

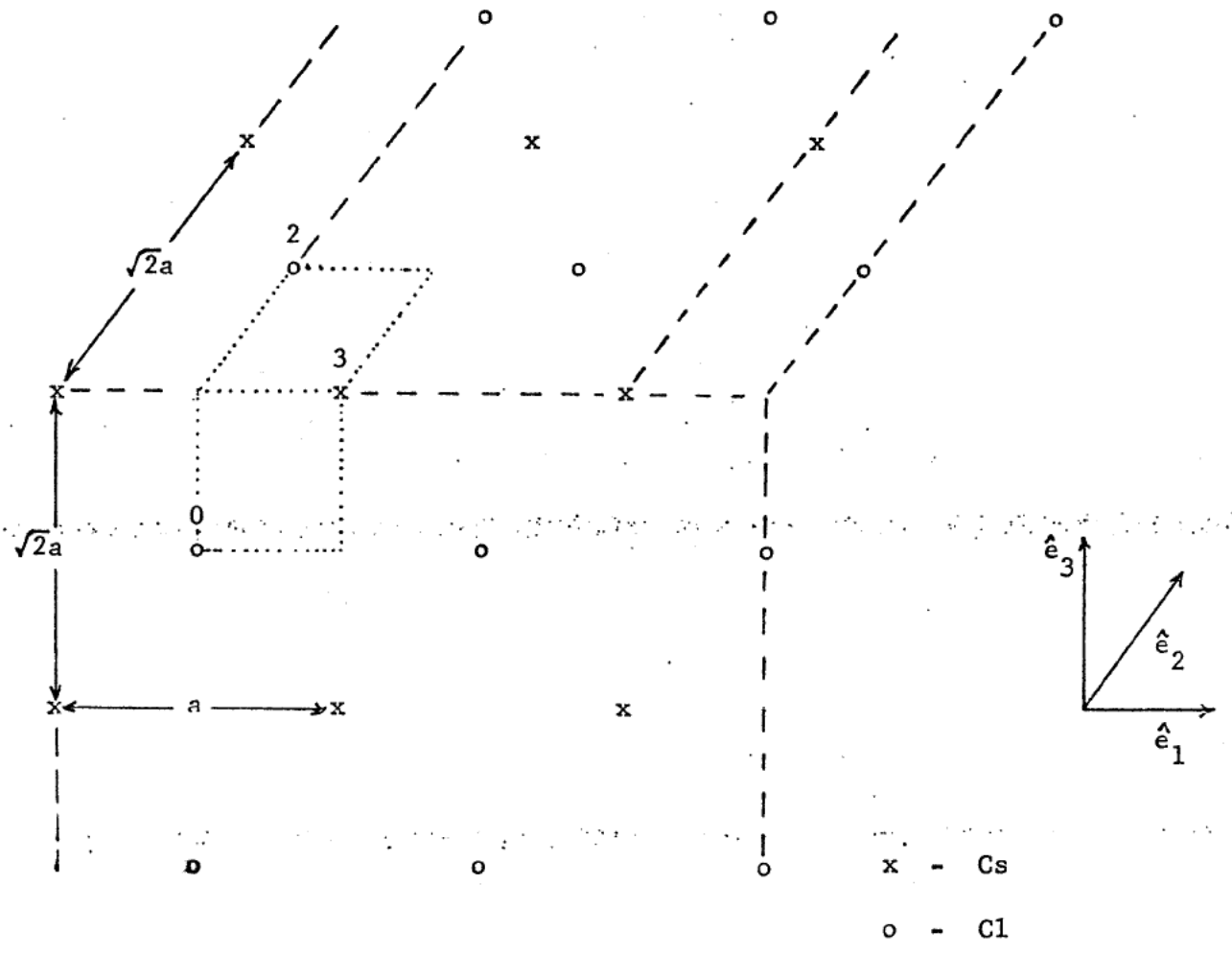

Figure 5.4

A (110) Surface of CsCl

Top and side view of the lattice array of CsCl with a (110) plane at the surface. The numbers labelling the ion sites are the k values assigned to the sub-lattices.

same m_3 value. This means that the crystal may be constructed using only one c.r.u. For $m_3 \gtrsim 5$, the terms in eq (5.3.16) containing negative exponentials in m_3, may be neglected. This is almost equivalent to letting one of the slab surfaces be at infinity (i.e. the case Tosi considered). The only difference is that we retain m_3 in the linear terms of eq (5.3.16).

Thus, summing (5.3.16) over the sub-lattices, within the above approximation, to obtain the electrostatic potential, we have

$$V_e^i(\vec{z}) = \sum_k^r \frac{q^k}{4\pi\epsilon_o} \frac{2\pi N}{V} \left\{ 2(m_3+\tfrac{1}{2})a_3 \frac{}{\beta} - \frac{a_3^2}{12} + (z_3^k)^2 - 2z_3^k a_3 (m_3+\tfrac{1}{2}) \right.$$
$$\left. + \tfrac{1}{2}a_3 \sum_{\substack{\vec{h} \\ h_3=0}}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}}}{|\vec{y}(\vec{h})|} \frac{e^{-\vec{z}\,|\vec{y}(\vec{h})|}}{\sinh|\vec{y}(\vec{h})|\tfrac{1}{2}a_3} \right\}$$

$$= \frac{1}{\epsilon_o} \left\{ P_{33} + \{z_3 - a_3(m_3+\tfrac{1}{2})\} P_3 + \tfrac{1}{2}Na_3 \sum_{\substack{\vec{h} \\ h_3=0}}' \sum_k^r q^k \frac{e^{-i\vec{y}(\vec{h}).\vec{x}^k} e^{-\vec{x}_3^k|\vec{y}(\vec{h})|}}{\vec{y}(\vec{h}) \sinh|\vec{y}(\vec{h})|\tfrac{1}{2}a_3} X \right.$$
$$\left. e^{i\vec{y}(\vec{h}).\vec{z}} e^{-z_3|\vec{y}(\vec{h})|} \right\} \quad 5.4.1$$

The terms in P_{33} and P_3 are the ones we would obtain by approximating the thin slab by an ellipsoid (see comment *1 of Section C). We note that the singularity arising from the $1/\beta$ has vanished due to charge neutrality of the c.r.u.

To simplify writing we will introduce a dimensionless function $\alpha_e(\vec{z})$, (cf $\alpha_i(\vec{z})$, eq (4.4.3)), as follows

$$\alpha_e(\vec{z}) \overset{\text{defn}}{=} 4\pi\epsilon_o b V_e^i(\vec{z})/(me) \quad 5.4.2$$

where b is an appropriate scaling distance and m is the greatest common factor of q^k/e with k ranging over the c.r.u.

Substituting (5.4.1) into (5.4.2), we have

$$\alpha_e(\vec{z}) = \frac{4\pi b}{me}\left\{ P_{33} + \{z_3 - a_3(m_3+\tfrac{1}{2})\} P_3 \right. \qquad 5.4.3$$

$$\left. + \tfrac{1}{2}\frac{Na_3}{V} \sum_{\substack{\vec{h} \\ h_3=0}}{}' \sum_{k}^{r} q^k \frac{e^{-i\vec{y}(\vec{h}).\vec{x}^k} e^{-x_3^k|\vec{y}(\vec{h})|}}{|\vec{y}(\vec{h})| \sinh |\vec{y}(\vec{h})| \tfrac{1}{2}a_3} e^{i\vec{y}(\vec{h}).\vec{z}} e^{-z_3|\vec{y}(\vec{h}} \right.$$

We will now evaluate $\alpha_e(\vec{z})$ for the three cases mentioned earlier by substituting for $\vec{x}^k$ and q^k from Table 5.1

(1) NaCl (100)

$$\alpha_e(\vec{z}) = -\frac{\pi Na}{V} \sum_{\substack{\vec{h} \\ h_3=0}}{}' \frac{-(1-e^{-iy_1(h_1)\frac{1}{2}a_1})(1-e^{-iy_2(h_2)\frac{1}{2}a_2})(1-e^{-|\vec{y}(\vec{h})|\frac{1}{2}a_3})}{|\vec{y}(\vec{h})| \sinh |\vec{y}(\vec{h})| \frac{1}{2}a_3} e^{i\vec{y}(\vec{h}).\vec{z}} e^{-z_3|\vec{y}(\vec{h})|}$$

$$= 2 \sum_{\substack{m_1,m_2 \\ \text{odd}}} \frac{(1 - e^{-\pi(m_1^2+m_2^2)^{\frac{1}{2}}}) e^{i2\pi(m_1z_1+m_2z_2)/a} e^{-2\pi z_3(m_1^2+m_2^2)^{\frac{1}{2}}/a}}{(m_1^2+m_2^2)^{\frac{1}{2}} \sinh(m_1^2+m_2^2)^{\frac{1}{2}}\pi} \qquad 5.4.4$$

where we have set $y_1(h_1) = 2\pi m_1/a$ and $y_2(h_2) = 2\pi m_2/a$. The terms with m_1, m_2 odd vanished and hence have not been included in the sum over m_1, m_2 in eq (5.4.4). We note that the c.r.u. does not have a dipole or quadrupole moment, (see Table 5.1).

(2) NaCl (110)

$$\alpha_e(\vec{z}) = -\frac{Na}{V}3 \sum_{\substack{\vec{h} \\ h=0}}{}' \frac{(1-e^{-iy_1(h_1)\frac{1}{2}a_1})(1-e^{iy_2(h_2)\frac{1}{2}a_2} e^{-\frac{1}{2}a_3|\vec{y}(\vec{h})|})}{|\vec{y}(\vec{h})| \sinh |\vec{y}(\vec{h})| \frac{1}{2}a_3} e^{i\vec{y}(\vec{h}).\vec{z}} e^{-z_3|\vec{y}(\vec{h})|} \qquad 5.4.5$$

Setting $y_1(h_1) = 2\pi m_1/a_1 = 2\pi m_1/a$ and $y_2(h_2) = 2\pi m_2/a_2 = 2\pi\sqrt{2}m_2/a$

in eq (5.4.5), we obtain

$$\alpha_e(\vec{z}) = \sqrt{2} \sum_{\substack{m_1,\text{odd} \\ m_2}} \frac{(1-(-1)^{m_2} e^{-\pi(m_1^2+2m_2^2)^{\frac{1}{2}}/\sqrt{2}})}{(m_1^2+2m_2^2)^{\frac{1}{2}} \sinh(m_1^2+2m_2^2)^{\frac{1}{2}}\frac{\pi}{\sqrt{2}}} e^{i2\pi(m_1 z_1 + m_2 z_2\sqrt{2})/a} e^{-2\pi z_3 (m_1^2+2m_2^2)^{\frac{1}{2}}/a} \qquad 5.4.6$$

We note again that the c.r.u. does not have a dipole or quadrupole moment, (see Table 5.1).

(3) CsCl (110)

$$\alpha_e(\vec{z}) = \frac{\pi N a_3}{V} \sum_{\substack{\vec{h} \\ h_3=0}}' \left\{-(1-e^{-i\pi[y_1(h_1)\frac{1}{2}a_1 + y_2(h_2)\frac{1}{2}a_2]}) + e^{-\frac{1}{2}a_3|\vec{y}(\vec{h})|}(e^{-iy_1(h_1)\frac{1}{2}a_1} - e^{-iy_2(h_2)\frac{1}{2}a_2})\right\} \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}}\, e^{-z_3|\vec{y}(\vec{h})|}}{|\vec{y}(\vec{h})|\, \sinh|\vec{y}(\vec{h})|\frac{1}{2}a_3}$$

$$= \frac{1}{2\sqrt{2}} \sum_{m_1,m_2}' \left\{\frac{(1-(-1)^{m_1+m_2}) - ((-1)^{m_1}-(-1)^{m_2} e^{-\sqrt{2}\pi(m_1^2+\frac{1}{2}m_2^2)^{\frac{1}{2}}})}{(m_1^2+\frac{1}{2}m_2^2)^{\frac{1}{2}} \sinh(m_1^2+\frac{1}{2}m_2^2)^{\frac{1}{2}}\pi\sqrt{2}}\right\} \times \qquad 5.4.7$$

$$e^{-2\pi(m_1 z_1 + m_2 a_2/\sqrt{2})/a} e^{-2\pi z_3 (m_1^2+\frac{1}{2}m_2^2)^{\frac{1}{2}}/a}$$

We have set $y_1(h_1) = 2\pi m_1/a$, $y_2(h_2) = 2\pi m_2/a_2 = \sqrt{2}\pi m_2/a$. We note that the c.r.u. has a dipole moment (see Table 5.1), but since it is not in the $\hat{e}_3$ direction, it does not appear explicitly.

We have evaluated the above $\alpha_e(\vec{z})$ for points with $z_1 = z_2 = 0$ and z_3 equal to the location of the planes of ions (i.e. $z_3 = n\frac{1}{2}a_3$, n an integer). The results are given in Table 5.2. We have denoted the leading term in each of the $\alpha_e(\vec{z})$ by $\alpha_e^o(\vec{z})$. By leading term, we mean the exponential with the smallest coefficient of z_3/a_3. From Table 5.2, we see that $\alpha_e^o(\vec{z})$ is the dominant term in each case.

This knowledge is of interest if one is attempting to solve for the displacements of the ions at the surface which are needed to satisfy equilibrium conditions. It gives a reasonable guess as tc the type of position dependence that one should assume these displacements have.

(1) NaCl (100)

k	q^k	$\vec{x}^k$	k	q^k	$\vec{x}^k$
0	-q	$(0,0,0)\frac{1}{2}a$	1	q	$(1,0,0)\frac{1}{2}a$
2	-q	$(1,1,0)\frac{1}{2}a$	3	q	$(0,1,0)\frac{1}{2}a$
4	-q	$(1,0,1)\frac{1}{2}a$	5	q	$(0,0,1)\frac{1}{2}a$
6	-q	$(0,1,1)\frac{1}{2}a$	7	q	$(1,1,1)\frac{1}{2}a$

(2) NaCl (110)

k	q^k	$\vec{x}^k$	k	q^k	$\vec{x}^k$
0	-q	$(0,0,0)\frac{1}{2}a$	1	q	$(1,0,0)\frac{1}{2}a$
2	-q	$(1,\frac{1}{\sqrt{2}},\frac{1}{\sqrt{2}})\frac{1}{2}a$	3	q	$(0,1,1)\frac{1}{2}a/\sqrt{2}$

(3) CsCl (110)

k	q^k	$\vec{x}^k$	k	q^k	$\vec{x}^k$
0	-q	$(0,0,0)\frac{1}{2}a$	1	q	$(1,\sqrt{2},0)\frac{1}{2}a$
2	-q	$(0,1,1)\frac{1}{2}a\sqrt{2}$	3	q	$(1,0,\sqrt{2})\frac{1}{2}a$

Table 5.1

Charge and Position of Each Ion in the C.R.U.

	(1) NaCl (100)		(2) NaCl (110)		(3) CsCl (110)	
Leading terms	$m_1=1,\ m_2=1$		$m_1=1,\ m_2=0$		$m_1=0,\ m_2=1$	
$\alpha_e^o(z_3)$	$4\sqrt{2}\frac{(1-e^{-\sqrt{2}\pi})e^{-2\sqrt{2}\pi(z_3/a_3)}}{\sinh\pi\sqrt{2}}$		$2\sqrt{2}\frac{(1-e^{-\frac{\pi}{\sqrt{2}}})e^{-\sqrt{2}\pi(z_3/a_3)}}{\sinh(\pi/\sqrt{2})}$		$\frac{(1-e^{-\pi})e^{-2\pi(z_3/a_3)}}{\sinh\pi}$	
$\alpha_i(x^*)$	3.4591		3.4591		2.0354	
z_3/a_3	$\alpha_e^o(z_3)$	$\alpha_e(z_3)$	$\alpha_e^o(z_3)$	$\alpha_e(z_3)$	$\alpha_e^o(z_3)$	$\alpha_e(z_3)$
0.0	1.3153×10^{-1}	1.3202×10^{-1}	2.7674×10^{-1}	3.5284×10^{-1}	1.6570×10^{-1}	2.0106×10^{-1}
0.5	1.5470×10^{-3}	1.5470×10^{-3}	3.0013×10^{-2}	3.1537×10^{-2}	7.1604×10^{-3}	7.5570×10^{-3}
1.0	1.8196×10^{-5}	same	3.2550×10^{-3}	3.2874×10^{-3}	3.0943×10^{-4}	3.1409×10^{-4}
1.5	2.1403×10^{-7}	same	3.5302×10^{-4}	3.5371×10^{-4}	1.3372×10^{-5}	1.3427×10^{-5}
2.0	2.5175×10^{-9}	same	3.8286×10^{-5}	3.8301×10^{-5}	5.7786×10^{-7}	5.7851×10^{-7}

Table 5.2

Variation of the Extrinsic Electrostatic Potential with Distance from the Surface

E. Summary

We have considered two cases:

1. an ellipsoid in which a dipole moment is present, and

2. a thin slab with no dipole moment perpendicular to the surface.

In the first case, the extrinsic terms contribute significantly in the bulk of the sample. In both the electrostatic energy and the derivatives of the electrostatic potential (which are the significant quantities physically), we found that the extrinsic terms were of the same magnitude as the intrinsic terms

In the second case, the extrinsic term decreases exponentially as the point of interest recedes from the surface. At the surface the extrinsic terms are of comparable magnitude ($\sim$10%) with the corresponding intrinsic terms.

We note from eq (5.4.1), that if a dipole moment is present which is perpendicular to the surface of the slab, then the electrostatic potential diverges as $m_3 \to \infty$ i.e. for the semi-infinite crystal.

CHAPTER VI

SUMMARY

In this part of the thesis we have succeeded in doing the following:*1

A. evaluate the electrostatic potential $V(\vec{z})$, eq (1.3.6), of a finite ionic crystal,

B. compare the electrostatic potential $V^{\infty}(\vec{z})$, eq (1.3.9), and the electrostatic energy of an infinite ionic crystal with those of the finite ionic crystal, and

C. determine when the finiteness is significant.

A.

We found the electrostatic potential of a finite ionic crystal can be written in the form

$$V(\vec{z}) = V_i(\vec{z}') + V_e(\vec{z}) \qquad (3.3.71)$$

where $V_i(\vec{z}')$ is the intrinsic electrostatic potential (which may be considered to be a periodic function of $\vec{z}$ with the period of the lattice) given by

$$V_i(\vec{z}') = \sum_k^b \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'^k|} - \frac{N f(\vec{z}'^k, V_n)}{V} \right\} \qquad (3.3.69)$$

and $V_e(\vec{z})$ is the extrinsic electrostatic potential (which is not a periodic function of $\vec{z}$) given by

$$V_e(\vec{z}) = \sum_k^r \frac{N q^k}{4\pi V \epsilon_o} f(\vec{z}^k, V) \qquad (3.3.70)$$

*1 See footnote *1 of Section 4.6.

where

$$\vec{z}^{k} = \vec{z} - \vec{x}^{k} \qquad (3.1.6)$$
$$\vec{z}'^{k} = \vec{z}^{k} - \vec{x}_{z}$$

$\vec{x}_z$ is the k=0 lattice site nearest $\vec{z}$. $f(\vec{z},V)$ is a solution of the differential equation

$$\hat{\Gamma} f(\vec{z},V) = \iiint_{V} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad (3.3.26)$$

subject to the boundary conditions

1. f must not contain a solution of the homogeneous differential equation

$$\hat{\Gamma}\, \tilde{f} = 0 \qquad (3.3.28)$$

which is not an explicit function of V, and

2. $\frac{Nf}{V}$ must have the same V dependence as

$$\phi(\vec{z},V) = \sum_{\vec{l}\in V}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}|}$$

We derived the above equations for the special case of cubic symmetry but the results are easily generalized to more complex symmetries.

B.

We found that there are two ways in which the summation over the lattice sites in the expressions for the electrostatic potential of an infinite crystal may be made absolutely convergent.

The first ways is by choosing a charge basis unit (c.b.u.) which has

(a) charge neutrality $\sum_{k}^{b} q^{k} = 0$

(b) vanishing dipole moment $p_i = 0$

(c) vanishing quadrupole moment $p_{ij} = 0$

The second way is by introducing a vanishing exponential. i.e.

$$V'(\vec{z}) = \lim_{\beta \to 0} \lim_{V \to \infty} \sum_{k}^{b} \frac{q^{k}}{4\pi\epsilon_0} \sum_{\vec{l} \in V}{}' \frac{e^{-\beta|\vec{x}(\vec{l})-\vec{z}|}}{|\vec{x}(\vec{l})-\vec{z}|} \qquad (1.3.11)$$

In both cases the electrostatic potential of the infinite crystal is equal to our intrinsic electrostatic potential $V_i(\vec{z})$.

Similarily there are two ways in which the summation over the lattice sites in the expression for the electrostatic energy of an infinite crystal may be made absolutely convergent.

The first is by choosing a c.b.u. which has

(a) charge neutrality

(b) vanishing dipole moment

The second way is the introduction of the vanishing exponential as for the electrostatic potential.

We note that the conditions on the c.b.u. for absolute convergence are different for the cases of the electrostatic potential and electrostatic energy.

C.

There are two situations in which the fact that we are dealing with a finite system is important.

The first is when either a dipole moment or a quadrupole moment is present in the system. For example, for the electrostatic energy

per c.r.u., the dependence on the shape of the sample (from the extrinsic electrostatic energy) is of the same order as the intrinsic electrostatic energy which is equivalent to the value obtained using an infinite crystal (see eq (5.2.12)).

The second case is when neither a dipole moment nor a quadrupole moment is present but we are considering the electrostatic potential near the surface. This is inherently a finite crystal problem. The deviation from bulk properties is significant ($\sim$ 10%, see Table 5.2).

The problem that remains is how to observe these effects experimentally. The simplest way to investigate these effects would be through observation of lattice spacings.

The lattice spacing may be evaluated theoretically in two ways:

1. minimization of the potential energy of the system with respect to the lattice spacing, and

2. through equilibrium conditions.

We note that when a dipole moment is present, this adds a term (the extrinsic electrostatic energy), which depends on the shape of the sample, to the potential energy. Thus when the potential energy is minimized, we find that the lattice spacing is dependent on the shape of the sample. Unfortunately, if a dipole moment is present in a real finite crystal, then free electrons and ions from outside the crystal would collect on the surface to exactly compensate for the dipole moment, making the detection of the shape dependent lattice spacing very difficult.

We note that in CsCl with a dipole moment perpendicular to the surface of the sample, that Huang[20] was unable to find a lattice spacing which would satisfy the equilibrium conditions.

Since the electrostatic potential depends on the distance from the surface, this causes the equilibrium conditions to change as one goes away from the surface. This causes the lattice spacing to change near the surface.

