A STATISTICAL THERMODYNAMICS OF A CRYSTAL LATTICE

THESIS

SUBMITTED BY

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1.

The Free Energy of a Lattice

an elastic solid

The free energy A of a rigid body is a function of the temperature and of the six homogeneous strain components. All other thermodynamic properties are found by differentiation,

the entropy $S = -\frac{\partial A}{\partial T}$,

the energy $E = A + ST$,

and the generalized forces corresponding to any molar parameter $F_r = -\frac{\partial A}{\partial a_r}$.

Let us consider the free energy of a cubic lattice of the Bravais type (simple, face-centred or body-centred). The cell of such a lattice is described by the three lattice vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$. The shape of the cell is given by the scalar products of these vectors with one another

(1.1) $\underline{a}_1^2, \underline{a}_2^2, \underline{a}_3^2, \underline{a}_2 \cdot \underline{a}_3, \underline{a}_3 \cdot \underline{a}_1, \underline{a}_1 \cdot \underline{a}_2$;

i.e. by three lengths and three angles. These six parameters are invariant with respect to rigid motion of the crystal; they play the part of the molar

parameters for this type of lattice.

Assuming that thermic motion can be considered as harmonic we obtain the following expression for the free energy of a crystal lattice at high temperatures

$$(1.2) \qquad A = \Phi_0 + 3NkT \log \frac{k\bar{\omega}}{kT} ,$$

where Φ_0 is the potential energy of the non-vibrating but homogeneously deformed lattice and $\bar{\omega}$ is a logarithmic mean frequency per 2π seconds.

The Mean Frequency and Potential Energy

The position of any lattice point is represented by the vector $\underline{r}^l$ where for equilibrium

$$(2.1) \qquad \underline{r}_0^l = \underline{a}_1 l_1 + \underline{a}_2 l_2 + \underline{a}_3 l_3 ,$$

l_1, l_2, l_3 being three arbitrary integers. Consider a small displacement $\underline{u}^l$ from the equilibrium position so that the vector

$$(2.2) \qquad \underline{r}^l = \underline{r}_0^l + \underline{u}^l$$

now defines the position of the particle l. The distance between two particles l and l' will be

$$(2.3) \qquad r^{ll'} = |\underline{r}^{ll'}| = |\underline{r}^l - \underline{r}^{l'}| .$$

We assume that the potential energy between two such particles depends only on their distance

apart $r^{ll'}$, and we denote it by $\varphi^{ll'}$.

For the undeformed lattice one has

$$(2.4) \qquad \varphi_0^{ll'} = \varphi(|\underline{r}_0^l - \underline{r}_0^{l'}|) = \varphi(|\underline{r}_0^{l-l'}|).$$

Omitting the suffix zero which denotes the equilibrium values we introduce the notation,

$$\varphi^l = \varphi(|\underline{r}^l|),$$

$$(2.5) \qquad \varphi_x^l = x^l D\varphi^l,$$

$$\varphi_{xy}^l = \delta_{xy} D\varphi^l + x^l y^l D^2\varphi^l.$$

where D is the operator $\frac{1}{r}\frac{\partial}{\partial r}$.

For the deformed lattice $\varphi^{ll'}$ can be expanded as a series in ascending powers of $\underline{u}^{ll'}$

$$(2.6) \qquad \varphi^{ll'} = \varphi^{l-l'} + \sum_x \varphi_x^{l-l'} u_x^{ll'} + \tfrac{1}{2}\sum_{xy} \varphi_{xy}^{l-l'} u_x^{ll'} u_y^{ll'} + \cdots.$$

The definitions (2.5) are meaningless when $l = 0$. We define φ_x^0, φ_{xy}^0 by

$$(2.7) \qquad \varphi_x^0 = 0 \qquad \sum_l \varphi_{xy}^l = 0.$$

If we sum the potential energy (2.6) over both l and l', we get twice the potential energy of the deformed lattice, since the potential between each pair of particles has been counted twice. This total potential energy of the deformed lattice Φ can be developed as a power series in $\underline{u}^{ll'}$

$$(2.8) \qquad \Phi = \Phi_0 + \Phi_1 + \Phi_2 + \cdots$$

where

$$\Phi_1 = \tfrac{1}{2} \sum_{ll'} \sum_{x} \varphi_x^{l-l'} u_x^{ll'}$$

(2.9)

$$\Phi_2 = \tfrac{1}{4} \sum_{ll'} \sum_{xy} \varphi_{xy}^{l-l'} u_x^{ll'} u_y^{ll'} .$$

Since $\underline{u}^{ll'} = \underline{u}^{l} - \underline{u}^{l'}$, we can with the help of (2.7) write (2.9) in the form

$$\Phi_1 = \sum_{l} \sum_{x} u_x^{l} \left[\sum_{l'} \varphi_x^{l-l'} \right]$$

(2.10)

$$\Phi_2 = -\tfrac{1}{2} \sum_{ll'} \sum_{xy} \varphi_{xy}^{l-l'} u_x^{l} u_y^{l'} .$$

The force of all particles on one is

(2.11) $$\underline{K}^{l} = -\frac{\partial \Phi}{\partial \underline{u}^{l}} .$$

The equilibrium condition is $\underline{K}^{l} = 0$, and this is satisfied since $\sum_{l'} \varphi_x^{l-l'}$ vanishes.

The equation of motion of any particle l, of mass μ is

(2.12) $$\mu \ddot{u}_x^{l} = K_x^{l} = -\frac{\partial \Phi_2}{\partial u_x^{l}}$$

$$= \sum_{l'} \sum_{y} \varphi_{xy}^{l-l'} u_y^{l'} .$$

We write the solution in the form

$$\underline{u}^{l} = \underline{U}^{l} e^{-i\omega t}$$

(2.13)

$$\underline{U}^{l} = \underline{U} e^{i(l,\alpha)} ,$$

where ω is the frequency of one of the independent normal modes of vibration and $(l,\alpha) = l_1\alpha_1 + l_2\alpha_2 + l_3\alpha_3$. Then if we restrict our choice of wave vector by the cyclic lattice condition * which postulates

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* Born, M. 'Atomtheorie des Festen Zustandes', 2nd ed. (1923) Leipzig, p.588.

that the displacement shall be periodic in a volume having the same shape as the elementary cell and containing $N(=n^3)$ cells, we can write the equations of motion in the form

$$\mu\omega^2 U_x = \sum_y [xy] U_y \tag{2.14}$$

where

$$[xy] = -\sum_\ell \varphi^\ell_{xy} e^{-i(\ell,\alpha)} . \tag{2.15}$$

It follows from (2.7) that

$$[xy] = -\sum_\ell{}' \varphi^\ell_{xy} e^{-i(\ell,\alpha)} - \varphi^\circ_{xy} \tag{2.16}$$

$$= \sum_\ell{}' \varphi^\ell_{xy} \left(1 - e^{-i(\ell,\alpha)}\right)$$

where the dash denotes that the term corresponding to $\ell_1 = \ell_2 = \ell_3 = 0$ is omitted.