APPENDIX I

In this appendix, we will derive the expansion for $I(\vec{z},d)$. It is defined as

$$I(\vec{z},d) = \iiint_{V_d} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad \text{(see eq (3.3.39))} \qquad A.1.1$$

We will divide the region of integration into two parts: V_1 - a sphere of radius $r > |\vec{z}|$ and $V_2 = V_d - V_1$.*1

Thus

$$I(\vec{z},d) = I_1 + I_2 \qquad A.1.2$$

where

$$I_1 = \iiint_{V_1} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad A.1.3$$

and

$$I_2 = \iiint_{V_2} \frac{d\vec{y}}{|\vec{y}-\vec{z}|} \qquad A.1.4$$

We will first evaluate I_1, then evaluate I_2.

Writing the limits of integration of I_1 explicitly, we have

$$I_1 = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \int_0^{r} dy \frac{y^2}{(y^2+z^2-2yz\cos\theta)^{\frac{1}{2}}} \qquad A.1.5$$

---

*1 This is a valid procedure for all $I(\vec{z},d)$ related to the intrinsic partial potentials. For the extrinsic partial potentials, there may be points such that a sphere of radius greater than $|\vec{z}|$ cannot be enclosed in V_d. If this is the case, then a different approach must be taken. For our calculations, this second approach is of no interest to us.

This integral is easily evaluated to give

$$I_1 = 4\pi\left(-\frac{z^2}{6} + \tfrac{1}{2}r^2\right) \qquad \text{A.1.6}$$

To evaluate I_2, we introduce the expansion

$$\frac{1}{|\vec{y}-\vec{z}|} = \frac{4\pi}{y}\sum_{m=0}^{\infty}\sum_{p=-m}^{m}\frac{1}{(2m+1)}(z/y)^m Y_m^p(\theta,\phi)Y_m^{p*}(\theta',\phi') \qquad \text{A.1.7}$$

(see eq (3.3.40)) which is valid for all $y > z$. This inequality is satisfied for all y in the region of integration of I_2. Thus

$$I_2 = 4\pi\iint_{4\pi} d\Omega' \int_r^{d/\eta} dy\, y^2 \sum_{m=0}^{\infty}\frac{z^m y^{-(m+1)}}{(2m+1)}\sum_{p=-m}^{m} Y_m^p(\theta,\phi)Y_m^{p*}(\theta',\phi') \qquad \text{A.1.8}$$

where $d\Omega' = d\phi' d\theta' \sin\theta'$ and η is a function of (θ',ϕ') which specifies the surface (see Table 3.3 for η for a cube). Rearranging terms in (A.1.8), we obtain

$$I_2 = 4\pi\sum_{m=0}^{\infty}\frac{z^m}{(2m+1)}\sum_{p=-m}^{m} Y_m^p(\theta,\phi)\iint_{4\pi} d\Omega' Y_m^{p*}(\theta',\phi')\int_r^{d/\eta} dy\, y^{1-m} \qquad \text{A.1.9}$$

The integral over y may be performed to give

$$I_2 = 4\pi\sum_{m=0}^{\infty}\frac{z^m}{(2m+1)}\sum_{p=-m}^{m} Y_m^p(\theta,\phi)\iint_{4\pi} d\Omega' Y_m^{p*}(\theta',\phi')\left[\left\{-\frac{(\eta/d)^{m-2}}{(m-2)}(1-\delta_{m,2})+\delta_{m,2}\ln(\eta)\right\}\right.$$

$$\left. + \left\{\frac{y^{2-m}}{(m-2)}(1-\delta_{m,2}) + \delta_{m,2}\ln(d/y)\right\}\right] \qquad \text{A.1.10}$$

The term in the second set of curly brackets is independent of (θ',ϕ'). Thus all the terms, except m=0, vanish due to the orthogonality relations possessed by the spherical harmonics. The contribution of this second term is just $-2\pi r^2$. Hence

$$I_2 = -2\pi r^2 - 4\pi d^2 \sum_{m=0}^{\infty} \frac{(z/d)^m}{(2m+1)} \sum_{p=-m}^{m} Y_m^p(\theta,\phi) \iint_{4\pi} d\Omega' Y_m^{p*}(\theta',\phi') \left\{ \frac{\eta^{m-2}}{(m-2)} (1-\delta_{m,2}) + \delta_{m,2} \ln(\eta) \right\} \quad \text{A.1.11}$$

Substituting (A.1.6) and (A.1.7), into A.1.2), we obtain

$$I(\vec{z},d) = -\frac{2\pi z^2}{3} - 4\pi d^2 \sum_{m=0}^{\infty} \frac{(z/d)^m}{(2m+1)} \sum_{p=-m}^{m} Y_m^p(\theta,\phi) \iint_{4\pi} d\Omega' Y_m^{p*}(\theta',\phi') \left\{ \frac{\eta^{m-2}}{(m-2)} (1-\delta_{m,2}) + \delta_{m,2} \ln(\eta) \right\}$$

$$= -\frac{2\pi z^2}{3} - d^2 \sum_{m=0}^{\infty} (z/d)^m \sum_{p=-m}^{m} Y_m^p(\theta,\phi) \alpha'_{mp} \quad \text{A.1.12}$$

where

$$\alpha'_{mp} = \frac{4\pi}{(2m+1)} \iint_{4\pi} d\Omega' Y_m^{p*}(\theta',\phi') \left\{ \frac{\eta^{m-2}}{(m-2)} (1-\delta_{m,2}) + \delta_{m,2} \ln(\eta) \right\} \quad \text{A.1.13}$$

If the integral in (A.1.1) is invariant under inversion and reflection operations, then the terms α'_{mp} with m or p odd vanish. In this case

$$I = -\frac{2\pi z^2}{3} - d^2 \sum_{m=0}^{\infty} (z/d)^{2m} \sum_{p=-m}^{m} Y_{2m}^{2p}(\theta,\phi) \alpha_{mp} \quad \text{A.1.14}$$

where

$$\alpha_{mp} = \alpha'_{2m,2p} \quad \text{A.1.15}$$

are functions of the shape of V_d, see eq (A.1.13).

APPENDIX II

In this appendix we will find the solution which is common to the two differential equations

$$\hat{\Gamma}\,\tilde{f} = 0 \qquad \text{A.2.1}$$

and

$$\nabla^2 \tilde{f} = 0 \qquad \text{A.2.2}$$

Provided $\tilde{f}$ has no singularities in the region of integration, we may use the identity

$$\hat{\Gamma}\,\tilde{f} = \frac{N}{V} \iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y}\,\tilde{f}(\vec{z}+\vec{y}) \qquad \text{(see eq (3.2.9))} \qquad \text{A.2.3}$$

Thus (A.4.1) may be written as

$$\iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y}\,\tilde{f}(\vec{z}+\vec{y}) = 0 \qquad \text{for all } \vec{z} \qquad \text{A.2.4}$$

Since $\vec{z}$ ranges over a finite region, we may introduce a cube of side La, (L an integer) which encloses the region V (see fig. A.1). We may represent any function within V as a fourier series in the harmonics of the cube. Thus

$$\tilde{f}(\vec{z}) = \sum_{\vec{h}} C(\vec{h})\, e^{i2\pi\vec{h}.\vec{z}/La} \qquad \text{A.2.5}$$

where $\vec{h}$ is a vector (h_1, h_2, h_3) whose components are integers and the $C(\vec{h})$ are constants. The sum is over all possible $\vec{h}$. Thus

$$\iiint_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y}\,\tilde{f}(\vec{z}+\vec{y}) = \sum_{\vec{h}} C(\vec{h})\, e^{i2\pi\vec{h}.\vec{z}/La} \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_1 e^{i2\pi h_1 y_1/La} \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_2 e^{i2\pi h_2 y_2/La} \int_{-\frac{1}{2}a}^{\frac{1}{2}a} dy_3 e^{i2\pi h_3 y_3/La}$$

$$= 0 \qquad \text{for all } \vec{z} \qquad \text{A.2.6}$$

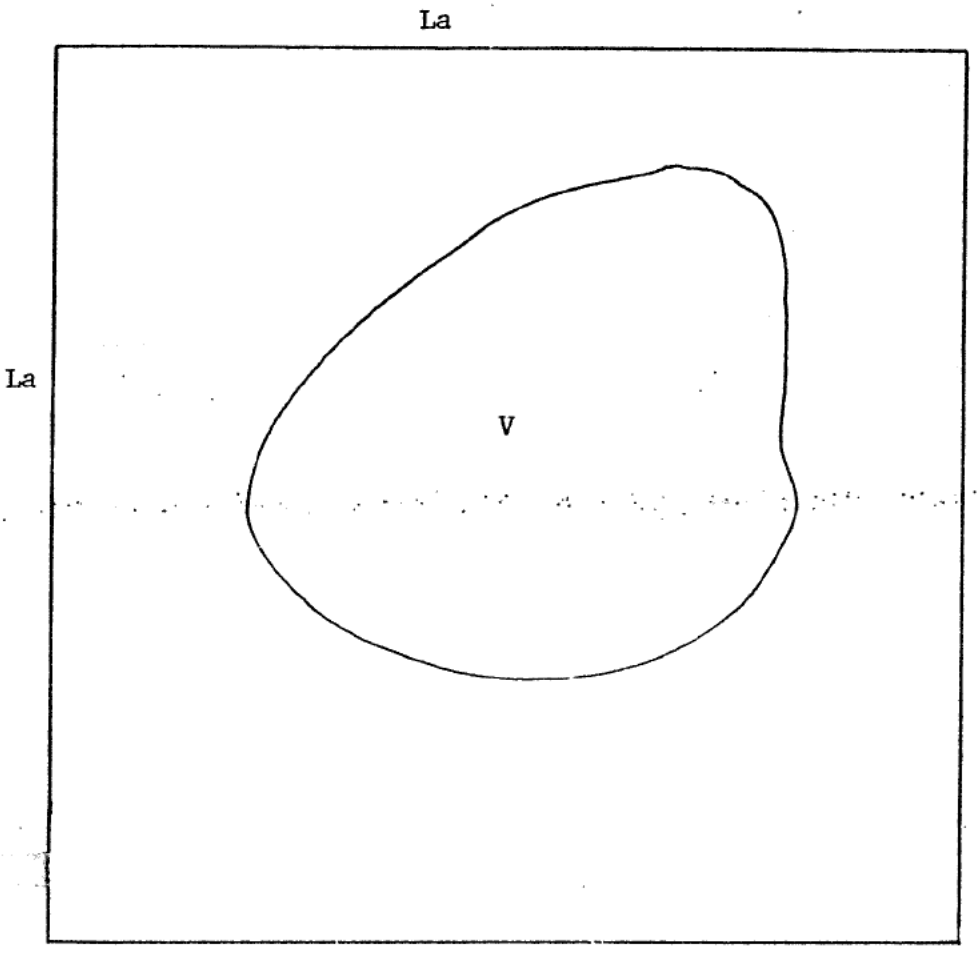

Figure A.1

A Cubic Region of Side La Enclosing an Arbitrary Finite Region V

Performing the integrations, (A.2.6) reduces to

$$0 = \frac{La}{\pi} \sum_{\vec{h}} C(\vec{h}) e^{i2\pi \vec{h}\cdot\vec{z}/La} \sin(\pi h_1/L)\sin(\pi h_2/L)\sin(\pi h_3/L) \qquad A.2.7$$

This equation is satisfied if

$$C(\vec{h}) = 0 \qquad A.2.8$$

for all $\vec{h}$ except those which have at least one component satisfying

$$h_i = h_i' L \qquad i = 1,2, \text{ or } 3 \qquad A.2.9$$

where h_i is a non-zero integer. Thus

$$\tilde{f}(\vec{z}) = \sum_{i,j,k} \sum_{h_i'} e^{i2\pi h_i' z_i/a} \sum_{h_j, h_k} C(\vec{h}) e^{i2\pi(h_j z_j + h_k z_k)/La} \qquad A.2.10$$

where i,j,k are summed over all permutations of 1,2,3. We may seperate the terms with h_j and h_k satisfying (A.2.9) as follows:

$$\sum_{h_j,h_k} C(\vec{h}) e^{i2\pi(h_j z_j + h_k z_k)/La} = \sum_{h_j,h_k}' e^{i2\pi(h_j z_j + h_k z_k)/La} C(\vec{h})$$

$$+ \sum_{h_j'} e^{i2\pi h_j' z_j/a} \sum_{h_k}' C(\vec{h}) e^{i2\pi h_k z_k/La} + \sum_{h_j', h_k'} C(\vec{h}) e^{i2\pi (h_j' z_j + h_k' z_k)}$$

$$= g'(z_j, z_k, h_i') + \sum_{h_j'} e^{i2\pi h_j z_j/a} g(z_k, h_i', h_j') + \sum_{h_j', h_k'} C(\vec{h}) e^{i2\pi(h_j' z_j + h_k' z_k} \qquad A.2.11$$

where the ' one the summations indicates the exclusions of the terms with h_i's satisfying (A.2.9). The functions g' and g do not have the periodicity of the lattice.

---

*1 The Einstein summation convention will not be used in this Appendix.

In terms of our previous notation

$$\frac{2\pi}{a} h_i' = y_i(h_i') \qquad \text{(see eq (1.2.4))} \qquad \text{A.2.12}$$

is a component of a reciprocal lattice vector.

Thus the general solution of the homogeneous equation (A.2.1) is

$$\tilde{f}(\vec{z}) = \sum_{\vec{h}}{}' C(\vec{h}) e^{i\vec{y}(\vec{h})\cdot\vec{z}} + \sum_{i,j,k} \Bigg\{ \sum_{\substack{h_i, h_j \\ h_k = 0}}{}' e^{i\vec{y}(\vec{h})\cdot\vec{z}} g(z_k, \vec{h}) + \sum_{h_i}{}' e^{iy_i(h_i)z_i} g'(z_j, z_k, h_i \quad \text{A.2.13}$$

where the C's are arbitrary constants and g, g' arbitrary non-periodic (with period of the lattice) functions. The ' on the sums over $\vec{h}$ indicates that the term with $\vec{h} = 0$ is to be omitted. We have dropped the ' on the $\vec{h}'$ for convenience.

We will now show what restrictions Laplace's equation, eq (A.2.2), impose on the C's, g, and g'. Operating on (A.2.13) with the Laplacian operator, we have

$$\nabla^2 \tilde{f} = 0$$

$$= -\sum_{\vec{h}}{}' C(h) e^{i\vec{y}(\vec{h})\cdot\vec{z}} |\vec{y}(\vec{h})|^2 + \sum_{i,j,k} \sum_{\substack{h_i, h_j \\ h_k = 0}}{}' e^{i\vec{y}(\vec{h})\cdot\vec{z}} \left\{ -|\vec{y}(\vec{h})|^2 g + \frac{\partial^2 g}{\partial z_k^2} \right\} \qquad \text{A.2.14}$$

$$+ \sum_{h_i}{}' e^{iy_i(h_i)z_i} \left\{ -y_i^2(h_i) g' + \left(\frac{\partial^2}{\partial z_j^2} + \frac{\partial^2}{\partial z_k^2}\right) g' \right\}$$

The three expressions on the R.H.S. of (A.2.14) are mutually orthogonal. Since each of the terms is also made up of orthogonal functions, the only way in which eq (A.2.14) may be satisfied is if

$$C(\vec{h}) = 0 \qquad \text{for all } \vec{h} \qquad \text{A.2.15}$$

$$-|\vec{y}(\vec{h})|^2 g + \frac{\partial^2 g}{\partial z_k^2} = 0 \qquad \text{A.2.16}$$

and

$$- y_i^2(h_i)g' + \left(\frac{\partial^2}{\partial z_j^2} + \frac{\partial^2}{\partial z_k^2}\right)g' = 0 \qquad \text{A.2.17}$$

Thus

$$g = B^+(\vec{h})e^{|y(\vec{h})|\, z_k} + B^-(\vec{h})e^{-|y(\vec{h})|\, z_k} \qquad \text{A.2.18}$$

and

$$g' = \int_0^{2\pi} d\theta C(h_i,\theta)e^{y_i(h_i)(z_j\cos\theta+z_k\sin\theta)} \qquad \text{A.2.19}$$

where B^+, B^-, and C are arbitrary constants which are functions of $\vec{h}$.

Therefore the common solutions of equations (A.2.1) and (A.2.2) is

$$\tilde{f} = \sum_{i,j,k}\left\{\sum_{\substack{h_i,h_j \\ h_k=0}}{}' e^{i\vec{y}(\vec{h})\cdot\vec{z}}\left[B^+(\vec{h})e^{|\vec{y}(\vec{h})|\, z_k} + B^-(\vec{h})e^{-|\vec{y}(\vec{h})|\, z_k}\right]\right. \qquad \text{A.2.20}$$

$$\left. + \sum_{h_i}{}' e^{iy_i(h_i)z_i}\int_0^{2\pi} d\theta C(h_i,\theta)e^{y_i(h_i)(z_j\cos\theta+z_k\sin\theta)}\right\}$$

APPENDIX III

The intrinsic partial potential at a point P (which is not near the surface), with position vector $\vec{z}'$, due to the k=0 sub-lattice is

$$V_i(\vec{z}',0) = \frac{q^0}{4\pi\epsilon_o}\left\{\sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l}) - \vec{z}'|} - \frac{N}{V} f(\vec{z}',V_n)\right\} \qquad A.3.1$$

where the ' indicates that the $\vec{l} = 0$ term is to be excluded from the sum when $\vec{z}' = 0$ and $f(\vec{z}',V_n)$ is a solution of the differential equation

$$\hat{\Gamma} f(\vec{z}',V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{y}-\vec{z}'|} \qquad A.3.2$$

subject to the boundary conditions that

(1) f must not contain a solution $\tilde{f}$ of the homogeneous differential equation

$$\hat{\Gamma}\tilde{f} = 0 \qquad A.3.3$$

which is not an explicit function of V_n, and

(2) $\frac{N}{V} f$ must have the same V_n dependence as

$$\phi(\vec{z}',V_n) = \sum_{\vec{l}\in V_n}{}' \frac{1}{|\vec{x}(\vec{l})-\vec{z}'|} \qquad A.3.4$$

When the ion occupies a lattice site at the surface, we may still write the intrinsic partial potential by eq (A.3.1). However V_n no longer has the same number of degrees of freedom (only 5) as the V_n used in Chapter III where V_n has 6 degrees of freedom (although we used only one by setting V_n equal to a cube). By degree of freedom we mean that one of the sides may vary in distance from the origin - six sides: six degrees of freedom (see fig. A.2). In this case, we find

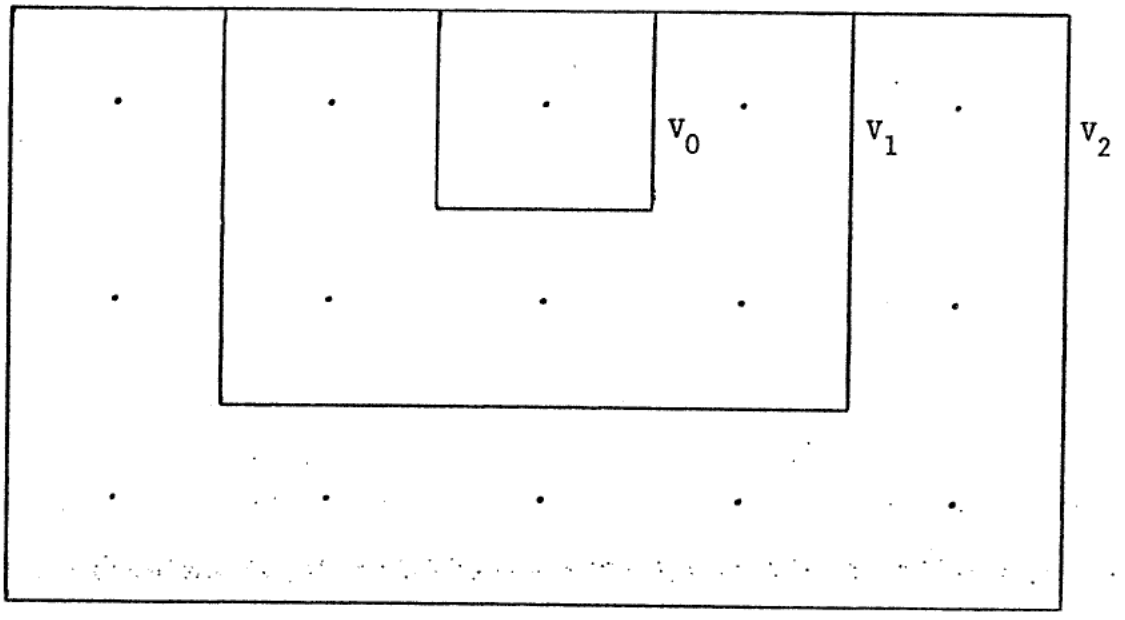

Figure A.2

V_n at the Surface of a Crystal

The above diagram shows the regions V_n which must be considered when the ion is at the surface. One surface of V_n is always fixed by the surface of the crystal. The other five surfaces are allowed to vary.

that the two boundary conditions are insufficient to uniquely define f.

To show this, we will consider the infinite slab discussed in Chapter V. This is the only case for which we have been able to evaluate all three of the electrostatic potentials $V(\vec{z})$, $V_i(\vec{z}')$, and $V_e(\vec{z})$.

From Chapter IV, we have that, for a box of sides of length $[(2m_1+1)a_1,(2m_2+1)a_2,(2m_3+1)a_3]$, the electrostatic potential $V(\vec{z})$ is

$$V(\vec{z}) = \lim_{\beta\to 0} \sum_{k}^{r} \frac{q^k}{4\pi\epsilon_o} \frac{1}{2\tau^2} \iiint \frac{d\vec{k}\, e^{i\vec{k}\cdot\vec{z}^k}}{(k^2+\beta^2)} \prod_{j=1}^{3} \frac{\sin(m_j+\frac{1}{2})k_j a_j}{\sin\frac{1}{2}k_j a_j} \qquad \text{A.3.4}$$

where we have used the generalized form of eq (4.6.12) and the point P is assumed to be not at an ion site.