Writing the determinant of the coefficients $[xy]$ as $|[xy]|$, we obtain for the mean logarithmic frequency used in equation (1.2) * :-

$$\log\bar{\omega} = \tfrac{1}{6}\langle \log|[xy]|\rangle_{AV} - \tfrac{1}{2}\log\mu , \tag{2.17}$$

where the average taken over $\alpha_1\alpha_2\alpha_3$, the phases of the waves is

$$f_{AV} = \frac{1}{(2\pi)^3}\int_{-\pi}^{+\pi}\!\!\int\!\!\int f(\alpha_1\alpha_2\alpha_3)\, d\alpha_1 d\alpha_2 d\alpha_3 . \tag{2.18}$$

For an undeformed lattice of N particles the total potential energy is

$$\Phi_0 = \tfrac{1}{2} N \sum_\ell{}' \varphi^\ell . \tag{2.19}$$

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* Born, M. 'Atomtheorie des Festen Zustandes', 2nd ed. (1923), Leipzig. p.677.

3.

The Expansion of the Frequency

Let us consider a cubic lattice, in which the cells have sides of length a, then

$$r^l = a(l_1^2 + l_2^2 + l_3^2)^{1/2} = al$$

$$x^l = al_1, \quad y^l = al_2, \quad z^l = al_3 \tag{3.1}$$

where l_1, l_2 and l_3 take all integral values for the simple lattice, are either all even or all odd for the body-centred lattice and are either all even or two odd and one even in the case of a face-centred lattice.

In order to obtain an explicit expression for $[xy]$ we must choose a suitable function φ^l. We take a law of force of the form

$$\varphi^l = \frac{nm}{n-m}\left\{-\frac{1}{m}\left(\frac{r_0}{rl}\right)^m + \frac{1}{n}\left(\frac{r_0}{rl}\right)^n\right\} \tag{3.2}$$

where the first term denotes the attractive and the second term the repulsive effect of the potential; n must be greater than m. r_0 is the equilibrium distance for two particles since $\left(\frac{\partial \varphi}{\partial r}\right)_{r=r_0} = 0$.

Differentiating (3.2) since $D = \frac{1}{r}\frac{\partial}{\partial r}$

$$D\varphi^{l} = \frac{umm}{r_0^2(n-m)}\left\{\left(r_0/rl\right)^{m+2} - \left(r_0/rl\right)^{n+2}\right\}$$

(3.3)
$$D^2\varphi^{l} = \frac{umm}{r_0^4(n-m)}\left\{-(m+2)\left(r_0/rl\right)^{m+4} + (n+2)\left(r_0/rl\right)^{n+4}\right\}.$$

Substituting these expressions in equations (2.5)

(3.4)
$$\varphi^{l}_{xx} = \frac{umm}{r_0^2(n-m)}\left\{\left(r_0/rl\right)^{m+2} - (m+2)\left(r_0/rl\right)^{m+4}\left(x^{l}/r_0\right)^2 - \left(r_0/rl\right)^{n+2} + (n+2)\left(r_0/rl\right)^{n+4}\left(x^{l}/r_0\right)^2\right\}$$

$$= \frac{umm}{r_0^2(n-m)}\left(r_0/a\right)^{m+2}\left\{1/l^{m+2} - (m+2)\,l_1^2/l^{m+4} - \left(r_0/a\right)^{n-m}\left[1/l^{n+2} - (n+2)\,l_1^2/l^{n+4}\right]\right\}$$

where $l = \left(l_1^2+l_2^2+l_3^2\right)^{1/2}$; and

(3.5)
$$\varphi^{l}_{xy} = -\frac{umm}{r_0^2(n-m)}\left(r_0/a\right)^{m+2}\left\{\frac{(m+2)\,l_2l_3}{l^{m+4}} - \left(r_0/a\right)^{n-m}\frac{(n+2)\,l_2l_3}{l^{n+4}}\right\}.$$

Now if we write

(3.6)
$$S_n^{k_1k_2k_3}(\alpha) = \sum' \frac{l_1^{k_1}l_2^{k_2}l_3^{k_3}}{l^n}\,e^{-i(l,\alpha)},$$
$$S_n^{k} = S_n^{k}(0),$$

from symmetry considerations

(3.7) (i)
$$S_{n+2}^{200} = S_{n+2}^{020} = S_{n+2}^{002} = \tfrac{1}{3}S_n^{0},$$

and

(3.7) (ii)
$$S_n^{011} = S_n^{101} = S_n^{110} = 0.$$

Hence by summing (3.4) and by summing (3.5) we find the coefficients (2.16) are

$$(3.8)\quad [xx] = \frac{\mu nm}{r_0^2(n-m)}\left(\frac{r_0}{a}\right)^{m+2}\left\{-\rho_{11}^{(n)} + \rho_{11}^{(n)}\left(\frac{r_0}{a}\right)^{n-m}\right\}$$

$$(3.9)\quad [yz] = \frac{\mu nm}{r_0^2(n-m)}\left(\frac{r_0}{a}\right)^{m+2}\left\{-\rho_{23}^{(n)} + \rho_{23}^{(n)}\left(\frac{r_0}{a}\right)^{n-m}\right\},$$

where

$$(3.10)\quad \begin{aligned}\rho_{11}^{(n)} &= S^{0}_{n+2}(\alpha) - (n+2)\,S^{200}_{n+4}(\alpha) + \frac{n-1}{3}S^{0}_{n+2}\\ \rho_{23}^{(n)} &= -(n+2)\,S^{011}_{n+4}(\alpha);\end{aligned}$$

with similar expressions for $[yy]$, $[zz]$ and $[zx]$, $[xy]$.

In general the sums denoted by S_n mean the sums over all points in the lattice; the same results hold however if we only consider the effect of a limited number of near neighbours and sum over those. We shall work out the results for the general case in which we assume that the same law of force acts between all lattice points.

As we are concerned with deviations from the equilibrium position we introduce a_0, the equilibrium value of a, given by $\left[\frac{\partial \Phi_0}{\partial a}\right]_{a=a_0} = 0$, instead of r_0. From (2.19) and (3.2)

$$(3.11)\quad \Phi_0 = \tfrac{1}{2}N\sum_{l}{}'\varphi^{l} = \frac{N\mu nm}{2(n-m)}\left\{-\tfrac{1}{m}\left(\frac{r_0}{a}\right)^{m}S^{0}_{m} + \tfrac{1}{n}\left(\frac{r_0}{a}\right)^{n}S^{0}_{n}\right\}$$

Therefore

$$(3.12)\quad \frac{\partial \Phi_0}{\partial a} = \frac{N\mu nm}{2r_0(n-m)}\left\{\left(\frac{r_0}{a}\right)^{m+1}S^{0}_{m} - \left(\frac{r_0}{a}\right)^{n+1}S^{0}_{n}\right.$$

so that for equilibrium

$$S^{\circ}_{m} - \left(r_0/a_0\right)^{n-m} S^{\circ}_{n} = 0 .$$

It follows that

(3.13) $$r_0^{n-m} = \gamma a_0^{n-m}$$

where

(3.14) $$\gamma = S^{\circ}_{m}/S^{\circ}_{n} .$$

If first neighbours only act a_0 is the projection of r_0 on the cubic axes, so that $\gamma^{\frac{1}{n-m}}$ is 1 for a simple lattice, $\sqrt{3}$ for a body-centred lattice and $\sqrt{2}$ for a face-centred lattice. Considering the effect of more neighbours γ assumes values slightly larger than these values.

Equations (3.8) and (3.9) now become

(3.15) $$[xx] = C\left(a_0/a\right)^{m+2}\left\{-\rho_{11}^{(m)} + \rho_{11}^{(n)}\gamma\left(a_0/a\right)^{n-m}\right\}$$

(3.16) $$[yz] = C\left(a_0/a\right)^{m+2}\left\{-\rho_{23}^{(m)} + \rho_{23}^{(n)}\gamma\left(a_0/a\right)^{n-m}\right\}$$

where

(3.17) $$C = \frac{mn\gamma^{m/n-m}}{a_0^2\,(n-m)} .$$

We now introduce, instead of the lattice constant a, the volume v of a cell

(3.18) $$v_0/v = \left(a_0/a\right)^3 .$$

Further since we are concerned with deviations from the equilibrium and wish to express the frequency in terms of change of volume, we write

(3.19) $$\left(v_0/v\right)^{\frac{n-m}{3}} = 1 + \zeta .$$

We now write for shortness

$$(3.20)\qquad \begin{vmatrix} \rho_{11}^{(p)} & \rho_{12}^{(q)} & \rho_{13}^{(r)} \\ \rho_{12}^{(p)} & \rho_{22}^{(q)} & \rho_{23}^{(r)} \\ \rho_{13}^{(p)} & \rho_{23}^{(q)} & \rho_{33}^{(r)} \end{vmatrix} = \left| \rho_1^{(p)} \ \rho_2^{(q)} \ \rho_3^{(r)} \right|$$

and let

$$D_0 = \left| \rho_1^{(m)} \ \rho_2^{(m)} \ \rho_3^{(m)} \right| .$$

$$D_1 = \left| \rho_1^{(n)} \ \rho_2^{(m)} \ \rho_3^{(m)} \right| + \left| \rho_1^{(m)} \ \rho_2^{(n)} \ \rho_3^{(m)} \right| + \left| \rho_1^{(m)} \ \rho_2^{(m)} \ \rho_3^{(n)} \right|$$

$$(3.21)\qquad D_2 = \left| \rho_1^{(m)} \ \rho_2^{(n)} \ \rho_3^{(n)} \right| + \left| \rho_1^{(n)} \ \rho_2^{(m)} \ \rho_3^{(n)} \right| + \left| \rho_1^{(n)} \ \rho_2^{(n)} \ \rho_3^{(m)} \right|$$

$$D_3 = \left| \rho_1^{(n)} \ \rho_2^{(n)} \ \rho_3^{(n)} \right| .$$

Then the determinants $|[xy]|$ can be expressed as a function of ζ :-

$$(3.22)\qquad |[xy]| = C^3 \left(\omega_{/r}\right)^{m+2} \left\{ \Delta_0 + \Delta_1 \zeta + \Delta_2 \zeta^2 + \Delta_3 \zeta^3 \right\}$$

where

$$\Delta_0 = \left| -\rho_1^{(m)} + \gamma \rho_1^{(n)} \quad -\rho_2^{(m)} + \gamma \rho_2^{(n)} \quad -\rho_3^{(m)} + \gamma \rho_3^{(n)} \right|$$

$$= -D_0 + \gamma D_1 - \gamma^2 D_2 + \gamma^3 D_3$$

$$\Delta_1 = \left| \gamma \rho_1^{(n)} \quad -\rho_2^{(m)} + \gamma \rho_2^{(n)} \quad -\rho_3^{(m)} + \gamma \rho_3^{(n)} \right| + \left| -\rho_1^{(m)} + \gamma \rho_1^{(n)} \quad \gamma \rho_2^{(n)} \quad -\rho_3^{(m)} + \gamma \rho_3^{(n)} \right| + \left| -\rho_1^{(m)} + \gamma \rho_1^{(n)} \quad -\rho_2^{(m)} + \gamma \rho_2^{(n)} \quad \gamma \rho_3^{(n)} \right|$$