Taking the limits m_1, $m_2 \to \infty$ to obtain the infinite slab, we have

$$V(\vec{z}) = \lim_{\beta\to 0} \sum_{k}^{r} \frac{q^k}{4\pi\epsilon_o} \sum_{\substack{\vec{h} \\ h_3=0}} 2e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} \int_{-\infty}^{\infty} \frac{dk_3 e^{ik_3 z_3^k}}{\{|\vec{y}(\vec{h})|^2 + z_3^2 + \beta^2\}} \frac{\sin(m_3+\frac{1}{2})k_3 a_3}{\sin\frac{1}{2}k_3 a_3} \qquad \text{A.3.5}$$

From Chapter V, eq (5.3.11), we have that the extrinsic electrostatic potential for this system is

$$V_e(\vec{z}) = \lim_{\beta\to 0} \sum_{k}^{r} \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\substack{\vec{h} \\ h_3=0}} 2e^{i\vec{y}(\vec{h})\cdot\vec{z}^k} \int_{-\infty}^{\infty} \frac{dk_3 e^{ik_3 z_3^k}}{\{|\vec{y}(\vec{h})|^2 + z_3^2 + \beta^2\}} \frac{\sin(m_3+\frac{1}{2})k_3 a_3}{\sin\frac{1}{2}k_3 a_3} \right.$$

$$\left. - \frac{4\pi N}{V} \sum_{\vec{h}}{}' \frac{e^{i\vec{y}(\vec{h})\cdot\vec{z}^k}}{|\vec{y}(\vec{h})|^2} \right\} \qquad \text{A.3.6}$$

If we calculate the intrinsic electrostatic potential $V_i^S(\vec{z}')$ of a surface ion using only the two boundary conditions, we find

$$V_i^S(\vec{z}') = V^\infty(\vec{z}';S) \qquad \text{A.3.7}$$

where $V^{\infty}(\vec{z}';S)$ is the electrostatic potential at the surface of a semi-infinite crystal.

If we take the difference between $V(\vec{z})$ and $V_e(\vec{z})$, we find

$$V(\vec{z}) - V_e(\vec{z}) = \sum_{k}^{r} \frac{Nq^k}{V\epsilon_o} \sum_{\vec{h}}' \frac{e^{i\vec{y}(\vec{h}).\vec{z}^k}}{|\vec{y}(\vec{h})|^2} \qquad \text{A.3.8}$$

$$= V_i(\vec{z}') \qquad \text{(see eq (4.6.24))} \qquad \text{A.3.8}$$

where $V_i(\vec{z}')$ is the intrinsic electrostatic potential as calculated in the bulk of the sample. We note that the derivations of $V(\vec{z})$ and $V_e(\vec{z})$ do not depend on where the point P is. Therefore since

$$V_i(\vec{z}') \neq V(\vec{z}',S) = V_i^S(\vec{z}') \qquad \text{A.3.9}$$

we conclude that the method used to calculate $V_i^S(\vec{z}')$ is in error and this error we believe arises because of the inadequacy of the first boundary condition.

Since the intrinsic electrostatic potential may be calculated in the bulk of the sample and the extrinsic electrostatic potential is not affected by this inadequacy, the total potential at any point may be obtained by summing $V_i(\vec{z}')$ and $V_e(\vec{z})$ whether the point P is in the bulk or at the surface of the sample. Thus we do not think it is necessary to give a new set of boundary conditions for calculating the intrinsic electrostatic potential of a surface lattice site.

We have given this discussion only to show that the inconsistancy exists and how it is avoided. It is of no interest to us in any other way.

CHAPTER I

INTRODUCTION

A. Introduction

In Part One, we evaluated the electrostatic potential of a finite ionic crystal whose ions occupy lattice sites. In this part of the thesis, we will consider the more general problem of solving for the electrostatic potential in a finite crystal whose ions are displaced from the lattice sites.

In Section B of this chapter, we will introduce the terminology which we will require and specify the system more exactly.

Chapter II will give a discussion of the previous methods used to define macroscopic fields. In Chapter III, we will solve for the electrostatic potential of the system described in Section B. Using this electrostatic potential, we give a generalized definition of the macroscopic electric field $\vec{E}$ and the electric displacement field $\vec{D}$. Unfortunately, we are unable to give a perscription for uniquely defining either $\vec{E}$ or $\vec{D}$. Thus we will investigate the properties of our $\vec{E}$ and $\vec{D}$ to see how they compare with the other definitions of $\vec{E}$ and $\vec{D}$ in common use. In Chapter IV, we will require that the ions in the finite crystal satisfy equilibrium conditions. These equilibrium conditions will be used to find a relationship (i.e. an equation of state) between the displacements, $\vec{E}$, and $\vec{D}$, in addition to the defining relation of $\vec{D}$ (see eq (3.4.14)).

B. Terminology

This section will be devoted to a discussion of the system we will consider in the following chapters and the terms we will use to describe it.

Since we will be considering a system which undergoes changes, we will call the unchanged state the initial state and the state which the crystal is in after all the changes have been performed, the final state.

For Chapters II and III, the following descriptions of the initial and final states will hold. The initial state will be the finite*1 crystal defined in Part One. i.e.

'A finite crystal is one which is constructed by associating a charge repetition unit (c.r.u.) with every Bravais lattice site within some finite region V.'

There are assumed to be no applied fields in the initial state. The final state is one in which all the ions are displaced by amounts $\vec{u}(\vec{l},k)$ from the positions $\vec{x}(\vec{l},k)$*2 in the initial state. The volume of the crystal in the final state will be denoted by V_d. There may be applied fields such as applied electric fields $\vec{E}_{ap}$ or applied stresses in the final state but, for Chapters II and III, we do not assume any

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*1 In Chapter II, the crystal may be either finite or infinite.

*2 Whenever possible, we will be using capital letters to denote position vectors in the final state and small letters to denote position vectors in the initial state.

---

explicit connection between the applied fields and the displacement fields $\vec{u}(\vec{l},k)$.

In Chapter IV, we also assume that the ions in both the initial*3 and final states are in equilibrium. This causes $\vec{u}(\vec{l},k)$ to be a function of the applied electric field and the applied stresses.

The position vector $\vec{X}(\vec{l},k)$ of the ions in the final state are given by

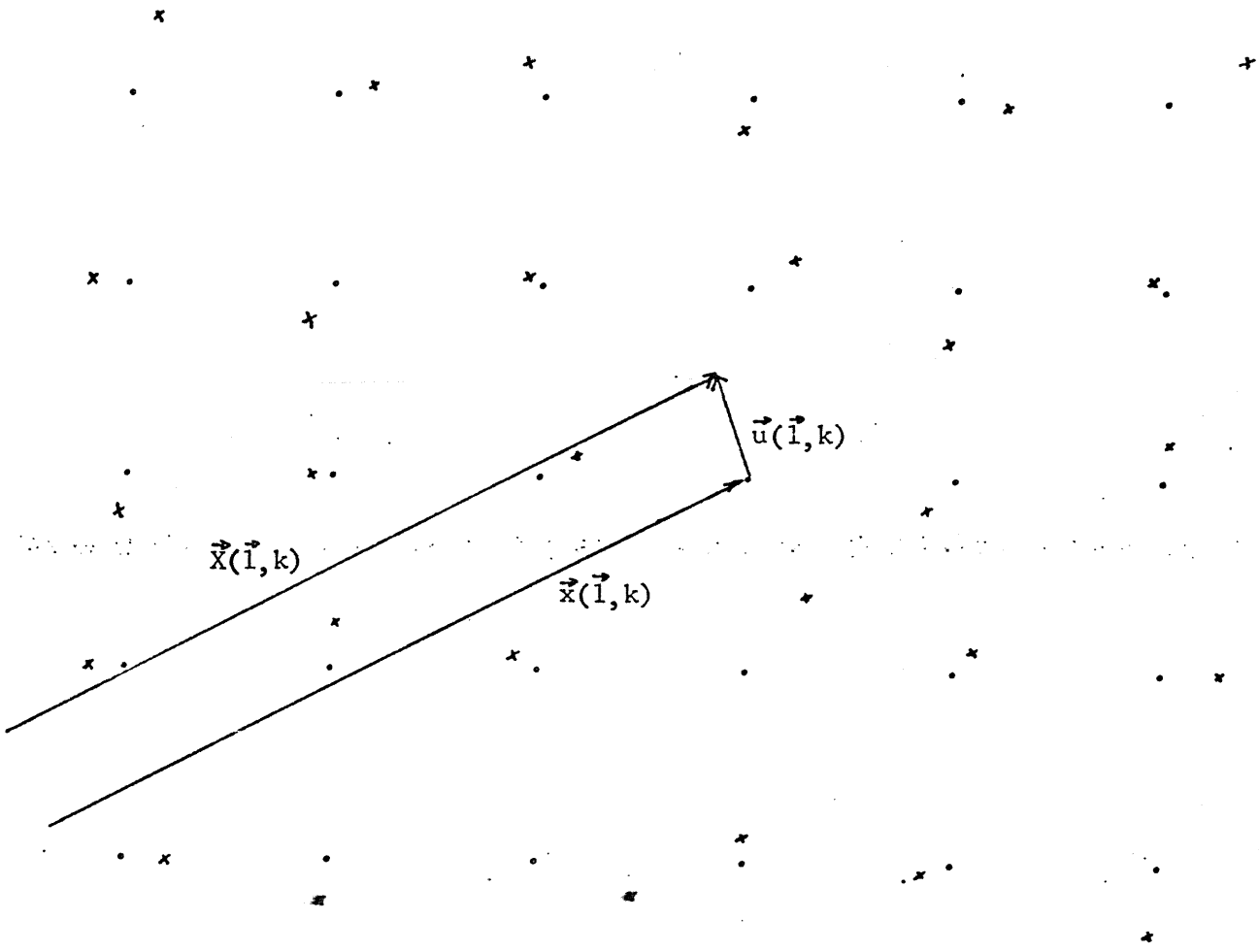
$$\vec{X}(\vec{l},k) = \vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) \qquad 1.2.1$$

(See figure 1.1). We allow only deformations which uniformly deform the surface of the sample. This means that the displacements of the ions at the surface may be written in the form

$$u_i(\vec{l},0) \overset{\text{defn}}{=} u_{ij}x_j(\vec{l},0) + u_i(\vec{l};S) \qquad 1.2.2$$

where u_{ij} is the displacement gradient of the surface ions (of type k=0) defined by the above relation and $u_i(\vec{l};S)$ is a microscopic vector which may be an explicit function of the lattice indices $\vec{l}$. The S is to denote $\vec{u}(\vec{l};S)$ is a vector which is associated with the surface. We now

*3 The ions at the surface do not, in general, occupy lattice sites. This is a result of the symmetry conditions being different for the ions at the surface (from the ions in the bulk of the sample) which results in a different set of equilibrium conditions. However, numerical calculations, (H&G[19]), for the case of the slab show that this difference is significant ($\gtrsim 1\%$) only for ions within a few lattice parameters of the surface. We shall assume that this result holds in general.



. - Position of an ion in the initial state - it forms part of a Bravais lattice

× - Position of an ion in the final state - does not form part of a Bravais lattice

Figure 1.1

Positions of the k-type Ions in the Initial and Final States

assume that the quantity $\vec{u}^k(\vec{l};S)$ which is defined for the $k\neq 0$ ions by

$$u_i^k(\vec{l};S) \overset{\text{defn}}{=} u_i(\vec{l},k) - u_{ij}x_j(\vec{l},k) \qquad 1.2.3$$

is also a microscopic vector.

For ions which are not at the surface, we may define a vector $\vec{u}^k(\vec{l})$ as the difference between the displacement vector $\vec{u}(\vec{l},\vec{k})$ and the quantities $u_{ij}x_j(\vec{l},k)$. i.e.

$$u_i^k(\vec{l}) \overset{\text{defn}}{=} u_i(\vec{l},k) - u_{ij}x_j(\vec{l},k) \qquad 1.2.4$$

We will call this vector the interior displacement. It need not be a microscopic quantity in the interior of the crystal. However, we know from the definition of the u_{ij}, eq (1.2.2), and from the assumption of eq (1.2.3), that $\vec{u}^k(\vec{l})$ is a microscopic quantity at the surface. Rearranging the terms in eq (1.2.4), the displacement vector may be written as

$$u_i(\vec{l},k) = u_{ij}x_j(\vec{l},k) + u_i^k(\vec{l}) \qquad 1.2.5$$

for all $\vec{l}$ and k. At this point the $\vec{u}^k(\vec{l})$ are arbitrary functions of the lattice indices $\vec{l}$ in the interior of the crystal and the u_{ij} are arbitrary constants.

In later calculations we will need the inverse of $\delta_{jk}+u_{jk}$. We will denote it by v_{ij}. i.e.

$$v_{ij}(\delta_{jk}+u_{jk}) = \delta_{ik} \qquad 1.2.6$$

Whenever possible, we will be using the following notation. A vector written in capitol letters, say $\vec{X}$, is a vector in the final

state and may be written in terms of a vector in the intial state (written in small letters), say $\vec{x}$, as follows

$$X_i = x_i + u_{ij}x_j \qquad 1.2.7$$

We note that we may write $\vec{x}$ in terms of $\vec{X}$ as follows

$$v_{mi}X_i = v_{mi}(\delta_{ij} + u_{ij})x_j$$

$$= x_m \qquad 1.2.8$$

Since the displacements $\vec{u}(\vec{l},k)$ are arbitrary (up to the restrictions of eqs (1.2.2) and (1.2.3)), the $\vec{X}(\vec{l},k)$, eq (1.2.1), need not be lattice vectors. As in Part One, the position vectors, $\vec{x}(\vec{l},k)$, of ions in the initial state are given by

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k \qquad \text{(see eq (1:1.3.5)}^{*4}\text{)} \quad 1.2.9$$

where

$$\vec{x}(\vec{l}) = l_1 a_1 \hat{e}_1 + l_2 a_2 \hat{e}_2 + l_3 a_3 \hat{e}_3 \qquad \text{(see eq (1:1.2.1))} \quad 1.2.10$$

and

$$\vec{x}^k = x_1^k \hat{e}_1 + x_2^k \hat{e}_2 + x_3^k \hat{e}_3 \qquad \text{(see eq (1:1.3.3))} \quad 1.2.11$$

The electrostatic potential in the final state at a point P (with position vector $\vec{Z}$) in a finite crystal is given by

$$V(\vec{Z}) = \frac{1}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \sum_{k}^{r} \frac{q^k}{|\vec{X}(\vec{l},k) - \vec{Z}|} \qquad 1.2.12$$

---

*4 When referring to equations of Part One, we will use four numbers, e.g. (1:L,M,N). For equations in Part Two, we will use only three numbers, e.g. (L,M,N)

Substituting for $\vec{X}(\vec{l},k)$ using eq (1.2.1), the electrostatic potential may be written as

$$V(\vec{Z}) = \frac{1}{4\pi\epsilon_o} \sum_{\vec{l}\in V}{}' \sum_{k} \frac{q^k}{|\vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) - \vec{Z}|} \qquad 1.2.13$$

where, as in Part One, k is summed over all the ions in the c.r.u. and $\vec{l}$ is summed over all the Bravais lattice sites within the region V. We have dropped the r on the sum over k since we are only considering finite crystals in this part of the thesis and hence will not have to distinguish between c.r.u.'s and c.b.u.'s.

The applied electric field $\vec{E}_{ap}$ is produced by the free charges present in the system. These charges may be inside the crystal. $\vec{E}_{ap}$ satisfies the field equation

$$\nabla.\vec{E}_{ap} = \rho_f/\epsilon_o \qquad 1.2.14$$

where ρ_f is the free charge density. $\vec{E}_{ap}$ may be written in terms of the electrostatic potential V_{ap} of the free charges as follows

$$\vec{E}_{ap} = -\nabla V_{ap} \qquad 1.2.15$$

CHAPTER II

AVERAGING TECHNIQUES

A. Introduction

In the past, authors have obtained the macroscopic fields and field equations by averaging the corresponding microscopic fields and field equations. There are three principal types of averaging in use:

1. Time
2. Ensemble
3. Spatial

On the microscopic level, the ions in a real crystal have non-zero velocities but their motions are limited to the vicinity of a lattice site due to the presence of the other ions. These thermal motions cause the microscopic fields to be rapidly fluctuating functions of time and space.

Using time averaging techniques, the macroscopic fields are found by integrating over a time interval, then dividing by the time interval.

With ensemble averaging techniques, the macroscopic fields at a point in the crystal is evaluated for some configuration (position and momenta of all the ions), then averaged over all possible ensembles according to some distribution law such as Boltzmann's Distribution.

Both time and ensemble averaging are not suitable for considering the rigid ion model because there is no time dependence and only one ensemble. Thus the time and ensemble averaging would have no effect.

The remaining method, spatial averaging, is more acceptable since it may be applied to the rigid ion model (i.e. time independent case) to give macroscopic functions which are slowly varying functions of position. To give an example of spatial averaging, we will discuss a recent method developed by Russakoff[21]. His definition is similar to those of Lorentz[22] and of Rosenfeld[23] who were the first to give a comprehensive treatment of this problem.

In Section B we will discuss spatial averaging and in Section C we will use spatial averaging to derive the macroscopic fields $\vec{E}$ (the electric field) and $\vec{D}$ (the electric displacement field).

B. Spatial Averaging

We will be following Russakoff's article[21], as closely as possible in this and the following section. He considered molecular crystals but we have generalized his method to the ionic crystal. Where Russakoff refers to molecule we will refer to a c.r.u.

The spatial average of a microscopic function of position, $A(\vec{z})$, is defined as

$$\langle A(\vec{z})\rangle = \iiint d\vec{y} A(\vec{z}-\vec{y}) w(\vec{y}) \qquad 2.2.1$$

where the integration is over all space and $w(\vec{y})$ is a weighting function which depends on the type of spatial averaging that is being performed.

Normally one chooses $w(\vec{y})$ as follows:

$$\begin{aligned} w(\vec{y}) &= 1/v_o \qquad \vec{y} \in v_o \\ &= 0 \qquad\quad \vec{y} \notin v_o \end{aligned} \qquad 2.2.2$$

where v_o is some microscopic volume which is large compared to volume of the unit cell (see fig. 2.1). We note that $w(\vec{y})$ is normalized to unity. i.e.

$$\iiint d\vec{y} w(\vec{y}) = 1 \qquad 2.2.3$$

This is essentially the type of averaging used by Lorentz and by Rosenfeld.

However, if one uses the above form for $w(\vec{y})$, then the average is not continuous. Rather it is a step function. To obtain smooth averages, it is necessary to use a different form for $w(\vec{y})$.

$w(\vec{y})$ is chosen to be a non-uniform, real, positive, well-behaved

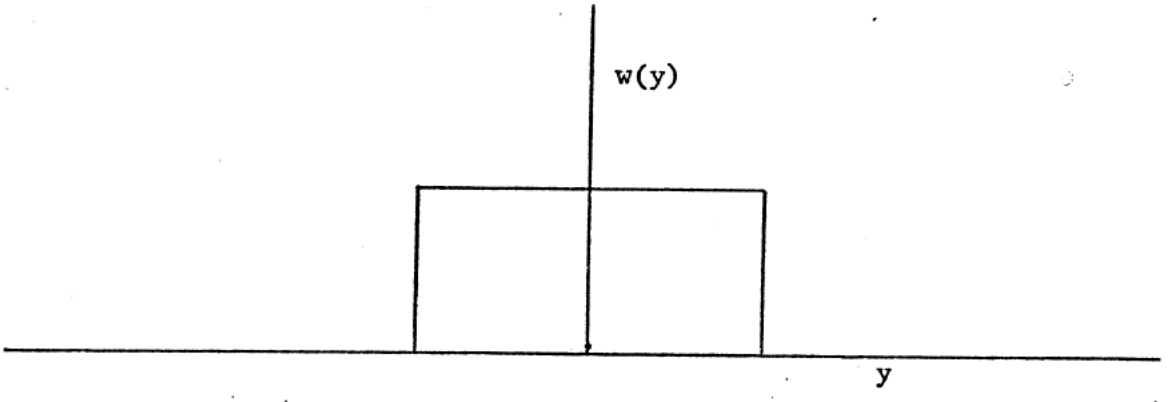


Figure 2.1

One Dimensional Weighting Function of the Type Used by Lorentz

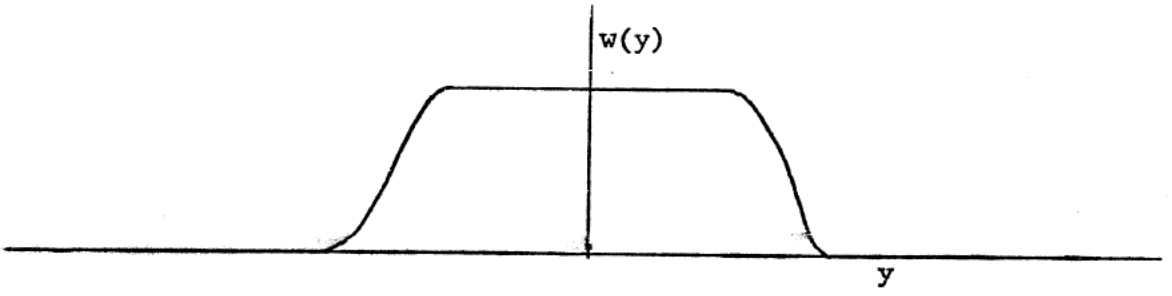


Figure 2.2

One Dimensional Weighting Function of the Type Used by Russakoff

function which is non-zero only in the vicinity of $\vec{y}=0$. (see fig 2.2). In addition $w(\vec{y})$ is normalized to unity. $w(\vec{y})$ is assumed to be sufficiently slowly varying so that only the first few terms of the expansion

$$w(\vec{y}+\vec{z}) = \sum_{m=0}^{\infty} \frac{(\vec{z}.\nabla_y)^m}{m!} w(\vec{y}) \qquad 2.2.4$$

need be considered for $\vec{z}$ of the order of the lattice parameters.

All the authors who used spatial averaging assumed that the derivatives with respect to $\vec{z}$ commute with the averaging process. i.e.

$$\frac{\partial \langle A(\vec{z}) \rangle}{\partial z_i} = \left\langle \frac{\partial A(\vec{z})}{\partial z_i} \right\rangle \qquad 2.2.5$$

They make no mention of the fact that eq (2.2.5) depends on the nature of the function $A(\vec{z})$. i.e. if $A(\vec{z}) = 1/|\vec{z}|^2$, then taking the spatial averages, we find

$$\frac{\partial \langle 1/|\vec{z}|^2 \rangle}{\partial z_i} \neq - \langle 2z_i/|\vec{z}|^4 \rangle \qquad 2.2.6$$

since the L.H.S. is finite and the R.H.S. is infinite.