$$(3.23)\qquad = \gamma D_1 - 2\gamma^2 D_2 + 3\gamma^3 D_3$$

$$\Delta_2 = \left| -\rho_1^{(m)} + \gamma \rho_1^{(n)} \quad \gamma \rho_2^{(n)} \quad \gamma \rho_3^{(n)} \right| + \left| \gamma \rho_1^{(n)} \quad -\rho_2^{(m)} + \gamma \rho_2^{(n)} \quad \gamma \rho_3^{(n)} \right| + \left| \gamma \rho_1^{(n)} \quad \gamma \rho_2^{(n)} \quad -\rho_3^{(m)} + \gamma \rho_3^{(n)} \right|$$

$$= -\gamma^2 D_2 + 3\gamma^3 D_3$$

$$\Delta_3 = \gamma^3 D_3 .$$

Taking logarithms the mean frequency (2.17) can be expressed as

$$(3.24)\quad \log \bar{\omega} = \tfrac{1}{2}\log \frac{c}{\mu} + \frac{(m+2)}{2(n-m)}\log(1+\xi) + \tfrac{1}{6}\left\langle \log\left(\Delta_0 + \Delta_1\xi + \Delta_2\xi^2 + \Delta_3\xi^3\right)\right\rangle_{AV}.$$

Expanding the logarithm

$$(3.25)\quad \log \bar{\omega} = \tfrac{1}{2}\log \frac{c}{\mu} + \frac{(m+2)}{2(n-m)}\log(1+\xi) + \tfrac{1}{6}\langle \log \Delta_0\rangle_{AV} + \tfrac{1}{6}\left\{A_1\xi + A_2\xi^2 + A_3\xi^3 + \cdots\right\}$$

where

$$(3.26)\quad A_1 = \left\langle \frac{\Delta_1}{\Delta_0}\right\rangle_{AV}$$

$$A_2 = \left\langle \frac{\Delta_2}{\Delta_0} - \frac{\Delta_1^2}{2\Delta_0^2}\right\rangle_{AV}$$

$$A_3 = \left\langle \frac{\Delta_3}{\Delta_0} - \frac{\Delta_1\Delta_2}{\Delta_0^2} + \frac{\Delta_1^3}{3\Delta_0^3}\right\rangle_{AV} \text{ etc.}$$

The Average Frequency

In order to express the energy of the crystal in terms of temperature and volume change we must determine the average of the A_k. It would appear impossible to integrate the functions of Δ_k

directly even if we consider the action of first neighbours only, so I have calculated the average for a face-centred lattice by numerical integration taking account of the action of all neighbours.

Having chosen a suitable range of values $\alpha_1, \alpha_2, \alpha_3$ of the phase, I have calculated the sums $\rho^{(n)}_{pq}$ for each of the set of α, and from these sums the corresponding determinants Δ_k. It is then only a short step to the actual coefficients of ζ in (3.25)

We can limit the number of points $(\alpha_1, \alpha_2, \alpha_3)$ which it is necessary to consider if we notice some simplifications due to cubic symmetry.

(4.1) (i) Consider $\overline{\rho}^{(n)}_{pq}$ where

$$\overline{\alpha}_1 = -\alpha_1 , \quad \overline{\alpha}_2 = \alpha_2 , \quad \overline{\alpha}_3 = \alpha_3 ,$$

then

$$\overline{\rho}^{(n)}_{pp} = \rho^{(n)}_{pp} \qquad (p = 1, 2 \text{ or } 3)$$

$$\overline{\rho}^{(n)}_{23} = \rho^{(n)}_{23} , \quad \overline{\rho}^{(n)}_{12} = -\rho^{(n)}_{12} , \quad \overline{\rho}^{(n)}_{13} = -\rho^{(n)}_{13}$$

Hence if we know the values of $\rho^{(n)}_{pq}$ for a set of $\alpha_1 \alpha_2 \alpha_3$ which lie in the positive octant of the cube bounded by

$$\alpha_1 = \pm\pi , \quad \alpha_2 = \pm\pi , \quad \alpha_3 = \pm\pi$$

we can determine all $\rho^{(n)}_{pq}$ for the whole cube.

We therefore restrict our α to values such that

$$0 \le \alpha_1 \le \pi , \quad 0 \le \alpha_2 \le \pi , \quad 0 \le \alpha_3 \le \pi .$$

(4.1) (ii) Consider $\bar{\rho}^{(n)}_{pq}$ where

$$\bar{\alpha}_1 = \alpha_2 \quad , \quad \bar{\alpha}_2 = \alpha_1 \quad , \quad \bar{\alpha}_3 = \alpha_3 \, ,$$

then

$$\bar{\rho}^{(n)}_{11} = \rho^{(n)}_{22} \quad , \quad \bar{\rho}^{(n)}_{22} = \rho^{(n)}_{11} \quad , \quad \bar{\rho}^{(n)}_{33} = \rho^{(n)}_{33}$$

$$\bar{\rho}^{(n)}_{23} = \rho^{(n)}_{13} \quad , \quad \bar{\rho}^{(n)}_{31} = \rho^{(n)}_{23} \quad , \quad \bar{\rho}^{(n)}_{12} = \rho^{(n)}_{12} \, .$$

Hence we can find all $\rho^{(n)}_{pq}$ corresponding to the permutations of $\alpha_1, \alpha_2, \alpha_3$. We can further restrict our phase by the planes

$$\alpha_1 = \alpha_2 \quad , \quad \alpha_2 = \alpha_3$$

and choose those points for which

$$\alpha_1 \geqslant \alpha_2 \geqslant \alpha_3 \, .$$

(iii) Finally consider $\bar{\rho}^{(n)}_{pq}$ where

$$\bar{\alpha}_1 = \alpha_1 \pm \pi \quad , \quad \bar{\alpha}_2 = \alpha_2 \pm \pi \quad , \quad \bar{\alpha}_3 = \alpha_3 \pm \pi \, .$$

Then

$$(\ell, \bar{\alpha}) = (\ell, \alpha) + \pi (\pm \ell_1 \pm \ell_2 \pm \ell_3) \, .$$

For a face-centred lattice $\ell_1 + \ell_2 + \ell_3$ is even so that we are only altering (ℓ, α) by some multiple of 2π . Hence

$$\bar{\rho}^{(n)}_{pp} = \rho^{(n)}_{pp} \quad , \quad \bar{\rho}^{(n)}_{pq} = \rho^{(n)}_{pq} \, .$$

Therefore together with condition (i)

$\alpha_1, \alpha_2, \alpha_3$ and $\pi - \alpha_1, \pi - \alpha_2, \pi - \alpha_3$

will give identical values of $\rho^{(n)}_{pq}$.