C. Macroscopic Fields and Field Equations

The following derivation also holds for time dependent fields, but since our work is with time independent case (i.e. the rigid ion model), we will consider only the time independent case. The microscopic field equations are

$$\nabla \times \vec{e} = 0 \qquad 2.3.1$$

$$\nabla \cdot \vec{e} = \rho / \epsilon_o \qquad 2.3.2$$

where $\vec{e}$ is the microscopic electric field and ρ is the charge density. Taking the average of the above equations, we have

$$\langle \nabla \times \vec{e} \rangle = 0 \qquad 2.3.3$$

$$\langle \nabla \cdot \vec{e} \rangle = \langle \rho \rangle / \epsilon_o \qquad 2.3.4$$

Assuming the averaging process commutes with the derivatives, then

$$\nabla \times \vec{E} = 0 \qquad 2.3.5$$

$$\nabla \cdot \vec{E} = \langle \rho \rangle / \epsilon_o \qquad 2.3.6$$

where

$$\vec{E} = \langle \vec{e} \rangle \qquad 2.3.7^{*1}$$

---

*1 We note that if we define an internal electric field $\vec{e}_i$ by

$$\vec{e}_i = \vec{e} - \vec{E}$$

then the average value of this function vanishes. i.e.

$$\langle \vec{e}_i \rangle = 0$$

Although it is seldom explicitly stated, this is one of the justifications for using the averaging techniques.

---

is the macroscopic electric field.

To transform (2.3.6) into a more familiar form, we need to evaluate $\langle\rho\rangle$. The charge density ρ is given by

$$\rho = \rho_f + \rho_i \qquad 2.3.8$$

where ρ_f is the free charge density and ρ_i is the charge density of the ions in the crystal. i.e.

$$\rho_i(\vec{x}) = \sum_k^r \sum_{\vec{l}\in V} q^k \delta(\vec{x} - \vec{x}(\vec{l},k)) \qquad 2.3.9$$

where $\delta(\vec{x})$ is the Dirac delta function.

Thus

$$\begin{aligned}\langle\rho\rangle &= \langle\rho_f\rangle + \langle\rho_i(x)\rangle \\ &= \rho_F(x) + \sum_{\vec{l}\in V} \sum_k^r q^k \langle\delta(\vec{x} - \vec{x}(\vec{l},k))\rangle \\ &= \rho_F(\vec{x}) + \sum_{\vec{l}\in V} \sum_k^r q^k w(\vec{x}-\vec{x}(\vec{l},k)) \qquad 2.3.10\end{aligned}$$

where

$$\rho_F(\vec{x}) = \langle\rho_f\rangle \qquad 2.3.11$$

is the average of the free charge density.

We now assume that the position vector $\vec{x}(\vec{l},k)$ of the ion in the crystal may be written in the form

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k(\vec{l}) \qquad \text{(c.f. eq (1.2.9))} \quad 2.3.12$$

where $\vec{x}(\vec{l})$ is the position vector of the Bravais lattice site with which the c.r.u. is associated and $\vec{x}^k(\vec{l})$ gives the position of the ion in the c.r.u., which may depend on the position vector $\vec{x}(\vec{l})$. (In Part One we assumed $\vec{x}^k$ was independent of $\vec{x}(\vec{l})$, our definition and use of c.r.u. is still valid when $\vec{x}^k$ depends on $\vec{x}(\vec{l})$. Since $\vec{x}^k(\vec{l})$

is of the order of the lattice parameters, we may expand $w(\vec{x}-\vec{x}(\vec{l},k))$ in a power series in $\vec{x}^k(\vec{l})$, and keep only the leading terms. i.e.

$$\langle\rho(\vec{x})\rangle = \rho_F + \sum_{\vec{l}\in V}\sum_k^r q^k \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\{\vec{x}^k(\vec{l}).\nabla_x\}^m w(\vec{x}-\vec{x}(\vec{l}))$$

$$= \rho_F + \sum_{\vec{l}\in V}\sum_k^r q^k\Big[w(\vec{x}-\vec{x}(\vec{l})) - \vec{x}^k(\vec{l}).\nabla w(\vec{x}-\vec{x}(\vec{l})) +$$

$$\tfrac{1}{2}\{\vec{x}^k(\vec{l}).\nabla\}^2 w(\vec{x}-\vec{x}(\vec{l}))\Big]$$

$$= \rho_F - \nabla_x.\Bigg\{\sum_{\vec{l}\in V}\sum_k^r q^k\vec{x}^k(\vec{l})\, w(\vec{x}-\vec{x}(\vec{l}))$$

$$- \tfrac{1}{2}\nabla.\Big[\sum_{\vec{l}\in V}\sum_k^r q^k\vec{x}^k(\vec{l})\vec{x}^k(\vec{l})\, w(\vec{x}-\vec{x}(\vec{l}))\Big]\Bigg\} \qquad 2.3.13$$

Defining

$$P_i(\vec{x}) = \sum_{\vec{l}\in V}\sum_k^r q^k x_i^k(\vec{l}) w(\vec{x}-\vec{x}(\vec{l})) \qquad i=1,2,3 \qquad 2.3.14$$

and

$$P_{ij}(\vec{x}) = \sum_{\vec{l}\in V}\sum_k^r q^k x^k(\vec{l}) x^k(\vec{l}) w(\vec{x}-\vec{x}(\vec{l})) \qquad i,j=1,2,3 \qquad 2.3.15$$

(c.f. P_i, eq (1:5.2.7) and P_{ij}, eq (1:5.2.8)), then eq (2.3.13) may be written as

$$\langle\rho(x)\rangle = \rho_F - \frac{\partial}{\partial x_i}\Big[P_i(\vec{x}) - \frac{\partial}{\partial x_j}P_{ij}(\vec{x})\Big] \qquad 2.3.16$$

Thus (2.3.6) becomes

$$\nabla.\vec{E} = \frac{1}{\epsilon_o}\rho_F - \frac{1}{\epsilon_o}\nabla.\{\vec{P}(\vec{x}) - \nabla.\underline{P}(\vec{x})\} \qquad 2.3.17$$

where we are using the dyadic notation for P_{ij} (i.e. $P_{ij} = (\underline{P})_{ij}$).

Hence

$$\nabla.(\epsilon_o \vec{E} + \vec{P} - \nabla.\underline{P}) = \rho_F \qquad 2.3.18$$

Therefore if we define a field $\vec{D}$ (this is not a unique definition for $\vec{D}$*2) by

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} - \nabla.\underline{P} \qquad 2.3.19$$

then

$$\nabla.\vec{D} = \rho_F \qquad 2.3.20$$

In summary we have defined two macroscopic fields $\vec{E}$ and $\vec{D}$ by

$$\vec{E} = \langle \vec{e} \rangle \qquad 2.3.21$$

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} - \nabla.\underline{P} \qquad 2.3.22$$

which satisfy the field equations

$$\nabla \times \vec{E} = 0 \qquad 2.3.23$$

$$\nabla.\vec{D} = \rho_F \qquad 2.3.24$$

where ρ_F is the average of the free charge density. Equations (2.3.23) and (2.3.24) are the field equations satisfied by the electric field and electric displacement field respectively. Therefore $\vec{E}$ is said to be the macroscopic electric field and $\vec{D}$ the macroscopic electric displacement field.

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*2 We could equally well have chosen a vector

$$\vec{D}' = \vec{D} + \nabla \times \vec{d}$$

where $\vec{d}$ is an arbitrary vector field and still have satisfied the field equation

$$\nabla.\vec{D}' = \rho_F$$

CHAPTER III

MACROSCOPIC FIELDS

A. Introduction

In this chapter, we will introduce a new method for defining macroscopic fields. We will not use averaging techniques such as spatial averaging described in Chapter II. Instead we will use a generalization of the method developed in Part One to obtain the quantities which we will consider to be the macroscopic fields.

In Section B, we derive a representation for the electrostatic potential at a point in a deformed finite crystal whose ions are displaced by $\vec{u}(\vec{l},k)$ from the lattice site $\vec{x}(\vec{l},k)$ of the undeformed crystal (see Section 1.2). As in Part One we are able to write the electrostatic potential as the sum of an intrinsic and an extrinsic electrostatic potential. In Section C, we use the extrinsic potential to define a macroscopic electric field, $\vec{E}$, as the sum of the applied electric field and the negative gradient of the extrinsic electrostatic potential. This quantity is well-defined both in the interior and exterior of the crystal. In Section D, we obtain a definition for the electric displacement field, $\vec{D}$, by manipulating the expression for $\nabla.\vec{E}$. This does not give a unique definition for $\vec{D}$ but it is the only method available to us (as it was for the $\vec{D}$ defined using spatial averaging (see eqs (2.3.18) and (2.3.19))).

B. The Electrostatic Potential

The electrostatic potential at a point P (with position vector $\vec{Z}$) in the deformed crystal described in Section 1.2, is

$$V(\vec{Z}) = \frac{1}{4\pi\epsilon_0} \sum_k q^k \sum_{\vec{l} \in V} \frac{1}{|\vec{X}(\vec{l},k) - \vec{Z}|} \qquad 3.2.1$$

where $\vec{X}(\vec{l},k)$ is the position vector in the final state of the ion (see eq (1.2.1)) which, in the initial state, was the k-th ion of the charge repetition unit (c.r.u.) associated with the $\vec{l}$-th lattice site. As in Part One, we sum over all lattice sites in the undeformed crystal, then sum over the ions in the c.r.u. We may do this since there is a one-to one correspondence between the ions in the deformed crystal and the ions in the undeformed crystal. Considering only the sum over $\vec{l}$ in eq (3.2.1), we define a quantity $\phi^k(\vec{Z},V)$ by

$$\phi^k(\vec{Z},V) \overset{\text{defn}}{=} \sum_{\vec{l} \in V} \frac{1}{|\vec{X}(\vec{l},k) - \vec{Z}|} \qquad 3.2.2$$

(c.f. the partial potential, eq (1:3.1.3)).

Thus

$$V(\vec{Z}) = \frac{1}{4\pi\epsilon_0} \sum_k q^k \phi^k(\vec{Z},V) \qquad 3.2.3$$

Substituting for $\vec{X}(\vec{l},k)$ using eq (1.2.1), $\phi^k(\vec{Z},V)$ becomes

$$\phi^k(\vec{Z},V) = \sum_{\vec{l} \in V} \frac{1}{|\vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) - \vec{Z}|} \qquad 3.2.4$$

where $\vec{x}(\vec{l},k)$ is the position vector of an ion site in the undeformed crystal (see eq (1.2.9)). Although we use the lattice site indices, $\vec{l}$, to label $\vec{u}(\vec{l},k)$ for convenience in writing, we implicitly assume $\vec{u}(\vec{l},k)$

can be written in the form

$$\vec{u}(\vec{l},k) = \vec{u}(\vec{x}(\vec{l}),k) \qquad 3.2.5$$

i.e. we treat $\vec{u}(\vec{l},k)$ as a function of $\vec{x}(\vec{l})$ rather than of $\vec{l}$.

The displacements can be considered in two ways:

1. As a set of N' vectors (N' being the number of ions in the crystal) with each vector being the displacement of an ion, or

2. as a continuous function of position (for a given k value) which gives the displacements of the ions when the position is a lattice site in the initial state.

Our method is valid only for displacements of the second kind.

In order that the generalization of the method of Part One will be as close as possible to the original method, we will assume that the undeformed lattice has cubic symmetry with lattice parameter a. The method is easily extended to more complex lattices. We note that the set of points defined by the vectors

$$X_i(\vec{l}) = (\delta_{ij} + u_{ij})x_j(\vec{l})$$

form a Bravais lattice (although, in general, not a cubic one). We will call this lattice the deformed lattice.

As in Part One, we split the sum into two parts - one over all the points within a cubic region V_n of side (2n+1)a, centered at $\vec{x}_z$ ($\vec{X}_Z$ is the deformed lattice site nearest $\vec{Z}$) ($l \in V_n$) and one over the rest of the crystal ($\vec{l} \notin V_n$).

Thus

$$\phi^k(\vec{Z},V) = \sum_{\vec{l}\in V_n} \frac{1}{|\vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) - \vec{Z}|} + \sum_{\vec{l}\notin V_n} \frac{1}{|\vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) - \vec{Z}|} \qquad 2.3.6$$

where n is any non-negative integer. Again following Part One, we define a new quantity $\phi'^{k}(\vec{Z})$ as the second term in eq (3.2.6), i.e.

$$\phi'^{k}(\vec{Z}) \overset{\text{defn}}{=} \sum_{\vec{l} \notin V_n} \frac{1}{|\vec{x}(\vec{l},k) + \vec{u}(\vec{l},k) - \vec{Z}|} \qquad 3.2.7$$

Although we have not written them explicitly, $\phi'^{k}(\vec{Z})$ is also a function of V, V_n, and $\vec{X}_Z$ (see definition of $v'(\vec{z}^k)$, eq (1:3.3.5)).

It is now necessary to expand $\phi'^{k}(\vec{Z})$ in a power series involving $\vec{u}(\vec{l},k)$. Eq (3.2.7) has only four practical expansion parameters involving $\vec{u}(\vec{l},k) - \vec{u}(\vec{l},k)$, $\vec{u}^k(\vec{l})$, $\vec{u}(\vec{l},k)+\vec{X}^k$, and $\vec{u}^k(\vec{l})+\vec{X}^k$. We find it necessary to use

$$\vec{u} = \vec{u}^k(\vec{l}) + \vec{X}^k \qquad \text{(see fig. 3.1)} \qquad 3.2.8$$

rather than one of the other three as the expansion parameter in order to obtain definitions consistent with those in present use. (See discussion following eq (3.2.10).) Although we have not written them explicitly (to avoid confusion with $\vec{u}(\vec{l},k)$), $\vec{u}$ is a function of k and of $\vec{x}(\vec{l})$.

Using eq (1.2.2), $\phi'^{k}(\vec{Z})$ may be written as

$$\phi'^{k}(\vec{Z}) = \sum_{\vec{l} \notin V_n} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} \qquad 3.2.9$$

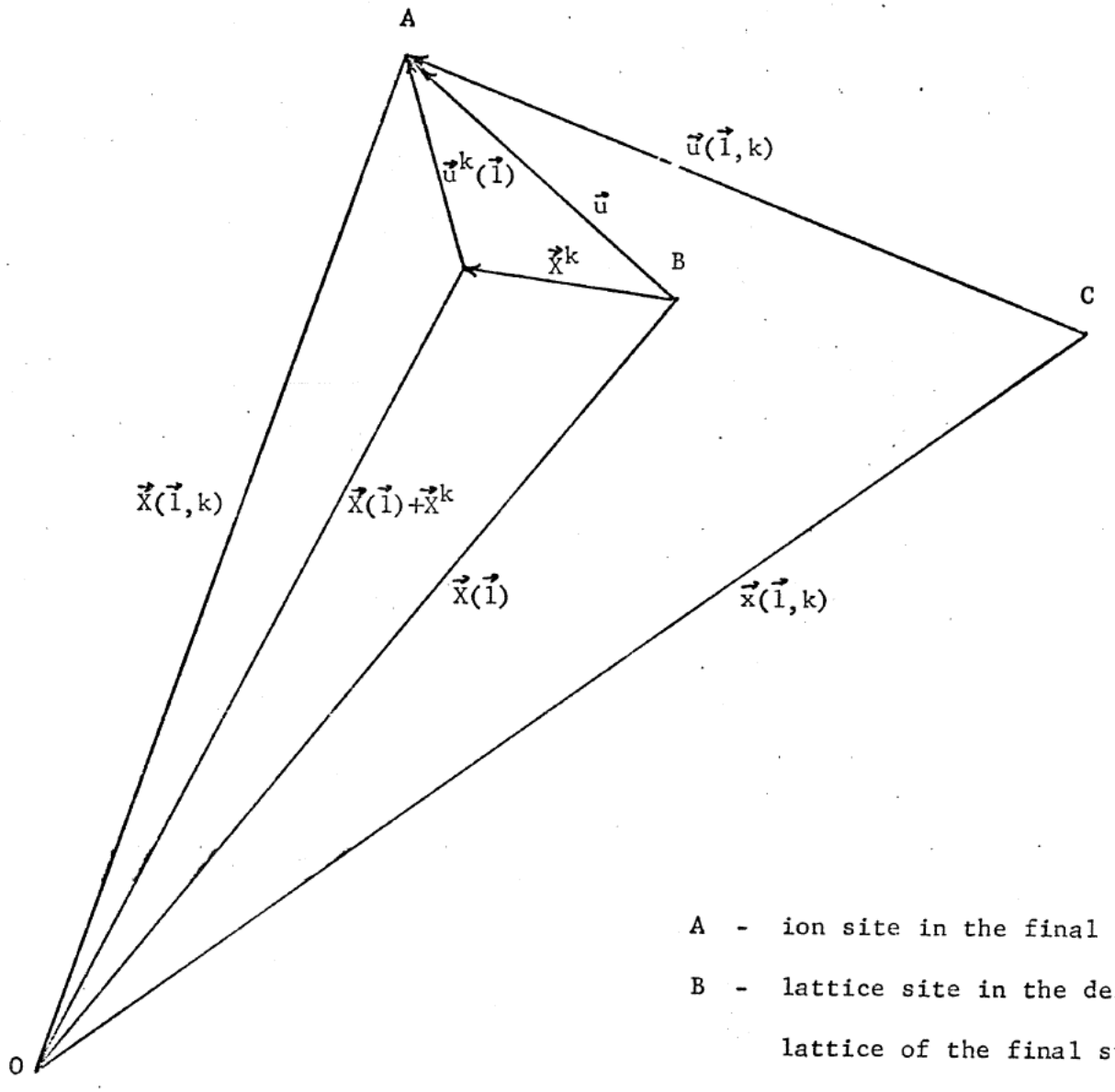
where we have set

$$X_i(\vec{l},k) = x_i(\vec{l},k) + u_i(\vec{l},k) \qquad \text{(see eq (1.2.1))}$$

$$= x_i(\vec{l},k) + u_{ij}x_j(\vec{l},k) + u_i^k(\vec{l}) \qquad \text{(see eq (1.2.5))}$$

$$= X_i(\vec{l}) + X_i^k + u_i^k(\vec{l}) \qquad \text{(see eqs (1.2.7) and (1.2.9))}$$

$$= X_i(\vec{l}) + u_i \qquad 3.2.9a$$



A - ion site in the final state

B - lattice site in the deformed lattice of the final state

C - ion site in the initial state

O - the origin

Figure 3.1

Vectors in the Final State

A diagram giving the relationships between the position vectors in the final state and the expansion parameter u.

We may now expand $\phi'^{k}(\vec{Z})$ in a power series in $\vec{u}$, provided the region V_n is such that

$$|\vec{u}| < |\vec{X}(\vec{l}) - \vec{Z}| \qquad \text{for all } \vec{l} \notin V_n \qquad 3.2.10$$

This restricts the lower limit which n may take.

We stated earlier that it is necessary to use displacements of the form

$$u_i(\vec{l},k) = u_{ij}x_j(\vec{l},k) + u_i^k(\vec{l}) \qquad \text{see eq (1.2.5)}$$

One of the reasons it is necessary, is related to eq (3.2.10). Let us assume $\vec{u}(\vec{l},k)$ is not of the above form and we are forced to use $\vec{u}(\vec{l},k)$ as our expansion parameter. i.e.

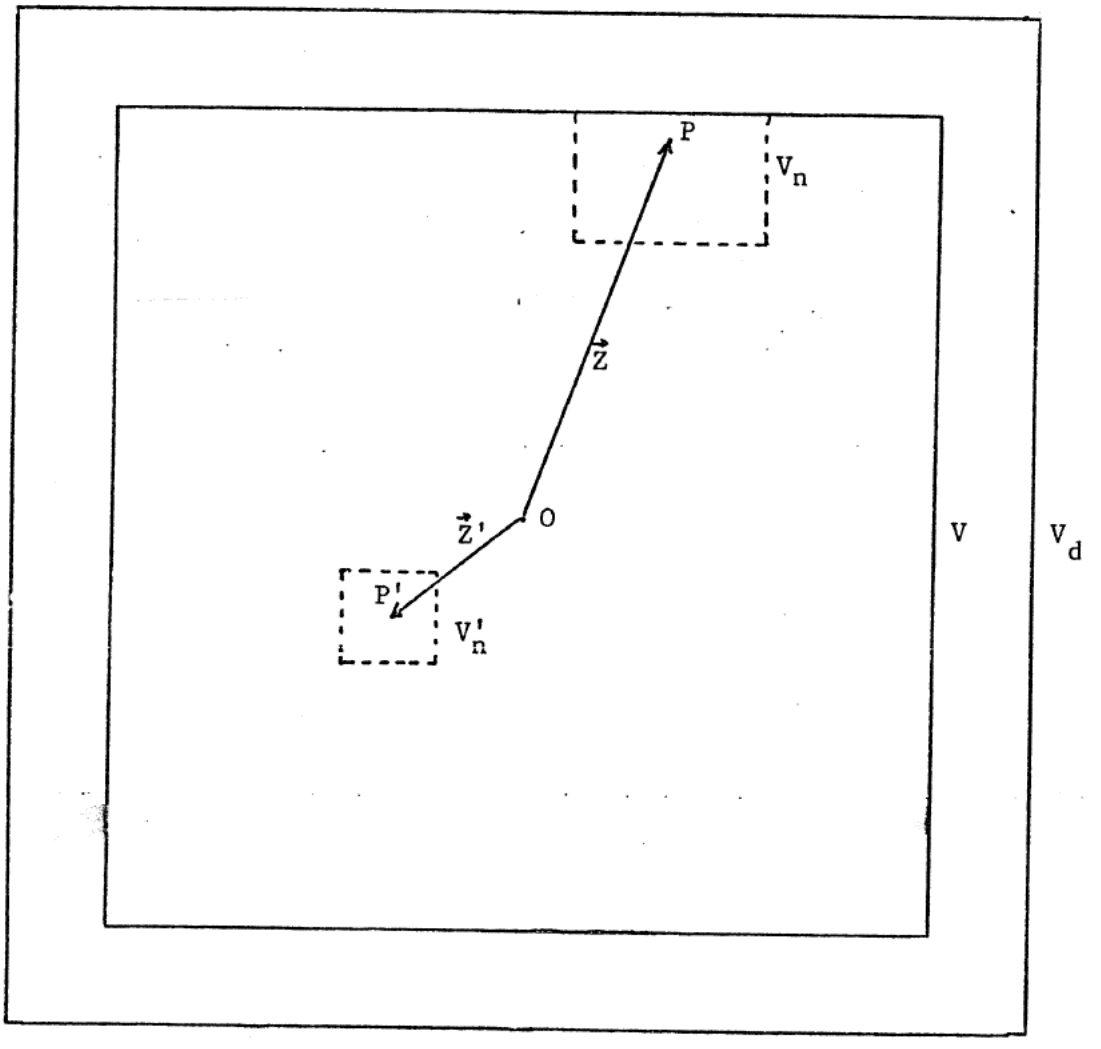
$$\vec{u} = \vec{u}(\vec{l},k)$$

rather than

$$\vec{u} = \vec{u}^k(\vec{l}) + \vec{X}^k \qquad \text{see eq (3.2.8)}$$

Consider the point P in fig. 3.2. With $\vec{u}(\vec{l},k)$ as our expansion parameter, we have to exclude the macroscopic region surrounding the point P since the $\vec{u}(\vec{l},k)$ can be macroscopic near the surface.

This would cause the analysis of this section to break down in the macroscopic region near the surface because the region V_n would be indirectly a function of $\vec{Z}$. It would depend on the distance the point P is from the surface. This distance fixes one side of V_n. Thus the boundary conditions given in Part One are invalidated and the difficulty discussed in Appendix III of Part One arises. Only now the difficulty



O - center of V

Figure 3.2

The Initial and Final States of a Crystal

The regions V_n which must be excluded if $\vec{u}(\vec{l},k)$ was chosen as the expansion parameter are shown for varicus points.

is important in a macroscopic region near the surface, rather than in a microscopic one as in Part One.

For a point such as P', the analysis would still hold since the region, which may be macroscopic in size, may be made independent of $\vec{Z}$. Thus in the interior of the crystal, it does not matter what quantity is chosen as the expansion parameter $\vec{u}$.

We note that the formalizm of this section would still apply in the macroscopic region near the surface. We would, however, have to give a new set of boundary conditions for this region.

By choosing $\vec{u}(\vec{l},k)$ of the form given in eq (1.2.5), we are able to use

$$\vec{u} = \vec{u}^{k}(\vec{l}) + \vec{\chi}^{k} \qquad \text{see eq (3.2.8)}$$

as our expansion parameter. By doing this, the problem still remains but now it is limited to a microscopic region near the surface (i.e. within a few lattice parameters of the surface).

A second reason is that the analysis would give fields which are defined with respect to the undeformed volume rather than the deformed volume as is done in other definitions for macroscopic fields in common use.

The expansion of $\phi'^{k}(\vec{Z})$ in terms of $\vec{u}$ is

$$\phi'^{k}(\vec{Z}) = \sum_{\vec{l}\notin V_n} \sum_{m=0}^{\infty} \frac{(-1)^m (\vec{u}.\nabla_Z)^m}{m!} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z}|} \qquad 3.2.11$$

At this point it simplifies writing if we introduce the outer product denoted by $\boxtimes$ (see Appendix I). We will use the symbol $\vec{A}^m$ to denote the m-th order outer product of a vector $\vec{A}$. i.e.

$$\vec{A}^m = \vec{A}\boxtimes\vec{A}\boxtimes\vec{A}\boxtimes\ldots.\boxtimes\vec{A} \qquad 3.2.12$$

where the symbol $\boxtimes$ appears m-1 times. $\vec{A}^m$ is a symmetric m-th order tensor whose components are given by

$$[\vec{A}^m]_{i_1\ldots.i_m} = \prod_{j=1}^{m} A_{i_j} \qquad i_j = 1,2,3 \qquad 3.2.13$$

In addition to the outer product, we need to introduce the generalized inner product denoted by $(\overset{m}{.})$. It has the property that

$$(\vec{A}.\vec{B})^m = \vec{A}^m(\overset{m}{.})\vec{B}^m \qquad 3.2.14$$

In terms of this notation, eq (3.2.11) may be written as

$$\begin{aligned}\phi'^{k}(\vec{Z}) &= \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sum_{\vec{l}\notin V_n} \vec{u}^m(\overset{m}{.})\nabla_Z^m \frac{1}{|\vec{X}(\vec{l}) - \vec{Z}|} \\ &= \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(\overset{m}{.}) \sum_{\vec{l}\notin V_n} \frac{\vec{u}^m}{|\vec{X}(\vec{l}) - \vec{Z}|} \qquad 3.2.15\end{aligned}$$

since $\vec{u}$ is independent of $\vec{Z}$ and hence ∇_Z commutes with $\vec{u}$.

The problem of evaluating the electrostatic potential at a point in a deformed crystal has now been reduced to evaluating

$$\underset{\sim}{S}(m) \overset{\text{defn}}{=} \sum_{\vec{l}\notin V_m} \frac{\vec{u}^m}{|\vec{X}(\vec{l}) - \vec{Z}|} \qquad 3.2.16^{*1}$$

By inspection $\underset{\leftrightarrow}{S}(m)$ is an m-th order tensor.

To proceed further, we have to assume the components of $\vec{u}^m$ can be written in the form

$$\begin{aligned}\left[\vec{u}^m\right]_{i_1..i_m} &= \left[\vec{u}^m(\vec{X}(\vec{l}))\right]_{i_1..i_m} \\ &= \left[\vec{u}^m(\vec{X}(\vec{l})-\vec{Z}+\vec{Z})\right]_{i_1..i_m} \\ &= \left[\sum_{p=0}^{\infty} g^k_{mp}(\vec{Z})h^k_{mp}(\vec{X}(\vec{l})-\vec{Z})\right]_{i_1..i_m} \qquad 3.2.17\end{aligned}$$

An example of this type of function is the exponential. i.e.

$$\begin{aligned}\vec{u} &= \vec{u}^o e^{i\vec{k}.\vec{X}(\vec{l})} \\ &= \vec{u}^o e^{i\vec{k}.\vec{Z}}\, e^{i\vec{k}.(\vec{X}(\vec{l})-\vec{Z})} \qquad 3.2.18\end{aligned}$$

where $\vec{k}$ is a vector in the reciprocal lattice. Another example of this type of function is any polynomial of finite order.

We note that although the R.H.S. of (3.2.17) contains functions which have $\vec{Z}$ as an explicit argument, the sum is independent of $\vec{Z}$. Up to this point $\vec{u}(\vec{l},\vec{k})$, and hence $\vec{u}$ by eq (3.2.8), has been an arbitrary function of $\vec{x}(\vec{l})$, and hence of $\vec{X}(\vec{l})$. Now it is restricted to the set of functions which satisfy (3.2.17). Substituting (3.2.17) for $\vec{u}^m$ in eq (3.2.16), we obtain

$$\left[\underset{\leftrightarrow}{S}(m)\right]_{i_1..i_m} = \sum_{\vec{l}\notin V_n}\left[\sum_{p=0}^{\infty}\frac{g^k_{mp}(\vec{Z})h^k_{mp}(\vec{X}(\vec{l})-\vec{Z})}{|\vec{X}(\vec{l})-\vec{Z}|}\right]_{i_1..i_m} \qquad 3.2.19$$

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*1 We will be using the notation $\underset{\leftrightarrow}{A}(m)$ to denote a tensor of rank m.

Hence

$$[\underline{S}^{(m)}]_{i_1..i_m} = \Big[\sum_{p=0}^{\infty} g^k_{mp}(\vec{Z}) \sum_{\vec{I}\notin V_n} \frac{h^k_{mp}(\vec{X}(\vec{I})-\vec{Z})}{|\vec{X}(\vec{I})-\vec{Z}|}\Big]_{i_1..i_m} \qquad 3.2.20$$

In order to be able to use eq (1:3.2.3), we must impose the constraint on V_n that

$$|\vec{X}(\vec{I}) - \vec{Z}| > \tfrac{1}{2}\sqrt{3}a \qquad \text{for all } \vec{I}\notin V_n \qquad 3.2.21$$

Thus the value which n may take is the greater of the two values as determined by eqs (3.2.10) and (3.2.21).

Therefore, for the functions $h^k_{mp}(\vec{X}(\vec{I})-\vec{Z})/|\vec{X}(\vec{I})-\vec{Z}|$ appearing in eq (3.2.20), we may write

$$\hat{\Gamma}(\vec{z})\,\frac{h^k_{mp}(\vec{X}(\vec{I})-\vec{Z})}{|\vec{X}(\vec{I})-\vec{Z}|} = \frac{N}{V}\int\!\!\int\!\!\int_{-\frac{1}{2}a}^{\frac{1}{2}a} d\vec{y}\,\frac{h^k_{mp}(\vec{X}(\vec{I})-\vec{Z})}{|\vec{X}(\vec{I})-\vec{Z}|} \qquad 3.2.22$$

where $|\vec{X}(\vec{I})-\vec{Z}| > \tfrac{1}{2}\sqrt{3}a$ for all $\vec{I}\notin V_n$ and hence the integrand does not have a singularity in the region of integration. In addition

$$Y_i = (\delta_{ij} + u_{ij})y_j \qquad \text{see eq (1.2.7)} \qquad 3.2.23$$

and

$$Z_i = (\delta_{ij} + u_{ij})z_j \qquad 3.2.24$$

Summing over $\vec{I}\notin V_n$ in eq (3.2.22), as in Part One, we obtain

$$\hat{\Gamma}(\vec{z}) \sum_{\vec{I}\notin V_n} \frac{h^k_{mp}(\vec{X}(\vec{I})-\vec{Z})}{|\vec{X}(\vec{I})-\vec{Z}|} = \frac{N}{V}\int\!\!\int\!\!\int_{V'} d\vec{y}\,\frac{h^k_{mp}(\vec{Y}-\vec{Z})}{|\vec{Y}-\vec{Z}|} \qquad 3.2.25$$

where V' is the region V from which the region V_n has been excluded.

This is the same type of differential equation as we solved in Part One, (see eqs (1:3.3.11) and (1:3.3.13)). Therefore, using the results of Part One, see eq (3.3.22), we may write the solution of

(3.2.22) as

$$\sum_{\vec{1}\in V_n} \frac{h^k_{mp}(\vec{X}(\vec{1})-\vec{Z})}{|\vec{X}(\vec{1}) - \vec{Z}|} = \frac{N}{V}\left\{f^k_{mp}(\vec{Z},V) - f^k_{mp}(\vec{Z}',V)\right\} \qquad 3.2.26$$

where

$$\vec{Z}' = \vec{Z} - \vec{X}_Z \qquad 3.2.27$$

$f^k_{mp}(\vec{Z},V)$ is a solution of the differential equation

$$\hat{\Gamma}(\vec{z}) f^k_{mp}(\vec{Z},V) = \iiint_V d\vec{y}\, \frac{h^k_{mp}(\vec{Y}-\vec{Z})}{|\vec{Y}-\vec{Z}|} \qquad 3.2.28$$

subject to the boundary conditions*2

1. $f^k_{mp}(\vec{Z},V)$ must not contain a solution $\tilde{f}$ of the homogeneous differential equation

$$\hat{\Gamma}\tilde{f} = 0 \qquad 3.2.29$$

which is not a function of V, and

2. $f^k_{mp}(\vec{Z},V)$ must have the same V dependence as the sum

$$H^k_{mp}(\vec{Z},V) \overset{\text{defn}}{=} \sum_{\vec{1}\notin V_n} \frac{h^k_{mp}(\vec{X}(\vec{1})-\vec{Z})}{|\vec{X}(\vec{1}) - \vec{Z}|} \qquad 3.2.30$$

The above statements with $\vec{Z} = \vec{Z}'$ and $V = V_n$ hold for $f^k_{mp}(\vec{Z}',V_n)$.

Substituting (3.2.26) into (3.2.20), S(m) becomes

$$\left[S(m)\right]_{i_1..i_m} = \left[\sum_{p=0}^{\infty} g^k_{mp}(\vec{Z})\frac{N}{V}\left\{f^k_{mp}(\vec{Z},V) - f^k_{mp}(\vec{Z}',V_n)\right\}\right]_{i_1..i_m} \qquad 3.2.31$$

*2 We note that the first boundary condition is the same as the first one introduced in Part One (following eq (1:3.3.29)). The second boundary condition is a generalization of the second boundary condition of Part One.

or

$$\underset{\leftrightarrow}{S}(m) = \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) - \underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}') \qquad 3.2.32$$

where

$$\left[\underset{\leftrightarrow}{R}^k(m,V,\vec{Z})\right]_{i_1..i_m} = \frac{N}{V}\left[\sum_{p=0}^{\infty} g_{mp}^k(\vec{Z}) f_{mp}^k(\vec{Z},V)\right]_{i_1..i_m} \qquad 3.2.33$$

and

$$\left[\underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}')\right]_{i_1..i_m} = \frac{N}{V}\left[\sum_{p=0}^{\infty} g_{mp}^k(\vec{Z}) f_{mp}^k(\vec{Z}',V_n)\right]_{i_1..i_m} \qquad 3.2.34$$

Substituting (3.3.32) into (3.2.15), we have

$$\phi'^k(\vec{Z}) = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(.)^m \left\{ \underset{\leftrightarrow}{R}^k(m,V,Z) - \underset{\leftrightarrow}{R}^k(m,V_n,Z,Z') \right\} \qquad 3.2.35$$

Thus

$$\phi^k(\vec{Z},V) = \sum_{\vec{l}\in V_n} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(.)^m \underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}')$$

$$+ \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(.)^m \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) \qquad 3.2.36$$

Therefore the electrostatic potential at the point P in the deformed crystal is

$$V(\vec{Z}) = \sum_k \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(.)^m \underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}') \right\}$$

$$+ \sum_k \frac{q^k}{4\pi\epsilon_o} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(.)^m \underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}') \quad \vec{Z}\in V_d \qquad 3.2.37$$

where V_d is the volume of the deformed crystal. V_d may be written in terms of the undeformed volume V as follows

$$V_d = JV \qquad 3.2.38$$

where J is the determinant of $\delta_{ij}+u_{ij}$. i.e.

$$J = |\delta_{ij} + u_{ij}| \qquad 3.2.39$$

As in Part One, (see eq (1:3.3.68)), eq (3.2.37) lends itself to

the definition of two new quantities - the intrinsic, $V_i(\vec{Z})$, and extrinsic, $V_e(\vec{Z})$, electrostatic potentials of a deformed crystal. i.e.

$$V_i(\vec{Z}) = \sum_k \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n} \frac{1}{|\vec{X}(\vec{l})-\vec{Z}+\vec{u}|} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(\cdot)^m \underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}') \right\} \qquad 3.2.40$$

and

$$V_e(\vec{Z}) = \sum_k \frac{q^k}{4\pi\epsilon_o} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(\cdot)^m \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) \qquad \vec{Z}\in V_d \qquad 3.2.41$$

Due to the method used to derive $\underset{\leftrightarrow}{R}^k(m,V_n,\vec{Z},\vec{Z}')$, it is not obvious that the potential $V_i(\vec{Z})$ is independent of V_n. To show that $V_i(\vec{Z})$ is independent of V_n, we proceed as follows.

From the second boundary condition, we know that $f^k_{mp}(\vec{Z}',V_n)$ has the same V_n dependence as $H^k_{mp}(\vec{Z}',V_n)$. Therefore the V_n dependence of the two quantities

$$\sum_{p=0}^{\infty} g^k_{mp}(\vec{Z}) f^k_{mp}(\vec{Z}') \quad \text{and} \quad \sum_{p=0}^{\infty} g^k_{mp}(\vec{Z}) H^k_{mp}(\vec{Z}')$$

is the same.

However, from eq (3.2.30),

$$\sum_{p=0}^{\infty} g^k_{mp}(\vec{Z}) H^k_{mp}(\vec{Z}') = \sum_{p=0}^{\infty} g^k_{mp}(\vec{Z}) \sum_{\vec{l}\in V_n} \frac{h^k_{mp}(\vec{X}(\vec{l})-\vec{Z}')}{|\vec{X}(\vec{l}) - \vec{Z}'|}$$

$$= \sum_{\vec{l}\in V_n} \frac{\vec{u}^m(\vec{X}(\vec{l})+\vec{X}_Z)}{|\vec{X}(\vec{l}) + \vec{X}_Z - \vec{Z}|} \qquad \text{(see eq (3.2.17) and eq (3.2.27))}$$

$$= \sum_{\vec{l}'\in V_n} \frac{\vec{u}^m}{|\vec{X}(\vec{l}') - \vec{Z}|} \qquad 3.2.42$$

where we have shifted the origin in the last step using the transformation

$$\vec{X}(\vec{l}') = \vec{X}(\vec{l}) + \vec{X}_Z \qquad 3.2.43$$

Thus

$$\sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m \binom{m}{\cdot} \underset{\leftrightarrow}{R}^k (m, V_n, \vec{Z}, \vec{Z}')$$

has the same V_n dependence as

$$\sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m \binom{m}{\cdot} \sum_{\vec{l} \in V_n} \frac{\vec{u}^m}{|\vec{X}(\vec{l}) - \vec{Z}|} \qquad 3.2.44$$

We will now consider the V_n dependence of the first expression on the R.H.S. of eq (3.2.40). From eq (3.2.10),

$$|\vec{u}| < |\vec{X}(\vec{l}) - \vec{Z}| \qquad \text{for all } \vec{l} \notin V_n \qquad 3.2.45$$

However, if V_n is sufficiently large, then

$$|\vec{u}| < |\vec{X}(\vec{l}) - \vec{Z}|$$

for some $\vec{l} \in V_n$. If we let n' be the minimum value of n for which eq (3.2.45) is satisfied, then we may set

$$\sum_{\vec{l} \in V_n} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} = \sum_{\vec{l} \in V_{n'}} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} + \sum_{\vec{l} \in V_n - V_{n'}} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} \qquad 3.2.46$$

We may expand the last term in a Taylor series to obtain

$$\sum_{\vec{l} \in V_n - V_{n'}} \frac{1}{|\vec{X}(\vec{l}) - \vec{Z} + \vec{u}|} = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m \binom{m}{\cdot} \sum_{\vec{l} \in V_n - V_{n'}} \frac{\vec{u}^m}{|\vec{X}(\vec{l}) - \vec{Z}|} \qquad 3.2.47$$

which has the same V_n dependence as (3.2.44) and hence $V_i(\vec{Z})$ is independent of V_n. It depends only on the crystal structure, the displacements, and the position of the point P in the sample. In contrast, in addition to depending on the above three quantities, $V_e(\vec{Z})$ also depends on the shape of the region V_d.

We note that using averaging techniques the quantity corresponding to V_i would have an average value of zero (see footnote of eq (2.3.7)). The average value of $V_i(\vec{Z})$ is, in general, not equal to zero. (When $\vec{u}(\vec{l},k) = 0$, the average value of $V_i(\vec{Z})$ is zero (see eq (1:4.2.9).)

In terms of the intrinsic an extrinsic electrostatic potentials, the total electrostatic potential at a point within the crystal is

$$V(\vec{Z}) = V_i(\vec{Z}) + V_e(\vec{Z}) \qquad \vec{Z} \in V_d \qquad 3.2.48$$

This is the potential at a point fixed in space. As we deform the crystal, the point P remains unchanged. Thus (3.2.48) gives the potential at the point P when the ions are displaced from the lattice sites by some applied fields. How the displacements are related to the applied fields is not of interest to us in this chapter. Thus, the quantities in (3.2.48) are suitable for defining fields such as the electric field and electric displacement fields since we are interested in how these two fields change at a fixed point when external fields (such as applied electric fields or applied stresses) are applied.

The intrinsic electrostatic potential is a rapidly fluctuating function of position since as we move from one ion to another, the potential can vary greatly in magnitude due to the singularities at the ion sites in the sum over V_n. It is also a rapidly varying function of the displacements since these can move the ions near the point of interest and hence cause the magnitude of $V_i(\vec{Z})$ vary greatly.

On the other hand, $V_e(\vec{Z})$ does not contain any singularities and may be expanded in a power series in $\vec{Z}$. For the case of uniform fields in an ellipsoid, $V_e(\vec{Z})$ is so slowly varying that only the first few terms in the power series are non-zero for points far from the surface.

C. The Electric Field

The total electric field, $\vec{E}_t$, which would act on a test charge (both in the interior and exterior of the crystal), is by definition

$$\vec{E}_t \overset{\text{defn}}{=} \vec{E}_{ap} - \nabla_Z V(\vec{Z}) \qquad 3.3.1$$

where $\vec{E}_{ap}$ is the applied electric field due to the free charges present in the system (see eq (1.2.15)) and $V(\vec{Z})$ is the electrostatic potential due to the ions of the crystal.

For points within the deformed crystal, we may use the results of Section B, eq (3.2.48), to immediately write

$$V(\vec{Z}) = V_i(\vec{Z}) + V_e(\vec{Z}) \qquad \vec{Z} \in V_d \qquad 3.3.2$$

where V_d is the volume of the deformed crystal. For points exterior to the crystal, we may go through the same analysis as given in Section B, to obtain a similar expression, i.e.

$$V(\vec{Z}) = V_i(\vec{Z}) + V_e(\vec{Z}) \qquad \vec{Z} \notin V_d \qquad 3.3.3$$

where

$$V_i(\vec{Z}) = 0 \qquad 3.3.4$$

and

$$V_e(\vec{Z}) = \sum_k \frac{q^k}{4\pi\epsilon_o} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m(\cdot)^m \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) \qquad 3.3.5$$

$\underset{\leftrightarrow}{R}^k(m,V,\vec{Z})$ $(\vec{Z} \notin V_d)$ is defined in the same way as for $\vec{Z} \in V_d$. i.e.

$$\left[\underset{\leftrightarrow}{R}^k(m,V,\vec{Z})\right]_{i_1..i_m} = \frac{N}{V}\left[\sum_{p=0}^{\infty} g_{mp}^k(\vec{Z}) f_{mp}^k(\vec{Z},V)\right]_{i_1..i_m} \qquad 3.3.6$$

(see eq (3.2.33)) with $f_{mp}^k(\vec{Z},V)$ a solution of eq (3.2.28)*1 and subject

to the boundary conditions which follow eq (3.2.28).

What we will now do is define a macroscopic electric field, then give some of its properties. In choosing definitions for macroscopic fields, one of the criteria we will impose is that it must be slowly varying over atomic distances. We have noted that $V_i(\vec{Z})$ is a rapidly fluctuating function of position and deformation. Thus we choose to define our macroscopic electric field as

$$\vec{E} \overset{\text{defn}}{=} \vec{E}_{ap} - \nabla_Z V_e(\vec{Z}) \qquad \text{for all } \vec{Z} \qquad 3.3.6$$

This definition is not unique since it is possible to include a slowly varying part of $-\nabla_Z V_i(\vec{Z})$. We have chosen to define $\vec{E}$ by eq (3.3.6) because it has the following properties:

1. it is a slowly varying function of position,

2. it has the same form both in the interior and exterior of the crystal,

3. the electrostatic potential at a point within the crystal and hence the electric field in the interior of the crystal is clearly

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*1 We note that although

$$\hat{\Gamma}(\vec{z}) f(\vec{Z},V) = \iiint_V d\vec{y}\, \frac{h(\vec{Y}-\vec{Z})}{|\vec{Y}-\vec{Z}|}$$

for points both in the interior and exterior of the crystal, the methods of solution for the two cases are different. In the interior of the crystal, we may use a polynomial expansion in powers of $|\vec{Z}|$ but in the exterior of the crystal, we need to expand in powers of $1/|\vec{Z}|$ so that f does not diverge as $|\vec{Z}| \to \infty$.

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separable into an intrinsic and an extrinsic part. The extrinsic part depends on the sample and hence changes if a different sample is considered. This is a property we would attribute to a macroscopic field.