This means that $\pi/2, \pi/2, \pi/2$ is a centre of symmetry, so we can divide our octant by the plane $\alpha_1 + \alpha_2 + \alpha_3 = \frac{3\pi}{2}$ and consider points

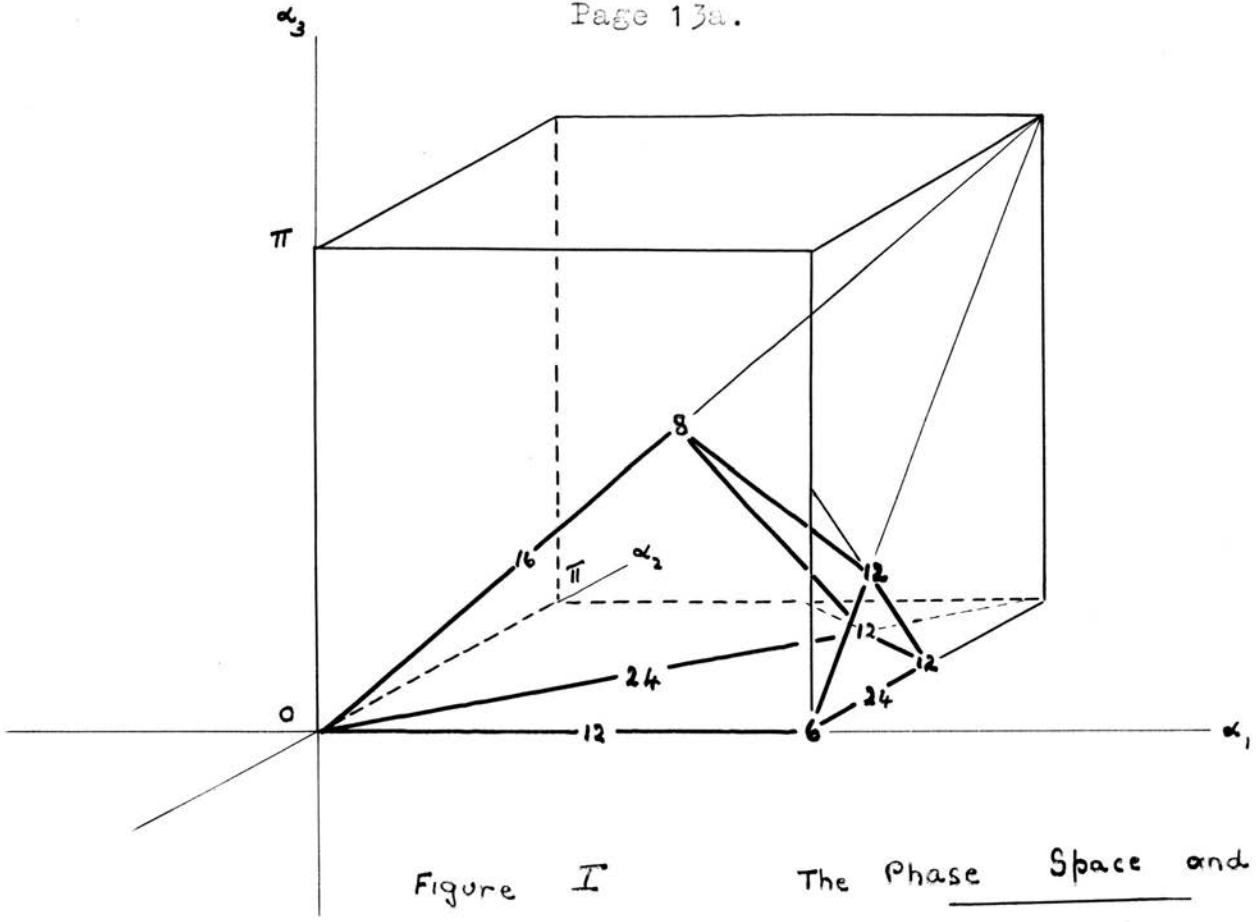

Figure I The Phase Space and Weights.

on one side of it only. We choose those for which

$$\alpha_1 + \alpha_2 + \alpha_3 \leq \frac{3\pi}{2}.$$

The portion of the phase space satisfying the three restrictions (4.1) is illustrated in Figure I.

I have divided my phase space into intervals $\pi/8$ and writing $\alpha = p\frac{\pi}{8}$, I have chosen integers p_1, p_2, p_3 such that p_1, p_2, p_3 are all odd or all even. From (4.1) it follows that we need only consider integers such that

$$0 \leq p_1 \leq 8, \quad 0 \leq p_2 \leq 8, \quad 0 \leq p_3 \leq 8$$

$$p_1 \geq p_2 \geq p_3 \tag{4.2}$$

$$p_1 + p_2 + p_3 \leq 12$$

In this way we get 29 distinct points in the phase space and each of these points has a certain weight depending on its position in the cube and on the number of similar points.

The sums $s_{pq}^{(n)}$ can be summed directly for a limited number of neighbours acting, or they can be transformed into rapidly convergent series and summed over all neighbours. These series have been calculated in the next part of the paper.

5.

Expressions for Periodic Lattice Sums

The elements $a^{(n)}_{pq}$ (3.10) involve two types of lattice sums, the periodic sums $S^k_n(\alpha)$ and the non-periodic S^0_n. The numerical values of the latter have been calculated for the Bravais cubic lattices for a large range of n. * We shall now calculate expressions for $S^k_n(\alpha)$ (3.6).

Unlike the non-periodic lattice sums, those $S^k_n(\alpha)$ which involve odd powers of l in the numerator are not identically zero, and in general simplifications of the kind (3.7) do not occur. The six sums obtained by permuting k_1, k_2, k_3 in (3.6) may be found from one another by suitably permuting $\alpha_1, \alpha_2, \alpha_3$; so for second order sums it is only necessary to calculate expressions for

$$S^2_n(\alpha) = S^{200}_n(\alpha) \quad , \quad S^{11}_n(\alpha) = S^{011}_n(\alpha) .$$

When we have calculated the zero order sum $S^0_n(\alpha)$ those involving higher powers of l in the numerator may be found by successive partial differentiation with respect to α_1, α_2 and (or) α_3.

There are two methods of transforming

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* Born, M. and Misra, R.D., Proc. Cambridge Phil. Soc. 36. (1940).

our sums into rapidly convergent series, and both methods lead to the same result. The methods are worked for the face-centred lattice, but they may equally well be applied to the simple and body-centred lattices.

6.

Summation by Use of ϑ -Functions

Using the well-known formula

$$(6.1)\qquad \Gamma(n/2)\, r^{-n} = \int_0^\infty e^{-r^2 u}\, u^{n/2-1}\, du$$

we get for any lattice sum of the form $S_n^0(\alpha)$ the integral representation

$$(6.2)\qquad S_n^0(\alpha) = \frac{1}{\Gamma(n/2)} \sum_\ell{}' e^{-i(\ell,\alpha)} \int_0^\infty e^{-\ell^2 u}\, u^{n/2-1}\, du .$$

Hence the sum for a face-centred lattice denoted by $[\ ]_f$ in which $\ell_1 \ell_2 \ell_3$ are all even or two odd and one even is

$$(6.3)\qquad S_n^0(\alpha) = \frac{1}{\Gamma(n/2)} \int_0^\infty u^{n/2-1}\, \sigma(u)\, du$$

where

$$(6.4)\qquad \sigma(u) = \left[\sum_\ell{}' e^{-\ell^2 u - i(\ell,\alpha)} \right]_f$$

$$= \sum_{\ell_1 = 0,\pm 2,\cdots} e^{-\ell_1^2 u - i\ell_1\alpha_1} \sum_{\ell_2 = 0,\pm 2,\cdots} e^{-\ell_2^2 u - i\ell_2\alpha_2} \sum_{\ell_3 = 0,\pm 2,\cdots} e^{-\ell_3^2 u - i\ell_3\alpha_3} +$$

$$+ \left\{ \sum_{\ell_1=0,\pm 2,\cdots} e^{-\ell_1^2 u - i\ell_1\alpha_1} \sum_{\ell_2=\pm 1,\pm 3,\cdots} e^{-\ell_2^2 u - i\ell_2\alpha_2} \sum_{\ell_3=\pm 1,\pm 3,\cdots} e^{-\ell_3^2 u - i\ell_3\alpha_3} \right\}_{\alpha_p}$$

$$- 1 .$$

$\{\ \}_{\alpha_p}$ denotes the sum of the three terms obtained by cyclic interchange of $\alpha_1, \alpha_2, \alpha_3$.

Now let us write

(6.5) $$4u = \pi\beta$$

and introduce instead of $\sigma(u)$

(6.6) $$\sigma_0(\beta) = \sigma_1(\beta) + \sigma_2(\beta) - 1$$

where

$$\sigma_1(\beta) = \sum_{\ell_1} e^{-\pi\ell_1^2\beta - 2i(\ell_1\alpha_1)} \sum_{\ell_2} e^{-\pi\ell_2^2\beta - 2i\ell_2\alpha_2} \sum_{\ell_3} e^{-\pi\ell_3^2\beta - 2i\ell_3\alpha_3}$$

(6.7) $$\sigma_2(\beta) = \left\{ \sum_{\ell_1} e^{-\pi\ell_1^2\beta - 2i\ell_1\alpha_1} \sum_{\ell_2} e^{-\pi(\ell_2+\frac{1}{2})^2\beta - i\alpha_2(2\ell_2+1)} \times \right.$$

$$\left. \times \sum_{\ell_3} e^{-\pi(\ell_3+\frac{1}{2})^2\beta - i\alpha_3(2\ell_3+1)} \right\}_{\alpha_p} .$$

Then

(6.8) $$S_n^0(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)} \int_0^\infty \beta^\eta \sigma_0(\beta)\, d\beta$$

where $\eta = n/2 - 1$.

We shall consider the integral as the sum of two integrals, between the limits 0 and 1, and 1 and ∞. The integral from 1 to ∞ may be obtained directly from $\sigma_0(\beta)$, but for the integral from 0 to 1 we must consider each part of $\sigma_0(\beta)$ in (6.6) separately so we write

$$(6.9)\qquad \int_0^\infty \beta^\eta \sigma_0(\beta)\, d\beta = \delta_0(\eta) + \delta_1(\eta) + \delta_2(\eta) - \frac{1}{\eta+1}$$

where

$$(6.10)\qquad \begin{aligned} \delta_0(\eta) &= \int_1^\infty \beta^\eta \sigma_0(\beta)\, d\beta \\ \delta_1(\eta) &= \int_0^1 \beta^\eta \sigma_1(\beta)\, d\beta \\ \delta_2(\eta) &= \int_0^1 \beta^\eta \sigma_2(\beta)\, d\beta . \end{aligned}$$

The complete expression for $\sigma_0(\beta)$ is

$$(6.11)\qquad \sigma_0(\beta) = \Big[\sum_{\ell}{}' e^{-\pi\ell^2\beta/4 - i(\ell,\alpha)}\Big]_f = \Big[2\sum_{\ell>0} \cos(\ell,\alpha)\, e^{-\pi\ell^2\beta/4}\Big]_f$$

where $\sum_{\ell>0}$ means that the sum is to be extended over half the lattice points in such a way that of the two points ℓ_1,ℓ_2,ℓ_3 and $-\ell_1,-\ell_2,-\ell_3$ one is omitted.

It follows immediately that

$$(6.12)\qquad \delta_0(\eta) = \Big[2\sum_{\ell>0} \cos(\ell,\alpha)\, \varphi_\eta\Big(\frac{\ell^2\pi}{4}\Big)\Big]_f$$

where $\varphi_\eta(x)$ are the well-known integrals

$$(6.13)\qquad \varphi_\eta(x) = \int_1^\infty \beta^\eta e^{-\beta x}\, d\beta .$$

The series for $\delta_0(\eta)$ may be written in the form

$$(6.14)\qquad \delta_0(\eta) = \sum_{k=1}^{\infty} a_k\, \varphi_\eta\Big(\frac{k\pi}{2}\Big)$$

where a_k are given in Table I, $(k \le 8)$.