4. $\vec{E}$ satisfies the field equation

$$\nabla_Z \times \vec{E} = 0 \qquad 3.3.7$$

$\vec{E}$ is easily shown to satisfy eq (3.3.7) as follows

$$\begin{aligned} \vec{E} &= \nabla_Z \times (\vec{E}_{ap} - \nabla_Z V_e) \\ &= \nabla_Z \times (-\nabla_Z V_{ap} - \nabla_Z V_e) \qquad \text{(see eq (1.2.15))} \\ &= -\nabla_Z \times \nabla_Z (V_{ap} + V_e) \\ &= 0 \end{aligned} \qquad 3.3.8$$

Subsituting for $V_e(\vec{Z})$ using eq (3.2.33) or (3.3.5), we have that the macroscopic electric field is given by

$$\vec{E} = \vec{E}_{ap} - \nabla_Z \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla_Z^m (\overset{m}{\cdot}) \underset{\leftrightarrow}{R}^k(m, V, \vec{Z})$$

$$= \vec{E}_{ap} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla_Z^{m+1} (\overset{m}{\cdot}) \underset{\leftrightarrow}{R}^k(m, V, \vec{Z}) \qquad \text{for all } \vec{Z} \quad 3.3.10$$

D. The Electric Displacement Field

Unlike the electric field, the electric displacement field, $\vec{D}$, is not usually defined on the microscopic level in terms of microscopic quantities. Instead it is a field which is defined in terms of other macroscopic fields. As we have shown in Chapter II, a common way of introducing $\vec{D}$ is as the quantity, resulting from the averaging procedure which satisfies the differential equation

$$\nabla.\vec{D} = \rho_F \qquad \text{(see eqs (2.3.18) and (2.3.19))} \qquad 3.4.1$$

where ρ_F is the average of the free charge density.

What we will do is to find a field which obeys a similar differential equation. Namely,

$$\nabla.D = \rho_f \qquad 3.4.2$$

where ρ_f is the free charge density. We note that ρ_F and ρ_f are related by the equation

$$\rho_F(\vec{Z}) = \iiint_{\substack{\text{all}\\\text{space}}} d\vec{y}\, w(\vec{y})\rho_f(\vec{Z}-\vec{y}) \qquad \text{(see eq (2.3.11))} \qquad 3.4.3$$

where $w(\vec{y})$ is a weighting function.

To find an expression for $\vec{D}$, we will manipulate the expression for $\nabla.\vec{E}$ since $\vec{E}$ is the only macroscopic vector field we have defined at present.

Taking the divergence of $\vec{E}$, as given by eq (3.3.10), we have

$$\nabla.\vec{E} = \nabla.\vec{E}_{ap} - \nabla.\nabla\Big\{\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\sum_k \frac{q^k}{4\pi\epsilon_o}\nabla^m(\overset{m}{\cdot})\overset{\leftrightarrow}{R}{}^k(m,V,\vec{Z})\Big\}$$

$$= \nabla.\vec{E}_{ap} - \sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\sum_k \frac{q^k}{4\pi\epsilon_o}\cdot\nabla^m(\overset{m}{\cdot})\nabla^2\overset{\leftrightarrow}{R}{}^k(m,V,\vec{Z}) \qquad 3.4.4$$

Rearranging terms and setting

$$\nabla.\vec{E}_{ap} = \rho_f/\epsilon_o \qquad \text{(see eq (1.2.14))} \qquad 3.4.5$$

we can write (3.4.4) in the form

$$\nabla.\left\{\vec{E} + \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla^{m-1}(\overset{m-1}{\cdot})\nabla^2_{\leftrightarrow} R^k(m,V,\vec{Z})\right\} = \rho_f/\epsilon_o - \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla^2_{\leftrightarrow} R^k(0,V,\vec{Z}) \qquad 3.4.6$$

The Laplacian of each element of $\underset{\leftrightarrow}{R}$ may be evaluated to give (see Appendix II)

$$\nabla^2_{\leftrightarrow} R^k(m,V,\vec{Z}) = -\frac{4\pi N}{V_d}\vec{u}^m \qquad \vec{Z} \in V_d \qquad 3.4.7$$

$$= 0 \qquad \vec{Z} \notin V_d \qquad 3.4.8$$

where $\vec{u}$ is now treated as a continuous function of $\vec{Z}$ (see discussion following eq (3.2.5)).

Thus eq (3.4.6) reduces to

$$\nabla.\left\{\epsilon_o E + \frac{N}{V_d} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{m!} \sum_k q^k \nabla^{m-1}(\overset{m-1}{\cdot})\vec{u}^m\right\} = \rho_f - \sum_k q^k N/V_d$$

$$= \rho_{f\,\vec{Z}\in V_d} \qquad 3.4.9$$

since

$$\sum_k q^k = 0 \qquad 3.4.10$$

from charge neutrality, and

$$\nabla.\{\epsilon_o \vec{E}\} = \rho_f \qquad \vec{Z} \notin V_d \qquad 3.4.11$$

Therefore if we define a quantity $\vec{D}$ as

$$\vec{D} \overset{\text{defn}}{=} \epsilon_o \vec{E} + \frac{N}{V_d} \sum_{m=1}^{\infty} \frac{(-1)^{m-1}}{m!} \sum_k q^k \nabla^{m-1}(\overset{m-1}{\cdot})\vec{u}^m \quad \vec{Z} \in V_d \qquad 3.4.12$$

and

$$\vec{D} \overset{\text{defn}}{=} \epsilon_o \vec{E} \qquad \vec{Z} \notin V_d \qquad 3.4.13$$

then we see immediately from (3.4.9) and (3.4.11), that $\vec{D}$ satisfies the field equation

$$\nabla . \vec{D} = \rho_f \qquad \text{for all } \vec{Z} \qquad 3.4.14$$

Thus, the quantity $\vec{D}$, defined by eqs (3.4.12) and (3.4.13), is an acceptable field to be chosen as the macroscopic electric displacement field since it satisfies the required Maxwell equation. As with the electric field, this definition is not unique; in the former case, we could add a term $\vec{D}' = \nabla \times \vec{d}'$ where $\vec{d}'$ is an arbitrary vector field and still have $\vec{D} + \vec{D}'$ satisfy (3.4.14). However, to our knowledge, there is no justification for introducing such a term. Thus we will use $\vec{D}$ as given by eqs (3.4.12) and (3.4.13) as our electric displacement field. This is the same philosophy in defining $\vec{D}$ as taken by the authors who used averaging techniques (see eqs (2.3.18) and (2.3.19)).

Setting

$$\underset{\sim}{P}(m, \vec{Z}) = \frac{1}{m!} \frac{N}{V_d} \sum_k q^k \vec{u}^m, \qquad 3.4.15$$

which is related to the multipole moment density per unit deformed volume, we can rewrite (3.4.12) in the more familiar form

$$\vec{D} = \epsilon_o \vec{E} + \sum_{m=1}^{\infty} (-1)^m \nabla^{m-1} \binom{m}{\cdot}^{-1} \underset{\sim}{P}(m, \vec{Z}) \qquad \vec{Z} \in V_d \qquad 3.4.16$$

This equation reduces to the same form as given in Chapter II, eq (2.3.22), if we retain only the terms up to m=2.

If the higher order multipole moments ($m \geq 2$) are negligible, then

$\vec{D}$ reduces to

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} \qquad 3.4.17$$

where

$$\vec{P} = \underset{\leftrightarrow}{P}(1, \vec{Z})$$

$$= \frac{N}{V_d} \sum_k q^k \vec{u} \qquad 3.4.18$$

is polarization.

E. Summary

In this chapter, we have defined the macroscopic electric field, $\vec{E}$, and the electric displacement field, $\vec{D}$, as follows:

$$\vec{E} = \vec{E}_{ap} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla^{m+1} \binom{m}{\cdot} \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) \qquad \text{for all } \vec{Z} \quad 3.5.1$$

(see eq (3.3.10)) and from eqs (3.4.16) and (3.4.13)

$$\vec{D} = \epsilon_o \vec{E} + \sum_{m=1}^{\infty} (-1)^m \nabla^{m-1} \binom{m-1}{\cdot} \underset{\leftrightarrow}{P}(m,\vec{Z}) \qquad \vec{Z} \in V_d \qquad 3.5.2$$

$$= \epsilon_o \vec{E} \qquad \vec{Z} \notin V_d \qquad 3.5.3$$

where

$$\underset{\leftrightarrow}{P}(m,\vec{Z}) = \frac{N}{V_d} \sum_k q^k \{\vec{X}^k + \vec{u}^k(\vec{Z})\}^m \quad \text{(see eq (3.4.15))} \qquad 3.5.4$$

These definitions of $\vec{E}$ and $\vec{D}$ are not unique (see footnote at the end of Section 2.3). To see how they compare with the definitions of $\vec{D}$ and $\vec{E}$ in common use, we will investigate the equation of state which relates $\vec{E}$ and $\vec{D}$. This will be done in the next chapter.

CHAPTER IV

EQUILIBRIUM CONDITIONS

A. Introduction

In Chapter III, we used a generalization of the method developed in Part One to define a macroscopic electric field and an electric displacement field. In this Chapter, we will use the results of Chapter III to solve an equilibrium condition problem for an ion in the system described in Chapter I.

Up to this point, the displacements have been arbitrary functions which were subject only to the two constraints that they satisfy eqs (1.2.2) and (3.2.17). Although there were applied fields present in the system we considered in Chapter III, we did not assume any explicit relationship between these applied fields and the $\vec{u}(\vec{l},k)$ of the ions. We will now assume that the displacements $\vec{u}(\vec{l},k)$ are produced by the applied fields, i.e. applied electric fields and/or applied stresses. The $\vec{u}(\vec{l},k)$ can be found in terms of the applied fields through the equilibrium conditions which the ions of a crystal must satisfy. If an ion, at say $\vec{x}(\vec{l},k)$ in the initial state, is part of a real, undisturbed crystal, then it must be in equilibrium, i.e. the net force $\vec{f}^{k}(\vec{l})$ acting on it must vanish.

$$\vec{f}^{k}(\vec{l}) = 0 \qquad 4.4.1$$

If fields are applied to the system, then the ions will be subject to non-zero forces. This causes the ions to redistribute themselves such that (4.1.1) holds for the ions in the new positions. i.e.

$$\vec{F}^k(\vec{l}) = 0 \qquad 4.4.2$$

where $\vec{F}^k(\vec{l})$ is the net force acting on the ion at $\vec{X}(\vec{l},k)$ in the final state.

In Chapter III, we assumed all the ions in the initial state occupied lattice sites. We now make the additional assumption that the ions are also in equilibrium in the initial state. We will further assume that there is no c.r.u. dipole moment (see eq (1:5.2.7)) in the intial state.

We now subject the crystal to applied electric fields and/or applied stresses. The ions in the final state will eventually reach an equilibrium state (if one exists, otherwise the crystal will destroy itself) and hence the net force acting on an ion in the final state will vanish, i.e.

$$\vec{F}^k(\vec{l}) = 0 \qquad 4.1.3$$

The net force $\vec{F}^k(\vec{l})$ acting on an ion (at $\vec{X}(\vec{l},k)$) is composed of two parts - the electrostatic contribution and a short range contribution, i.e.

$$\vec{F}^k(\vec{l}) = - q^k \nabla V_t(\vec{Z}) - \nabla \phi_s^k(\vec{Z})\Big|_{\vec{Z}=\vec{X}(\vec{l},\vec{k})} \qquad 4.1.4$$

where $V_t(\vec{Z})$ is the total electrostatic potential due to the crystal plus the free charges and $\phi_s^k(\vec{Z})$ is the potential energy due to the short range forces. The short range forces are assumed to be two body. $\vec{Z}$ is to be set equal to the position vector of the ion under consideration (i.e. $\vec{Z}=\vec{X}(\vec{l},k)$) after the derivatives have been taken. We have implicitly assumed that it is at a k-th ion site by the k superscripts

on q^k and $\phi_s^k(\vec{Z})$. Unlike the problem discussed in Chapter III, $\vec{Z}$ changes as we apply the fields (since it is an ion site).

We have already solved for the total electrostatic potential in Section 3.3, i.e.

$$V_t(\vec{Z}) = V_{ap} + V(\vec{Z}) \qquad \text{(c.f. eq (3.3.1))}$$

$$= V_{ap} + V_e + V_i \qquad 4.1.5$$

where

$$\vec{E} = -\nabla(V_{ap} + V_e) \qquad \text{(see eq (3.3.6))} \qquad 4.1.6$$

is the macroscopic electric field and

$$V_i(\vec{Z}) = \sum_k \frac{q^k}{4\pi\epsilon_o} \left\{ \sum_{\vec{l}\in V_n} \frac{1}{|\vec{X}(\vec{l})-\vec{Z}+\vec{u}|} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla^m(\cdot)^m \underset{\Rightarrow}{R}^k(m, V_n, \vec{Z}, \vec{Z}') \right\} \qquad 4.1.7$$

(see eq (3.2.40)). The two-body short range potential is usually expressed in the form

$$\phi_s^k(\vec{Z}) = \sum_{k'} \sum_{\vec{l}\in V_n} \psi^{k'k}[\vec{X}(\vec{l},k')-\vec{Z}] \qquad 4.1.8^{*1}$$

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*1 A common short range potential to use (for ionic crystals is the Born-Mayer potential, i.e.

$$\psi^{k'k}(\vec{Z}) = A^{k'k} e^{-\vec{Z}/\rho^{k'k}}$$

where $A^{k'k}$ and $\rho^{k'k}$ are constants. If only nearest neighbour interactions are allowed in diatomic crystals, then $A^{k'k}$ and $\rho^{k'k}$ need not carry k and k' superscripts.

The sum over $\vec{l}$ should be over $\vec{l}\in V$ but, due to the short range nature of $\phi_s^k(\vec{Z})$, the error in summing over $\vec{l}\in V_n$ is negligible.

where $\psi^{k'k}(\vec{Z})$ is the short range potential of the k-th ion in the field of the k'-th ion.

Substituting (4.1.5) and (4.1.4), and using (4.1.6), we can rewrite $\vec{F}^k(\vec{l})$ in the form

$$\vec{F}^k(\vec{l}) = q^k\left\{ -\nabla[V_e(\vec{Z}) + V_{ap}(\vec{Z})] - \nabla V_i(\vec{Z})\right\} - \bar{\Phi}_s^k(\vec{Z})\Big|_{\vec{Z}=\vec{X}(\vec{l},k)}$$

$$= q^k E(\vec{Z}) - \bar{\Phi}_{eff}^k(\vec{Z})\Big|_{\vec{Z}=\vec{X}(\vec{l},k)} \qquad 4.1.9$$

where

$$\bar{\Phi}_{eff}^k(\vec{Z}) = q^k V_i(\vec{Z}) + \bar{\Phi}_s^k(\vec{Z}) \qquad 4.1.10$$

is an effective short range potential energy.

Therefore the equilibrium condition of the ion at $\vec{X}(\vec{l},k)$ in the deformed crystal is

$$\left\{q^k E(\vec{Z}) - \bar{\Phi}_{eff}^k(\vec{Z})\right\}\Big|_{\vec{Z}=\vec{X}(\vec{l},k)} = 0 \qquad 4.1.11$$

We note that due to the way in which we have defined the macroscopic electric field $\vec{E}$, the equilibrium condition is not an explicit function of the shape of the sample.

Unfortunately, eq (4.1.11), is, in general, not solvable in closed form for the $\vec{u}(\vec{l},k)$. However a great deal of information can be obtained from eq (4.1.11) for the special case in which the fields are uniform.

In Section B, we investigate how eq (4.1.11) is simplified when the fields are uniform. In Section C, we discuss the equation of state and how it is related to the equilibrium conditions. In Section D, we obtain the set of equations from which the coefficients of the equation of state may be obtained. In Section E, we show that our electric

field is equivalent to the accepted macroscopic definition for the case of uniform fields in an ellipsoidal specimen.

B. Equilibrium Conditions in a Crystal with Uniform Displacements

To give an example of the calculations involved in a problem concerning equilibrium conditions, we will consider the case of a crystal whose ions are subjected to uniform displacements. These displacements are assumed to be caused by applied electric fields and/or applied stresses. The undeformed crystal is assumed to have all its ions occupying lattice sites and in equilibrium. The only systems known to the author in which uniform fields exist throughout the crystal are an ellipsoid and, to a good approximation, a thin slab.

The position vector of an ion in the initial state is

$$\vec{x}(\vec{l},k) = \vec{x}(\vec{l}) + \vec{x}^k \qquad \text{(see eq (1.2.9))} \qquad 4.2.1$$

where $\vec{x}^k$ is the position vector of the k-th ion in the c.r.u. with respect to the origin of the c.r.u. and $\vec{x}(\vec{l})$ is the position vector of the $\vec{l}$-th lattice site.

The position vector of the same ion in the final state is

$$X_i(\vec{l},k) = x_i(\vec{l},k) + u_{ij}x_j(\vec{l},k) + u^i_i$$

$$= X_i(\vec{l}) + X^k_i + u^k_i \qquad 4.2.2$$

(c.f. eq (3.2.9a)), where

$$X_i(\vec{l}) = x_i(\vec{l}) + u_{ij}x_j(\vec{l}) \qquad \text{(see eq (1.2.5))} \qquad 4.2.3$$

and

$$X^k_i = x^k_i + u_{ij}x^k_j \qquad 4.2.4$$

u_{ij} is the displacement gradient (of all the ions, not just the surface ions as in the definition (1.2.2)) and $\vec{u}^k$ is the internal strain vector

which is of microscopic size throughout the sample. We note that this internal strain vector is the quantity which we previously called the interior displacement. $\vec{u}^k$ is assumed*1 to be independent of $\vec{x}(\vec{l},k)$. The displacement vector can thus be written in the form

$$u_i(\vec{l},k) = u_{ij}x_j(\vec{l},k) + u_i^k \qquad 4.2.5$$

which is of the necessary form (see eq (1.2.2)). We note that it satisfies the criterion of eq (3.2.17) and hence we may use the analysis of Chapter III wherever it is appropriate. The expansion parameter $\vec{u}$, eq (3.2.8), is

$$\vec{u} = \vec{X}^k + \vec{u}^k \qquad 4.2.6$$

In a crystal on which uniform fields are acting we may shift all the ions by the same amount, i.e.

$$\vec{u}^{k'} = \vec{u}^o \qquad \text{for all } k' \qquad 4.2.7$$

and the equilibrium conditions will remain unchanged. Thus one of the $\vec{u}^{k'}$ is arbitrary. We will choose the ion (at $\vec{X}(\vec{l},k)$) whose equilibrium condition we are considering to have zero internal strain, i.e.

$$\vec{u}^k = 0 \qquad 4.2.8$$

In addition, we will choose the origin of the c.r.u. to be at the k-th ion. Thus

$$\vec{x}^k = 0 \qquad 4.2.9$$

Hence

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*1 This assumption is valid if, by using it, we obtain equilibrium conditions which are independent of the ion chosen, i.e. of $\vec{x}(\vec{l},k)$ (see eq (4.4.9) and the discussion following this equation).

$$\vec{X}(\vec{l},k) = \vec{X}(\vec{l}) \qquad 4.2.10$$

Therefore after we have taken all the required derivatives with respect to $\vec{Z}$ but before we take any derivatives with respect to the independent variables*2 (eg. $\vec{E}$, u_{ij} or $\vec{D}$, u_{ij} etc.), we must set $\vec{Z}$ equal to the lattice vector in the deformed state $\vec{X}(\vec{l})$. i.e.

$$\vec{Z} = \vec{X}(\vec{l}) \qquad 4.2.11$$

From eq (4.1.11), the equilibrium condition for the ion at $\vec{X}(\vec{l},k)$ is

$$\left\{q^k\vec{E}(\vec{Z}) - \nabla\mathfrak{C}^k_{eff}(\vec{Z})\right\}\Big|_{\vec{Z}=\vec{X}(\vec{l})} = 0 \qquad 4.2.12$$

We recall that we are dealing with the uniform field case in which E is independent of $\vec{Z}$ and $\mathfrak{C}^k_{eff}(\vec{Z})$ is given by

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*2 Up to this point, some of the fields we have introduced are

$\vec{E}_{ap}$, $\vec{E}$, $\vec{D}$, $\vec{u}(\vec{l},k)$, u_{ij}, $\vec{u}^k$, $\vec{u}$

These fields are not all independent of each other. However, we know that $\vec{E}_{ap}$ and $\vec{u}(\vec{l},k)$ may be considered as independent because the $\vec{u}(\vec{l},k)$ can be caused by applied stresses which are independent of the free charges which produce $\vec{E}_{ap}$.

Thus we have the liberty of choosing one of the electrostatic fields and one of the displacement fields as independent variables, say $\vec{E}$ and u_{ij}. Once the independent variables are chosen, then the other fields are considered to be functions of these independent variables. i.e.

$$\vec{E}_{ap}(\vec{E},u_{ij}),\ \vec{D}(\vec{E},u_{ij}),\ \vec{u}(\vec{E},u_{ij}),\ \vec{u}^k(\vec{E},u_{ij})$$

$$\Phi^{k}_{eff}(\vec{Z}) = \sum_{k'} \left\{ \sum_{1' \in V} \left[\psi^{k'k}(\vec{X}(\vec{1}',k') - \vec{Z}) + \frac{q^{k} q^{k'}}{4\pi\epsilon_o} \frac{1}{|\vec{X}(\vec{1}') - \vec{Z} + \vec{u}|} \right] \right.$$

$$\left. - \frac{q^{k} q^{k'}}{4\pi\epsilon_o} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla_Z^m (\overset{m}{\cdot}) \underset{\leftrightarrow}{R}^{k'}(m, V_n, \vec{Z}, \vec{Z}') \right\} \quad 4.2.13$$

The only quantities which are unknown in eq (4.2.13) are the internal strains $\vec{u}^{k'}$. This is assuming we know the short range potential (and hence $A^{k'k}$ and $\rho^{k'k}$). Due to the nature of eqs (4.2.12) and (4.2.13) (i.e. that it is an infinite power series in $\vec{u}^{k'}$), we are unable to solve for the $\vec{u}^{k'}$ explicitly in closed form. How eq (4.2.12) is used will be discussed in the next section.

C. The Equation of State

In Section B, we obtained a general expression, eq (4.2.12), for the equilibrium conditions which relate $\vec{u}^k$, $\vec{E}$, and u_{ij}. The equilibrium conditions can be written as the vanishing of an infinite power series in $\vec{u}^k$ and hence we cannot obtain $\vec{u}^k$ explicitly in a closed form in terms of $\vec{E}$, u_{ij}, and the parameters of the short range forces. However, it is possible to solve for the various derivatives of $\vec{u}^k$ with respect to $\vec{E}$ and u_{ij} (see Section D).