TABLE I

l	$\frac{l^2}{2} = k$	a_k
$(0, 1, 1)$	1	$4\{\cos\alpha_2 \cos\alpha_3\}_{\alpha_p}$
$(2, 0, 0)$	2	$2\{\cos 2\alpha_1\}_{\alpha_p}$
$(2, 1, 1)$	3	$8\{\cos 2\alpha_1 \cos\alpha_2 \cos\alpha_3\}_{\alpha_p}$
$(0, 2, 2)$	4	$4\{\cos 2\alpha_2 \cos 2\alpha_3\}_{\alpha_p}$
$(0, 1, 3)$	5	$4\{\cos\alpha_2 \cos 3\alpha_3 + \cos 3\alpha_2 \cos\alpha_3\}_{\alpha_p}$
$(2, 2, 2)$	6	$8\cos 2\alpha_1 \cos 2\alpha_2 \cos 2\alpha_3$
$(1, 2, 3)$	7	$8\{\cos\alpha_1 \cos 2\alpha_2 \cos 3\alpha_3 + \cos 3\alpha_1 \cos 2\alpha_2 \cos\alpha_3\}_{\alpha_p}$
$(4, 0, 0)$	8	$2\{\cos 4\alpha_1\}_{\alpha_p}$

To calculate $\lambda_1(\gamma)$ and $\lambda_2(\gamma)$ the second integrals in (6.10) we express $\sigma_1(\beta)$ and $\sigma_2(\beta)$ in terms of ϑ -functions and make use of Jacobi's imaginary transformation *. We can then changee our limits of integration from 0 and 1 to 1 and ∞, and obtain an expression involving the functions (6.13).

From definition

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* Whittaker and Watson, 'Modern Analysis' (1927) Cambridge. p.474.

$$(6.15)\qquad \vartheta_3(\alpha_1, e^{-\pi\beta}) = \sum_{\ell_1} e^{-\pi\ell_1^2\beta - 2i\ell_1\alpha_1}$$

and Jacobi's imaginary transformation is

$$(6.16)\qquad \vartheta_3(\alpha_1, e^{-\pi\beta}) = \beta^{-1/2}\exp\left(\frac{-\alpha_1^2}{\pi\beta}\right)\vartheta_3\left(\frac{i\alpha_1}{\beta}, e^{-\pi/\beta}\right).$$

Therefore

$$(6.17)\qquad \sigma_1(\beta) = \vartheta_3(\alpha_1, e^{-\pi\beta})\,\vartheta_3(\alpha_2, e^{-\pi\beta})\,\vartheta_3(\alpha_3, e^{-\pi\beta})$$
$$= \nu^{3/2}\exp\left\{-\frac{\nu}{\pi}(\alpha_1^2+\alpha_2^2+\alpha_3^2)\right\} \times$$
$$\times\,\vartheta_3(i\alpha_1\nu, e^{-\pi\nu})\,\vartheta_3(i\alpha_2\nu, e^{-\pi\nu})\,\vartheta_3(i\alpha_3\nu, e^{-\pi\nu})$$

where ν is the reciprocal of β.

Since

$$(6.18)\qquad \exp\left(\frac{-\nu\alpha_1^2}{\pi}\right)\vartheta_3(i\alpha_1\nu, e^{-\pi\nu}) = \sum_{\ell_1}\exp\left\{-\frac{\nu}{\pi}(\alpha_1+\ell_1\pi)^2\right\},$$

$$(6.19)\qquad \sigma_1(\beta) = \nu^{3/2}\sum_{\ell}\exp\left\{-\frac{\nu}{\pi}(\alpha+\ell\pi)^2\right\}$$

where

$$(6.20)\qquad (\alpha+\ell\pi)^2 = (\alpha_1+\ell_1\pi)^2 + (\alpha_2+\ell_2\pi)^2 + (\alpha_3+\ell_3\pi)^2$$

and where the sum is taken over all positive and negative integral values of $\ell_1\ell_2\ell_3$. It follows that

$$(6.21)\qquad \Lambda_1(\gamma) = \sum_{\ell}\int_1^\infty \nu^{-\gamma-1/2}\exp\left\{-\frac{\nu}{\pi}(\alpha+\ell\pi)^2\right\}d\nu$$
$$= \sum_{\ell}\varphi_{-\gamma-1/2}\frac{(\alpha+\ell\pi)^2}{\pi}.$$

The calculation of $\Lambda_2(\gamma)$ is similar. We have

$$(6.22)\qquad \vartheta_2(\alpha_2, e^{-\pi\beta}) = \sum_{l_2} e^{-\pi(l_2+\frac{1}{2})^2\beta - i(2l_2+1)\alpha_2}$$

and

$$(6.23)\qquad \vartheta_2(\alpha_2, e^{-\pi\beta}) = \beta^{-1/2}\exp\left(-\frac{\alpha_2^2}{\pi\beta}\right)\vartheta_4\left(\frac{i\alpha_2}{\beta}, e^{-\pi/\beta}\right).$$

Hence

$$(6.24)\qquad \sigma_2(\beta) = \left\{\vartheta_3(\alpha_1, e^{-\pi\beta})\,\vartheta_2(\alpha_2, e^{-\pi\beta})\,\vartheta_2(\alpha_3, e^{-\pi\beta})\right\}^{\alpha_p}$$
$$= \nu^{3/2}\sum_{l}\left[(-1)^{l_2+l_3} + (-1)^{l_3+l_1} + (-1)^{l_1+l_2}\right]\exp\left\{-\frac{\nu}{\pi}(\alpha+l\pi)^2\right\}$$

where the sum is again taken over all positive and negative values of l_1, l_2, l_3. It follows that

$$(6.25)\qquad \delta_2(\eta) = \sum_{l}\left[(-1)^{l_2+l_3} + (-1)^{l_3+l_1} + (-1)^{l_1+l_2}\right]\varphi_{-\eta-1/2}\frac{(\alpha+l\pi)^2}{\pi}.$$

Combining this with (6.21)

$$(6.26)\qquad \delta_1(\eta) + \delta_2(\eta) = 4\left[\sum_{l}\varphi_{-\eta-1/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_b$$

where $[\ \ ]_b$ means that $l_1 l_2 l_3$ are all even or all odd as in the case of a body-centred lattice.