To give an idea of how these derivatives are used, we will consider the electric displacement field $\vec{D}$. From eq (3.5.1), $\vec{D}$ may be written as

$$\vec{D}(\vec{Z}) = \epsilon_o \vec{E}(\vec{Z}) + \sum_{m=0}^{\infty} (-1)^m \nabla_Z^m (\overset{m}{\cdot}) \underset{\sim}{P}(m+1, \vec{Z}) \qquad 4.3.1$$

where

$$\underset{\sim}{P}(m+1, \vec{Z}) = \frac{N}{V} \sum_k q^k \vec{u}^{k \to m+1} \qquad \text{(see eq (3.4.15)} \qquad 4.3.2$$

From eq (4.2.6), the expansion parameter $\vec{u}$ may be written in the form

$$\vec{u} = \vec{X}^k + \vec{u}^k \qquad 4.3.3$$

which is independent of $\vec{Z}$. Therefore all the terms in eq (4.3.1) with $m \geq 1$ vanish and we are left with

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} \qquad \vec{Z} \in V_d \qquad 4.3.4$$

which is an exact relation for the case of uniform fields (for non-uniform fields, this relation would only be approximate, see eq (3.4.17)).

We have dropped the $\vec{Z}$ as an explicit argument since $\vec{E}$ is independent of $\vec{Z}$ by assumption (of uniform fields) and $\vec{P}$ is independent of $\vec{Z}$ by calculation. Thus $\vec{D}$ is also independent of $\vec{Z}$. $\vec{P}$ is the polarization which is given by

$$\vec{P} = \frac{N}{V_d} \sum_k q^k (\vec{X}^k + \vec{u}^k) \qquad \text{(see eq (3.4.18))}$$

$$= \frac{N}{V_d} \sum_k q^k \vec{u}^k \qquad 4.3.5$$

when the initial dipole moment vanishes.

In order to simplify the discussion as much as possible and yet not miss any significant results we will consider the expansion of u_i^k, which is needed to solve the equilibrium eq (4.2.12), only up to terms second order in E_i and u_{ij}. i.e.

$$u_i^k = \left(\frac{\partial u_i^k}{\partial E_j}\right)^o E_j + \left(\frac{\partial u_i^k}{\partial u_{mn}}\right)^o u_{mn} + \left(\frac{\partial^2 u_i^k}{\partial E_j \partial E_m}\right)^o E_j E_m + \left(\frac{\partial^2 u_i^k}{\partial E_i \partial u_{mn}}\right)^o E_j u_{mn}$$

$$+ \left(\frac{\partial^2 u_i^k}{\partial u_{mn} \partial u_{rs}}\right)^o u_{mn} u_{rs} \qquad 4.3.6$$

There is no non-zero term which is independent of E_i and u_{ij} since E_i, u_{ij}, and u_i^k vanish in the initial state. The ^{o} superscript indicates that E_i and u_{ij} are to be set equal to zero in the enclosed function.

To be consistent, we must also use a second order expansion for $\vec{D}$. Substituting eq (4.3.6) into (4.3.5), then subsituting the result into eq (4.3.4), we obtain

$$D_i = \epsilon_o E_i + \frac{N}{V}\sum_k q^k \left(\frac{\partial u_i^k}{\partial E_j}\right)^o E_j + \left(\frac{\partial u_i^k}{\partial u_{mn}}\right)^o u_{mn} + \left(\frac{\partial^2 u_i^k}{\partial E_j \partial E_m}\right)^o E_j E_m$$

$$+\left[\left(\frac{\partial^2 u_i^k}{\partial E_j \partial u_{mn}}\right) - \delta_{mn}\left(\frac{\partial u_i^k}{\partial E_j}\right)\right]^o E_j u_{mn} + \left[\left(\frac{\partial^2 u_i^k}{\partial u_{mn}\partial u_{rs}}\right) - \delta_{mn}\left(\frac{\partial u_i^k}{\partial u_{rs}}\right)\right]^o u_{mn}u_{rs}$$

$$= \left\{\epsilon_o \delta_{ij} + \frac{N}{V}\sum_k q^k \left(\frac{\partial u_i^k}{\partial E_j}\right)^o\right\} E_j + \left\{\frac{N}{V}\sum_k q^k \left(\frac{\partial u_i^k}{\partial u_{mn}}\right)^o\right\} u_{mn} + \left\{\frac{N}{V}\sum_k q^k \left(\frac{\partial^2 u_i^k}{\partial E_j \partial E_m}\right)^o\right\} E_j E_m$$

$$+\left\{\frac{N}{V}\sum_k q^k \left[\left(\frac{\partial^2 u_i^k}{\partial E_j \partial u_{mn}}\right) - \delta_{mn}\left(\frac{u_i^k}{E_j}\right)\right]^o\right\} E_j u_{mn} + \left\{\frac{N}{V}\sum_k q^k \left[\left(\frac{\partial^2 u_i^k}{\partial u_{mn}\partial u_{rs}}\right) - \delta_{mn}\left(\frac{\partial u_i^k}{\partial u_{rs}}\right)\right]^o\right\} u_{mn}u_{r} \qquad 4.3.6$$

where we have used the relation

$$\frac{1}{V_d} \cong \frac{1}{V}(1 - u_{ii}) \qquad \text{(see eq (3.2.38))} \qquad 4.3.7$$

Eq (4.3.6) is an equation of state relating $\vec{D}$, $\vec{E}$, and u_{ij}. This relation is usually written in the form

$$D_i = \epsilon_{ij}E_j + e_{imn}u_{mn} + Q_{ijk}E_jE_k + Q_{ijmn}E_ju_{mn} + Q_{imnrs}u_{mn}u_{rs} \qquad 4.3.8^{*1}$$

where ϵ_{ij}, e_{jmn}, Q_{ijmn} are, respectively, the dielectric, piezoelectric, and electrostrictive constants. The remaining constants have not been named to the author's knowledge. We note that we could equally well have expanded E_i as a function of D_i and u_{ij} to obtain a different

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*1 The coefficients in this equation are also obtainable from experiment. This serves as a check on the validity of our definition of the electric displacement field.

equation of state. We have chosen eq (4.3.8) in order to compare with eq (4.3.6). Thus the coefficients in eq (4.3.8) may be written in terms of the derivatives of $\vec{u}^k$ appearing in eq (4.3.6) as follows:

$$\epsilon_{ij} = \frac{N}{V} \sum_k q^k \left(\frac{\partial u_i^k}{\partial E_j} \right)^o + \epsilon_o \delta_{ij} \qquad 4.3.9$$

$$e_{imn} = \frac{N}{V} \sum_k q^k \left(\frac{\partial u_i^k}{\partial u_{mn}} \right)^o \qquad 4.3.10$$

$$Q_{ijm} = \frac{N}{V} \sum_k q^k \left(\frac{\partial^2 u_i^k}{\partial E_j \partial E_m} \right)^o \qquad 4.3.11$$

$$Q_{ijmn} = \frac{N}{V} \sum_k q^k \left\{ \left(\frac{\partial^2 u_i^k}{\partial E_j \partial u_{mn}} \right)^o - \delta_{mn} \left(\frac{\partial u_i^k}{\partial E_j} \right)^o \right\} \qquad 4.3.12$$

$$Q_{imnrs} = \frac{N}{V} \sum_k q^k \left\{ \left(\frac{\partial^2 u_i^k}{\partial u_{mn} \partial u_{rs}} \right)^o - \delta_{mn} \left(\frac{\partial u_i^k}{\partial u_{rs}} \right)^o \right\} \qquad 4.3.13$$

The derivatives of $\vec{u}^k$ appearing in eqs (4.3.9) to (4.3.13) must be determined from the equilibrium conditions. We note that equations (4.3.9) and (4.3.12) are the same as those derived by Grindlay and Wong[26].

D. The Derivatives of $\vec{u}^k$

In Section C, we showed how the electric displacement field, $\vec{D}$, may be written in terms of E_i, u_{ij} and the derivatives of $\vec{u}^k$ with respect to E_i and u_{ij} (see eq (4.3.6)). In this section, we will give the set of linear equations which the derivatives of $\vec{u}^k$ must satisfy due to the equilibrium conditions.

The equilibrium condition of an ion at $\vec{X}(\vec{l},k)$ is

$$\left\{q^k\vec{E} - \nabla \Phi^k_{eff}(\vec{Z})\right\}\Big|_{\vec{Z}=\vec{X}(\vec{l})} = 0 \qquad \text{(see eq (4.2.12))} \qquad 4.4.1$$

where $\Phi^k_{eff}(\vec{Z})$ is given by eq (4.2.13). Namely

$$\Phi^k_{eff}(\vec{Z}) = \Phi^k_s(\vec{Z}) + q^k V_i(\vec{Z})$$

$$= \sum_{k'}\left[\sum_{\vec{l}'\in V_n}\left\{\frac{q^k q^{k'}}{4\pi\epsilon_o}\frac{1}{|\vec{X}(\vec{l}')-\vec{Z}+\vec{u}^{k'}+\vec{X}^{k'}|} + \psi^{k'k}\left[\vec{X}(\vec{l}')-\vec{Z}+\vec{u}^{k'}+\vec{X}^{k'}\right]\right\}\right.$$

$$\left. - \frac{q^k q^{k'}}{4\pi\epsilon_o}\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\nabla^m(\cdot)^m \underset{\leftrightarrow}{R}^{k'}(m,V_n,\vec{Z},\vec{Z}')\right] \qquad 4.4.2$$

Assuming that

$$|\vec{u}^{k'}| < |\vec{x}^{k'}| \qquad \text{for all } k' \qquad 4.4.3$$

then we may expand the first term on the R.H.S. of eq (4.4.2) in a power series in $\vec{u}^{k'}$ as follows

$$\sum_{\vec{l}'\in V_n}\left\{\frac{q^k q^{k'}}{4\pi\epsilon_o}\frac{1}{|\vec{X}(\vec{l})+\vec{X}^{k'}-\vec{Z}'+\vec{u}^{k'}|} + \psi^{k'k}\left[\vec{X}(\vec{l})+\vec{X}^{k'}-\vec{Z}'+\vec{u}^{k'}\right]\right\} =$$

$$4.4.4$$

$$\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\nabla^m(\cdot)^m(\vec{u}^{k'})^m\sum_{\vec{l}'\in V_n}\left\{\frac{q^k q^{k'}}{4\pi\epsilon_o}\frac{1}{|\vec{X}(\vec{l})+\vec{X}^{k'}-\vec{Z}'|} + \psi^{k'k}\left[\vec{X}(\vec{l})+\vec{X}^{k'}-\vec{Z}'\right]\right\}$$

We have introduced the transformation

$$\vec{X}(\vec{l}') = \vec{X}(\vec{l}'') + \vec{X}(\vec{l}) \qquad 4.4.5$$

(and dropped the ") so that the origin of summation over $\vec{l}'$ is the center of V_n. Also

$$\vec{Z}' = \vec{Z} - \vec{X}(\vec{l}) \qquad 4.4.6$$

Since the quantity $\vec{u}^{k'}$ is independent of $\vec{X}(\vec{l})$, it immediately satisfies the condition (3.2.17), and the expression for $\underset{\leftrightarrow}{R}^{k'}(m,V_n,\vec{Z},\vec{Z}')$, eq (3.2.34), reduces to

$$\underset{\leftrightarrow}{R}^{k'}(m,V_n,\vec{Z},\vec{Z}') = (\vec{X}^{k'}+\vec{u}^{k'})^m \frac{N}{V} f(\vec{Z}',V_n) \qquad 4.4.7$$

where $f(\vec{Z}',V_n)$ is the solution of the differential equation

$$\hat{\Gamma}(\vec{z}')f(\vec{Z}',V_n) = \iiint_{V_n} \frac{d\vec{y}}{|\vec{Y}-\vec{Z}'|} \qquad 4.4.8$$

Thus

$$\sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\nabla^m(\overset{m}{\cdot})\underset{\leftrightarrow}{R}^{k'}(m,V_n,\vec{Z},\vec{Z}') = \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\nabla^m(\overset{m}{\cdot})(\vec{X}^{k'}+\vec{u}^{k'})^m f(\vec{Z}',V_n)$$

$$= \sum_{m=0}^{\infty} \frac{(-1)^m}{m!}\nabla^m(\overset{m}{\cdot})(\vec{u}^{k'})^m f(\vec{Z}'-\vec{X}^{k'},V_n) \qquad 4.4.9$$

Substituting (4.4.4) and (4.4.9) into eq (4.4.2), we can write $\bar{\Phi}^k_{eff}(\vec{Z})$ as

$$\bar{\Phi}^k_{eff}(\vec{Z}) = \sum_{k'} \sum_{m=0} \frac{(-1)^m}{m!}\nabla^m(\overset{m}{\cdot})(\vec{u}^{k'})^m \bar{\Phi}^{k'k}(\vec{Z}'-\vec{X}^{k'},u_{ij}) \qquad 4.4.10$$

where

$$\bar{\Phi}^{k'k}(\vec{Z}'-\vec{X}^{k'},u_{ij}) = \sum_{\vec{l}'\in V_n}\left\{\frac{q^k q^{k'}}{4\pi\epsilon_o}\frac{1}{|\vec{X}(\vec{l})-\vec{Z}'+\vec{X}^{k'}|} + \psi^{k'k}\left[\vec{X}(\vec{l})-\vec{Z}'+\vec{X}^{k'}\right]\right\}$$

$$- \frac{N}{V}\frac{q^k q^{k'}}{4\pi\epsilon_o} f(\vec{Z}'-\vec{X}^{k'},V_n) \qquad 4.4.11$$

We note that $\Phi^{k'k}(\vec{Z}'-\vec{X}^{k'}, u_{ij})$ is an explicit function of $\vec{Z}' = \vec{Z} - \vec{X}(\vec{l})$ where $\vec{X}(\vec{l})$ is the lattice site in the deformed state nearest $\vec{Z}$ ($\vec{Z}$ is to be set equal to $\vec{X}(\vec{l})$). Therefore when we set $\vec{Z} = \vec{X}(\vec{l})$ in eq (4.4.1), $\vec{Z}' = 0$ and hence the equilibrium condition is independent of $\vec{l}$ as required by our assumptions (see footnote *1 of Section B).

Equations (4.4.10) and (4.4.11) have enabled us to isolate the implicit $\vec{E}$ dependence of eq (4.4.1) since $\vec{u}^{k'}$ is an implicit function of $\vec{E}$. $\Phi^{k'k}$ is not a function of $\vec{E}$; it is only a function of u_{ij}.

In order to show clearly where the u_{ij} dependence arises, we must use the inverse of $\delta_{ij} + u_{ij}$, namely v_{ij} (see eq (1.2.6)).

$$z_i = Z_j v_{ij} \qquad \text{(see eq (1.2.8))} \qquad 4.4.12$$

Thus

$$\frac{\partial}{\partial Z_i} = \frac{\partial z_j}{\partial Z_i}\frac{\partial}{\partial z_j}$$

$$= v_{ji}\frac{\partial}{\partial z_j} \qquad 4.2.13$$

Thus the equilibrium condition, eq (4.4.1), may be written as

$$E_i - v_{ji}\frac{\partial}{\partial z_j}\sum_{k'}\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\left(\frac{\partial}{\partial z_r}v_{rs}u_s^{k'}(E,u_{pq})\right)^m \Phi^{k'k}((\delta_{pq}+u_{pq})(z'_q-x_q^{k'}),u_{pq})\Big|_{\vec{z}'=}$$

$$= 0 \qquad 4.4.14$$

where we have shown all the places where $\vec{E}$ and u_{ij} appear explicitly or implicitly.

Taking the derivatives of eq (4.4.14) with respect to E_i and u_{ij}, we obtain, (with the aid of the identity $\left(\frac{\partial v_{ij}}{\partial u_{mn}}\right)^0 = -\delta_{im}\delta_{jn}$),

$$\sum_{k'}\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial z_i}\right)^o = 0 \qquad 4.4.15$$

$$\sum_{k'}\left(\frac{\partial u_r^{k'}}{\partial E_j}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o = -q^k \delta_{ij} \qquad 4.4.16$$

$$\sum_{k'}\left(\frac{\partial u_r^{k'}}{\partial u_{mn}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o = \sum_{k'}\frac{\partial\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{mn}}\right)^o}{\partial z_i} \qquad 4.4.17$$

$$\sum_{k'}\left(\frac{\partial^2 u_r^{k'}}{\partial E_j \partial E_m}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o = \sum_{k'}\left(\frac{\partial u_r^{k'}}{\partial E_j}\right)^o\left(\frac{\partial u_s^{k'}}{\partial E_m}\right)^o\left(\frac{\partial^3 \bar{\Phi}^{k'k}}{\partial z_r \partial z_s \partial z_i}\right)^o \qquad 4.4.18$$

$$\sum_{k'}\left(\frac{\partial^2 u_r^{k'}}{\partial E_j \partial u_{rs}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o = \sum_{k'}\left(\frac{\partial u_m^{k'}}{\partial E_j}\right)^o\left\{\delta_{is}\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_m \partial z_r}\right)^o + \delta_{ms}\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o - \frac{\partial^2\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{rs}}\right)^o}{\partial z_i \partial z_m} + \left(\frac{\partial u_n^{k'}}{\partial u_{rs}}\right)^o\left(\frac{\partial^3 \bar{\Phi}^{k'k}}{\partial z_i \partial z_m \partial z_n}\right)^o\right\} \qquad 4.4.19$$

$$\sum_{k'}\left(\frac{\partial u_r^{k'}}{\partial u_{pq}\partial u_{rs}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o = \sum_{k'}\left\{-\delta_{iq}\frac{\partial\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{rs}}\right)^o}{\partial z_p} - \delta_{is}\frac{\partial\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{pq}}\right)^o}{\partial z_r} + \delta_{iq}\left(\frac{\partial u_m^{k'}}{\partial u_{rs}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_p \partial z_m}\right)^o + \delta_{ir}\left(\frac{\partial u_m^{k'}}{\partial u_{pq}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_s \partial z_m}\right)^o + \left(\frac{\partial u_s^{k'}}{\partial u_{pq}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_r}\right)^o + \left(\frac{\partial u_q^{k'}}{\partial u_{rs}}\right)^o\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_p}\right)^o - \left(\frac{\partial u_m^{k'}}{\partial u_{pq}}\right)^o\frac{\partial^2\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{rs}}\right)^o}{\partial z_i \partial z_m} - \left(\frac{\partial u_m^{k'}}{\partial u_{rs}}\right)^o\frac{\partial^2\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{rs}}\right)^o}{\partial z_i \partial z_m} + \frac{\partial\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial u_{rs}\partial u_{pq}}\right)^o}{\partial z_i} + \left(\frac{\partial u_m^{k'}}{\partial u_{pq}}\right)^o\left(\frac{\partial u_n^{k'}}{\partial u_{rs}}\right)^o\left(\frac{\partial^3 \bar{\Phi}^{k'k}}{\partial z_i \partial z_m \partial z_n}\right)^o\right\} \qquad 4.4.20$$

The problem of solving for the derivatives of $\vec{u}^{k'}$ has now been reduced to finding the microscopic quantities $\left(\bar{\Phi}^{k'k}\right)^o$ *2, $\left(\frac{\partial \bar{\Phi}^{k'k}}{\partial u_{mn}}\right)^o$, and

and $\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial u_{pq} \partial u_{rs}}\right)^o$ as functions of $\vec{z}$, (see eq (4.4.11)). What we have done is to give a recipe based on our definitions of $\vec{E}$ and $\vec{D}$ for calculating the coefficients in eq (4.3.8), and hence for comparing our definitions with experimental results.

We note that eqs (4.4.16) and (4.4.19) are of the same form as the corresponding ones obtained by Grindlay and Wong[26] (eqs (28) and (29) of their paper). Our definition of $\bar{\Phi}^{k'k}$ differs slightly from the definition of the corresponding quantity used by Wong and Grindlay.

$$\left(\frac{\partial^2 \bar{\Phi}^{k'k}}{\partial z_i \partial z_j}\right)^o \quad \text{-------} \quad \lambda_{ij}^{k'k} + \frac{q^k q^{k'}}{4\pi\epsilon_o} (\gamma_{ij}^{k'k})^o$$

They sum over a sphere while ours involves a sum over a cube. The limiting value as the sphere goes to infinity is the value of our expression.

We recall that in Part One, Section 4.6, we proved that our intrinsic electrostatic potential was equivalent to the electrostatic potential as evaluated using Ewald's method. Since the $V_i(\vec{Z})$ is a simple generalization of the $V_i(\vec{z})$ of Part One, we conclude that our results are equivalent to those of B&H who used Ewald's method in calculating the electrostatic contribution to the total potential energy (the short range forces are treated the same in most theories). This means that our equation of state for the finite crystal is equivalent to the equation of state of the infinite crystal. This is

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*2 The electrostatic contribution of this term is the intrinsic electrostatic potential calculated in Part One.

a further justification of the infinite crystal methods.

E. The Electric Field in an Ellipsoid

The standard result for the electric field in a uniformly deformed ellipsoid is

$$E_i = (\vec{E}_{ap})_i - \frac{1}{\epsilon_o} L_{ij} P_j \qquad 4.5.1$$

where P_j is the polarization given by

$$P_j = \frac{N}{V_d} \sum_k q^k (X_i^k + u_i^k) \qquad \text{(see eq (3.4.18))}$$

where both L_{ij} and V_d are functions of u_{ij}.

From eq (3.3.10), our electric field is given by

$$E_i = (\vec{E}_{ap})_i - \frac{\partial}{\partial Z_i} \sum_{k'} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \nabla^m (\cdot)^m R^{k'}(m, V, \vec{Z})$$

$$= (\vec{E}_{ap})_i - \frac{\partial}{\partial Z_i} \sum_{k'} \sum_{m=0} \frac{(-1)^m}{m!} \nabla^m (\cdot)^m (\vec{u}^{k'} + \vec{X}^{k'})^m \frac{N}{V} f(\vec{Z}, V) \qquad 4.5.3$$

where we have used eq (4.4.5). For the deformed ellipsoid, $f(\vec{Z},V)$ is

$$f(\vec{Z},V) = -\frac{1}{J}\left\{ 2\pi L_{ij} \vec{Z}_j \vec{Z}_j - \frac{\pi}{6} \right\} \qquad 4.5.4$$

Thus

$$E_i = (\vec{E}_{ap})_i - \frac{N}{VJ} \frac{1}{4\pi\epsilon_o} 4\pi \sum_{k'} q^{k'} L_{ij} (u_j^{k'} + X_j^{k'})$$

$$= (\vec{E}_{ap})_i - \frac{1}{\epsilon_o} L_{ij} P_j \qquad 4.5.5$$

where

$$P_j = \frac{N}{V_d} \sum_{k'} q^{k'} (u_j^{k'} + X_j^{k'}) \qquad 4.5.6$$

which is in agreement with the relation, eq (4.5.1), in common usage. We have used the relation $V_d = JV$ in writing eq (4.5.5).

F. Summary

In this chapter, we investigated the relationship between $\vec{E}$ and $\vec{D}$ when the fields are uniform.

We found that

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} \qquad \text{(see eq (4.3.4))} \qquad 4.6.1$$

and when the specimen is an ellipsoid, the further relation

$$E_i = (\vec{E}_{ap})_i - \frac{1}{\epsilon_o} L_{ij} P_j \qquad \text{(see eq (4.5.5))} \qquad 4.6.2$$

which are the accepted relations between $\vec{E}$ and $\vec{D}$ when the fields are uniform.

In addition, we showed that the equation of state relating $\vec{D}$ and $\vec{E}$ which results from the equilibrium conditions is equivalent to the equation of state derived by Born and Huang.

CHAPTER V

SUMMARY

In this part of the thesis we have done two things:

A. defined a macroscopic electric field and an electric displacement field, and

B. investigated the relationship between them.

A.

The definitions we used for $\vec{E}$ and $\vec{D}$ are

$$\vec{E} = \vec{E}_{ap} - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \sum_k \frac{q^k}{4\pi\epsilon_o} \nabla^{m+1} \binom{m}{\cdot} \underset{\leftrightarrow}{R}^k(m,V,\vec{Z}) \quad \text{for all } \vec{Z} \qquad (3.3.10)$$

and

$$\vec{D} = \epsilon_o \vec{E} + \sum_{m=1}^{\infty} (-1)^m \nabla^{m-1} \binom{m-1}{\cdot} \underset{\leftrightarrow}{P}(m,\vec{Z}) \qquad \vec{Z} \in V_d \qquad (3.4.16)$$

$$= \epsilon_o \vec{E} \qquad \vec{Z} \notin V_d \qquad (3.4.13)$$

where $\underset{\leftrightarrow}{R}^k(m,V,\vec{Z})$ is given by eq (3.2.33) and

$$\underset{\leftrightarrow}{P}(m,\vec{Z}) = \frac{N}{V_d} \sum_k q^k \left\{ \vec{X}^k + \vec{u}^k(\vec{Z}) \right\}^m \qquad (3.5.4)$$

These fields are slowly varying over atomic distances and satisfy the field equations

$$\nabla \times \vec{E} = 0 \qquad (3.3.7)$$

$$\nabla \cdot \vec{D} = \rho_f \qquad (3.4.14)$$

where ρ_f is the free charge density.

B.

When the fields are uniform, the relationship between $\vec{D}$ and $\vec{E}$ takes the simple form

$$\vec{D} = \epsilon_o \vec{E} + \vec{P} \qquad \vec{Z} \epsilon V_d \qquad (4.3.4)$$

When the sample is an ellipsoid, then $\vec{E}$ also has a simple form given by (for uniform fields)

$$E_i = (\vec{E}_{ap})_i - \frac{1}{\epsilon_o} L_{ij} P_j \qquad \vec{Z} \epsilon V_d \qquad (4.5.5)$$

which are the accepted relations between $\vec{E}$ and $\vec{D}$ when the fields are uniform.

In additon, we showed that the equation of state relating $\vec{D}$ and $\vec{E}$ which results from the equilibrium conditions is equivalent to the equation of state derived by Born and Huang who used an infinite crystal.

To our knowledge, no absolute criteria have been put forward in the literature to uniquely define $\vec{E}$ or $\vec{D}$. Thus we have been unable to prove that our definitions of $\vec{E}$ and $\vec{D}$ are the ones that should be used. However, they have satisfied all the conditions, (which the electric field and electric displacement field must satisfy), which we have been able to investigate.

APPENDIX I

The direct product W of two quantities U and V will be denoted by the symbol ⊠ (see Leech and Newmann[24]). i.e.

$$W = U \boxtimes V \qquad \text{A.1.1}$$

As an example, let U and V be a pair of 2x2 matrices.

$$U = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}; \quad V = \begin{pmatrix} V_{11} & V_{12} \\ V_{21} & V_{22} \end{pmatrix}, \qquad \text{A.1.2}$$

then the direct product of U and V is given by

$$W = U \boxtimes V = \begin{pmatrix} U_{11}V_{11} & U_{11}V_{12} & U_{12}V_{11} & U_{12}V_{12} \\ U_{11}V_{21} & U_{11}V_{22} & U_{12}V_{21} & U_{12}V_{22} \\ U_{21}V_{11} & U_{21}V_{12} & U_{22}V_{11} & U_{22}V_{12} \\ U_{21}V_{21} & U_{21}V_{22} & U_{22}V_{21} & U_{22}V_{22} \end{pmatrix} \qquad \text{A.1.3}$$

For our purposes, the quantities U and V will be vectors. i.e.

$$\vec{U} = (U_1, U_2, U_3); \quad \vec{V} = \begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix} \qquad \text{A.1.4}$$

Thus the direct product of the two vectors $\vec{U}$ and $\vec{V}$ is

$$U \boxtimes V = \begin{pmatrix} U_1V_1 & U_2V_1 & U_3V_1 \\ U_1V_2 & U_2V_2 & U_3V_2 \\ U_1V_3 & U_2V_3 & U_3V_3 \end{pmatrix} \qquad \text{A.1.5}$$

which is a 3x3 matrix.

When we are taking the direct product between two vectors which are the same, we will use the following notation

$$\vec{U}^2 \overset{\text{defn}}{=} \vec{U} \otimes \vec{U}_t \qquad \text{A.1.6}$$

where $\vec{U}_t$ is the transpose of $\vec{U}$. i.e. $\begin{pmatrix} U_1 \\ U_2 \\ U_3 \end{pmatrix}$ rather than (U_1, U_2, U_3).

The vector symbol on $\vec{U}^2$ is retained to avoid confusion with U^2 where $U = |\vec{U}|$. We note that $\vec{U}^2$ is a symmetric 3x3 matix.

Generalizing eq (A.1.6), we will use the notation $\vec{U}^n$ to denote the following n-th order direct product

$$\vec{U}^n \overset{\text{defn}}{=} \vec{U} \otimes \vec{U}_t \otimes \ldots \otimes \vec{U} \otimes \vec{U}_t \quad n \text{ even}$$
$$= \vec{U} \otimes \vec{U}_t \otimes \ldots \otimes \vec{U}_t \otimes \vec{U} \quad n \text{ odd} \qquad \text{A.1.7}$$

where the symbol $\otimes$ appears n-1 times. We note that $\vec{U}^n$ is a tensor whose components are given by

$$[\vec{U}^n]_{i_1 \ldots i_n} = \prod_{j=1}^{n} U_{i_j} \qquad i_j = 1,2,3 \qquad \text{A.1.8}$$

In conjunction with the direct product, we need to introduce a generalized inner product which we will denote by the symbol (.). The inner product of a vector with a direct product reduces the order of the direct product by one. i.e.

$$\vec{V}(.)\vec{U}^n = (\vec{V}.\vec{U})\vec{U}^{n-1} \qquad \text{A.1.9}$$

where $\vec{V}.\vec{U}$ is the standard inner product between two vectors.

The m-th order inner product will be denoted by the symbol $(\overset{m}{.})$. If we take the m-th order inner product of two direct products $\vec{U}^m$ and

$\vec{V}^p$ where $p \geq m$, then

$$\vec{U}^m \overset{m}{(\cdot)} \vec{V}^p = (\vec{U}.\vec{V})^m \vec{V}^{p-m} \qquad \text{A.1.10}$$

We note that we could not have an m-th order inner product between $\vec{U}^n$, $\vec{V}^p$ where $n,p > m$. Either n or p must equal m.

Appendix II

Let us consider a function $R(\vec{Z},\vec{Z}-\vec{Y})$ given by

$$R(\vec{Z},\vec{Z}-\vec{Y}) = J \sum_{p=0}^{\infty} g_p(\vec{Z}) f_p(\vec{Z}-\vec{Y}) \qquad \text{A.2.1}$$

where $f_p(\vec{X})$ is a solution of the differential equation

$$\hat{\Gamma}(\vec{x}) f_p(\vec{X}) = \iiint d\vec{w} \frac{h_p(\vec{W}-\vec{X})}{|\vec{W}-\vec{X}|} \qquad \text{A.2.2}$$

with

$$X_j = (\delta_{ij}+u_{ij})x_j \qquad \text{A.2.3}$$

and

$$W_j = (\delta_{ij}+u_{ij})w_j \qquad \text{A.2.4}$$

J is the determinant of $(\delta_{ij}+u_{ij})$. i.e.

$$J = \det(\delta_{ij}+u_{ij}) \qquad \text{A.2.6}$$

In addition we have the relation

$$u(\vec{W}) = \sum_{p=0}^{\infty} g_p(\vec{X}) h_p(\vec{W}-\vec{X}) \qquad \text{A.2.7}$$

Introducing the transformation, eq A.2.4), into eq (A.2.2), we may rewrite it as

$$\hat{\Gamma}(\vec{x}) f_p(\vec{X}) = \frac{1}{J} \iiint d\vec{W} \frac{h_p(\vec{W}-\vec{X})}{|\vec{W}-\vec{X}|} \qquad \text{A.2.8}$$

What we want to do in this appendix is find an expression for the quantity $\nabla_Z^2 R(\vec{Z},\vec{Z})$.

Before taking the Laplacian of R, we first operate on eq (A.2.1) with $\hat{\Gamma}(\vec{y})$ to obtain

$$\hat{\Gamma}(\vec{y})R(\vec{Z},\vec{Z}-\vec{Y}) = J\sum_{p=0}^{\infty} g_p(\vec{Z})\,\hat{\Gamma}(\vec{y})\,f_p(\vec{Z}-\vec{Y})$$

$$= \sum_{p=0}^{\infty} g_p(\vec{Z}) \iiint d\vec{W}\, \frac{h_p(\vec{W}-\vec{Z}+\vec{Y})}{|\vec{W}-\vec{Z}+\vec{Y}|} \quad \text{(see eq (A.2.8))}$$

$$= \iiint d\vec{W} \sum_{p=0}^{\infty} \frac{g_p(\vec{Z})h_p(\vec{W}+\vec{Y}-\vec{Z})}{|\vec{W}-\vec{Z}+\vec{Y}|}$$

$$= \iiint \frac{d\vec{W}\, u(\vec{W}+\vec{Y})}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.9}$$

Taking the gradient of eq (A.2.9) with respect to $\vec{Z}$, we have

$$\hat{\Gamma}(\vec{y})\nabla_Z R(\vec{Z},\vec{Z}-\vec{Y}) = \nabla_Z \iiint \frac{dW\, u(W+Y)}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$= \iiint d\vec{W}\, u(\vec{W}+\vec{Y})\, \nabla_Z \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$= -\iiint d\vec{W}\, u(\vec{W}+\vec{Y})\, \nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$= -\iint dS\, \frac{\hat{n}u(\vec{W}+\vec{Y})}{|\vec{W}+\vec{Y}-\vec{Z}|} + \iiint \frac{d\vec{W}\, \nabla_Z u(\vec{W}+\vec{Y})}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.10}$$

Taking the divergence of eq (A.2.10), we obtain an equation involving $\nabla_Z^2 R$. i.e.

$$\hat{\Gamma}(\vec{y})\nabla_Z^2 R(\vec{Z},\vec{Z}-\vec{Y}) = -\iint_V dS\, u(\vec{W}+\vec{Y})\hat{n}.\nabla_Z \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} + \iiint_V d\vec{W}\nabla_W u(\vec{W}+\vec{Y}).\nabla_Z \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$= \iint_V dS u(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} - \iiint_V d\vec{W}\nabla_W u(\vec{W}+\vec{Y}).\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.11}$$

The first term on the R.H.S. of eq (A.2.11) has to be considered carefully. We write it as

$$\iint_V dS u(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} = \iint_V dS u(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} + \iint_S dS u(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$- \iint_S dS u(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.12}$$

where S is a spherical region of radius β centered at $\vec{W} = \vec{Z} - \vec{Y}$.

We may apply Gauss' theorem to the first two terms to get

$$\iint dSu(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} = \iiint_{V-S} d\vec{W}\nabla_W.\left\{u(\vec{W}+\vec{Y})\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}\right\} - \iint_S dSu(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$= \iiint_{V-S} d\vec{W}\,\nabla_W u(\vec{W}+\vec{Y}).\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} + \iiint_{V-S} d\vec{W}u(\vec{W}+\vec{Y})\nabla_W^2 \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|}$$

$$- \iint_S dSu(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.13}$$

However

$$\nabla_W^2 \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} = -4\pi\delta(\vec{W}+\vec{Y}-\vec{Z}) \qquad \text{A.2.14}$$

where $\delta(\vec{X})$ is the Dirac delta function and hence the second term on the R.H.S. of eq (A.2.13) vanishes. Substituting eq (A.2.13) into eq (A.2.11), we have

$$\hat{\Gamma}(y)\nabla_Z^2 R(\vec{Z},\vec{Z}-\vec{Y}) = -\iiint_S d\vec{W}\,\nabla_W u(\vec{W}+\vec{Y}).\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} + \iint_S dSu(\vec{W}+\vec{Y})\hat{n}.\nabla_W \frac{1}{|\vec{W}+\vec{Y}-\vec{Z}|} \qquad \text{A.2.15}$$

Introducing the transformation

$$\vec{V} = \vec{W} + \vec{Y} - \vec{Z} \qquad \text{A.2.16}$$

into eq (A.2.15), we have

$$\hat{\Gamma}(\vec{y})\nabla_Z^2 R(\vec{Z},\vec{Z}-\vec{Y}) = -\iiint_S d\vec{V}\nabla_V u(\vec{V}+\vec{Z}).\nabla_V\left(\frac{1}{V}\right) + \iint_S dSu(\vec{V}+\vec{Z})\hat{n}.\nabla_V\left(\frac{1}{V}\right) \qquad \text{A.2.17}$$

As we let $\beta \to 0$ (i.e. let the region S become vanishingly small), then the first term on the R.H.S. of (A.2.17) vanishes and the second term becomes

$$\lim_{\beta \to 0} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta V^2 u(\vec{V}+\vec{Z}) \frac{\partial}{\partial V}\left(\frac{1}{V}\right) \Big|_{V=\beta} = -\lim_{\beta \to 0} \int_0^{2} d\phi \int_0^{\pi} d\theta \sin\theta u(\vec{V}+\vec{Z})$$

$$= -4\pi u(\vec{Z}) \qquad \text{A.2.17}_a$$

Thus

$$\hat{\Gamma}(\vec{y}) \nabla_Z^2 R(\vec{Z}, \vec{Z}-\vec{Y}) = -4\pi u(\vec{Z}) \qquad \text{A.2.18}$$

We note that R is indirectly related to $\vec{u}$. Thus when $\vec{u}$ changes, so does R. The boundary condition we have assumed for R is that it must be a function of $\vec{u}$. Since $\vec{u}$ is an arbitrary function of position, R will not, in general, contain a term which satisfies

$$\hat{\Gamma}(\vec{y}) \tilde{f} = 0 \qquad \text{A.2.19}$$

Thus we assume the solution of eq (A.2.18) is

$$\nabla_Z^2 R(\vec{Z}, \vec{Z}-\vec{Y}) = -4\pi u(\vec{Z}) \qquad \text{A.2.20}$$

which is independent of $\vec{Y}$. We have been unable to prove that this solution is the complete one.

GLOSSARY OF SYMBOLS

PART ONE

$\vec{x}(\vec{l})$	a lattice vector
$\vec{l}$	a triplet of integers (l_1, l_2, l_3)- lattice site indices
a_i	a lattice parameter
$\hat{e}_i$	a unit vector in real space
$\vec{k}$	a vector in reciprocal space
$\vec{y}(\vec{h})$	a reciprocal lattice vector
$\hat{e}_i$	a unit vector in reciprocal space
δ_{ij}	the Kronecker delta function
q^k	charge of the k-th type ion
k	the symbol used to label the type of ion
e	the magnitude of the electronic charge
s^k	$= q^k/e$
$\vec{x}^k$	the position vector of the k-th ion relative to the center of the c.r.u.
$\vec{z}$	position vector of the point of interest
z	magnitude of $\vec{z}$
V	volume of the finite crystal; also the self-potential of the k=0 ion in an infinite crystal
$V(\vec{z})$	the electrostatic potential at a point with position vector $\vec{z}$ in a finite crystal
ϵ_o	permittivity of free space

$V^k(\vec{l})$ the electrostatic self-potential of the ion site at $\vec{x}(\vec{l},\vec{k})$

$V^\infty(\vec{z})$ the electrostatic potential at a point with position vector $\vec{z}$ in an infinite crystal

$V^\infty(k)$ the electrostatic self-potential of a k-type ion in an infinite crystal

$V'(\vec{z})$ the electrostatic potential defined by the introduction of a vanishing exponential

V'^k the electrostatic self-potential of a k-type ion associated with $V'(\vec{z})$

$V^L(\vec{z})$ the electrostatic potential due to a line of point charges

$V^P(\vec{z})$ the electrostatic potential due to a plane of point charges

$\phi(\vec{l}) = \frac{1}{e} \sum_k^b \frac{q^k}{|\vec{x}(\vec{l}) - \vec{x}^k|}$

w^k a weighting factor which depends on the position of the ion in the unit cell

$e^k = s^k w^k$

$\phi(\vec{z},k,\beta) = \lim_{V\to\infty} \sum_{\vec{l}\in V}{}' \frac{e^{i\vec{k}.\vec{x}(\vec{l})} e^{-\beta|\vec{x}(\vec{l})-\vec{z}|}}{|\vec{x}(\vec{l}) - \vec{z}|}$

$Q(x)$ the error function

$V'(\vec{z},0)$ the electrostatic potential of a neutralized Bravais lattice

v_a the volume of the unit cell

$\rho(\vec{z})$ charge density

$S(\vec{h})$ a structure factor

$V(\vec{z},k)$ the partial potential of the k-th type ion

$\hat{\Gamma}(\vec{x})$ a differential operator (see eq (3.2.5))

$\hat{D}_{2p}$ a differential operator which contains only derivatives of order 2p (see eq (3.2.8))

$\vec{x}_z$ the lattice site (of the k=0 ion) nearest $\vec{z}$

$v'(\vec{z}) = \sum_{\vec{l} \notin V_n} \frac{1}{|\vec{x}(\vec{l}) - \vec{z}^k|}$

$\vec{z}' = \vec{z} - \vec{x}_z$

$\vec{z}'^k = \vec{z}' - \vec{x}^k$

$\phi(\vec{z},V) = \sum'_{\vec{l} \in V} \frac{1}{|\vec{x}(\vec{l}) - \vec{z}|}$

$I(\vec{z},d) = \iiint_V \frac{d\vec{y}}{|\vec{y} - \vec{z}|}$

d a parameter which is a measure of the size of V

$f(\vec{z},V)$ a solution of the differential equation $\hat{\Gamma}(\vec{z}) f(\vec{z},V) = I(\vec{z},d)$

V_n a cube of side (2n+1)a

ϵ_m^{npo} a constant defined by eq (3.3.45)

α_{mp} a coefficient in the expansion of $I(\vec{z},d)$ in powers of $\vec{z}$ and d

Y_m^p a spherical harmonic

β_{ps}^m a coefficient in the expansion of $f(\vec{z},V)$ in powers of $\vec{z}$ and d

$\Delta f(\vec{z},V) = f(\vec{z},V_n) - f(\vec{z},V_{n+1})$

$V_i(\vec{z},k)$ the intrinsic partial potential of the k-th ion

$V_e(\vec{z},k)$ the extrinsic partial potential of the k-th ion

$V_i(\vec{z})$ the intrinsic electrostatic potential of the k-th ion

$V_e(\vec{z})$ the extrinsic electrostatic potential of the k-th ion

L_i (i=1,2,3) the principal values of the depolarization factor

S_m a symmetric combination of spherical harmonics of order m

$\eta(\theta,\phi)$ the function describing the surface of V

P_i dipole moment per unit volume of the c.b.u.

P_{ij} quadrupole moment per unit volume of the c.b.u.

α^{∞} madelung constant of the infinite crystal

α_i the intrinsic madelung constant

U_i the intrinsic electrostatic energy

U_e the extrinsic electrostatic energy

α_e the extrinsic madelung constant

$\alpha(\vec{z})$ a dimensionless quantity associated with the intrinsic electrostatic potential

P_i dipole moment per unit volume of the c.r.u.

P_{ij} quadrupole pole moment per unit volume of the c.r.u.

$\alpha_e(\vec{z})$ a dimensionless function associated with the extrinsic electrostatic potential

PART TWO

$\vec{E}$ the macroscopic electric field

$\vec{D}$ the electric displacement field

$\vec{u}(\vec{l},k)$ displacement of the ion which was at $\vec{x}(\vec{l},k)$

V_d volume of the deformed crystal

u_{ij} displacement gradient of the k=0 ion at the surface.

$\vec{u}^k(\vec{l})$ the internal displacement vector

v_{ij} the inverse of $\delta_{ij} + u_{ij}$

$\vec{Z}$ position vector of the point of interest in the deformed crystal

$\vec{X}(\vec{l},k)$ $= \vec{x}(\vec{l},k) + \vec{u}(\vec{l},k)$

ρ_f free charge density

$\vec{E}_{ap}$ the electric field due to the free charges

V_{ap} the electrostatic potential due to the free charges

$w(\vec{y})$ a weighting function

v_o a microscopic region which is much larger than the lattice parameter

$\vec{e}$ the microscopic electric field

$\phi'^{k}(\vec{z})$ $= \sum_{\vec{l} \notin V} \frac{1}{|\vec{X}(\vec{l},k) - \vec{z}|}$.

$\vec{u}$ expansion parameter of $\phi'^{k}(\vec{z})$

J $= \det(\delta_{ij} + u_{ij})$

$\underset{\sim}{P}(m,\vec{z})$ $= \frac{1}{m!} \frac{N}{V_d} \sum_k q^k (\vec{X}^k + \vec{u}^k(\vec{z}))^m$

$\vec{P}$ $= \underset{\sim}{P}(1,\vec{z})$ - the polarization

$\Phi_s^{kk'}$ the short range potential energy

$\Phi_{eff}^{kk'}$ $= \Phi_s^{kk'} + q^k V_i(\vec{z})$ - an effective short range potential energy

ϵ_{ij} the dielectric constant

e_{imn} the piezoelectric constant

Q_{ijmn} the electrostrictive constant

$\vec{F}^k(\vec{l})$ the net force acting on an ion of type k at the $\vec{l}$-th c.r.u.

$V_t(\vec{z})$ the total electrostatic potential

$\underset{\sim}{R}(m,V,\vec{z})$ see eq (3.2.33)

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