Our final expression for $S^{\circ}_{\eta}(\alpha)$ is

$$(6.27)\qquad \frac{4^{\eta/2}\Gamma(\eta/2)}{\pi^{\eta/2}}S^{\circ}_{\eta}(\alpha) = \left[2\sum_{l>0}\cos(l,\alpha)\,\varphi_{\eta}\left(\frac{l^2\pi}{4}\right)\right]_f + 4\left[\sum_{l}\varphi_{-\eta-1/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_b - \frac{1}{\eta+1}$$

$$(6.28)\qquad = \sum_{k=1}^{\infty}\alpha_k\,\varphi_{\eta}\left(\frac{k\pi}{2}\right) - \frac{1}{\eta+1} + 4\left[\sum_{l}\varphi_{-\eta-1/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_b.$$

7.

The Derivation of Sums of Higher Order

If we differentiate the sum $S_n^\circ(\alpha)$ partially with respect to α_1, α_2 or α_3 we obtain a sum involving l_1, l_2 or l_3 respectively in the numerator

$$(7.1) \qquad \frac{\partial}{\partial \alpha_1} S_n^\circ(\alpha) = \sum_l \frac{-i l_1 e^{-i(l,\alpha)}}{l^n}.$$

Repeating the partial differentiation we find

$$(7.2) \qquad \frac{\partial^2}{\partial \alpha_1^2} S_n^\circ(\alpha) = -\sum_l \frac{l_1^2 e^{-i(l,\alpha)}}{l^n} = -S_n^2(\alpha)$$

and similarly

$$(7.3) \qquad \frac{\partial^2}{\partial \alpha_2 \partial \alpha_3} S_n^\circ(\alpha) = -\sum_l \frac{l_2 l_3 e^{-i(l,\alpha)}}{l^n} = -S_n''(\alpha).$$

Differentiating an integral of the type (6.13) we find

$$(7.4) \qquad \frac{\partial}{\partial \alpha_1} \varphi_{-\gamma-\frac{1}{2}}\frac{(\alpha+l\pi)^2}{\pi} = -\frac{2}{\pi}(\alpha_1+l_1\pi)\varphi_{-\gamma+\frac{1}{2}}\frac{(\alpha+l\pi)^2}{\pi}.$$

Hence

$$(7.5) \qquad \frac{\partial^2}{\partial \alpha_1^2} \varphi_{-\gamma-\frac{1}{2}}\frac{(\alpha+l\pi)^2}{\pi} = -\frac{2}{\pi}\varphi_{-\gamma+\frac{1}{2}}\frac{(\alpha+l\pi)^2}{\pi} + \frac{4(\alpha_1+l_1\pi)^2}{\pi^2}\varphi_{-\gamma+\frac{3}{2}}\frac{(\alpha+l\pi)^2}{\pi}$$

$$(7.6) \qquad \frac{\partial^2}{\partial \alpha_2 \partial \alpha_3} \varphi_{-\gamma-\frac{1}{2}}\frac{(\alpha+l\pi)^2}{\pi} = \frac{4}{\pi^2}(\alpha_2+l_2\pi)(\alpha_3+l_3\pi)\varphi_{-\gamma+\frac{3}{2}}\frac{(\alpha+l\pi)^2}{\pi}.$$

Thus the expressions for the second order sums corresponding to (6.28) are

$$(7.7)\quad S_n^2(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)} \left\{ \sum_{k=1,2\cdots} b_k \varphi_n\left(\frac{k\pi}{2}\right) + \frac{8}{\pi}\left[\sum_l \varphi_{-n+1/2}\left(\frac{(\alpha+l\pi)^2}{\pi}\right)\right]_b - \frac{16}{\pi^2}\left[\sum_l (\alpha_1+l_1\pi)^2 \varphi_{-n+3/2}\left(\frac{(\alpha+l\pi)^2}{\pi}\right)\right]_b \right\}$$

$$(7.8)\quad S_n''(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)} \left\{ \sum_{k=1,2,\cdots} c_k \varphi_n\left(\frac{k\pi}{2}\right) - \frac{16}{\pi^2}\left[\sum_l (\alpha_2+l_2\pi)(\alpha_3+l_3\pi) \varphi_{-n+3/2}\left(\frac{(\alpha+l\pi)^2}{\pi}\right)\right]_b \right\}$$

where

$$(7.9)\quad b_k = -\frac{\partial^2}{\partial\alpha_1^2} a_k \;, \qquad c_k = -\frac{\partial^2}{\partial\alpha_2\partial\alpha_3} a_k$$

The b_k and c_k, corresponding to the a_k given in Table I, are to be found in Table II.

8.

Ewald's Method

If $\underline{a}^l = \underline{a}_1 l_1 + \underline{a}_2 l_2 + \underline{a}_3 l_3$

and $\underline{b}$ is the lattice vector of the reciprocal lattice

$$(8.1)\quad \underline{a}_i \cdot \underline{b}_j = \delta_{ij} \;, \qquad \underline{b}_1 = \frac{\underline{a}_2 \times \underline{a}_3}{v_a}$$

TABLE II

k	b_k	c_k
1	$4\cos\alpha_1(\cos\alpha_2+\cos\alpha_3)$	$-4\sin\alpha_2\sin\alpha_3$
2	$8\cos 2\alpha_1$	0
3	$32\cos 2\alpha_1\cos\alpha_2\cos\alpha_3$ $+8\cos\alpha_1(\cos 2\alpha_2\cos\alpha_3+\cos 2\alpha_3\cos\alpha_2)$	$-16\cos\alpha_1(\sin 2\alpha_2\sin\alpha_3+\sin\alpha_2\sin 2\alpha_3)$ $-8\cos 2\alpha_1\sin\alpha_2\sin\alpha_3$
4	$16\cos 2\alpha_1(\cos 2\alpha_2+\cos 2\alpha_3)$	$-16\sin 2\alpha_1\sin 2\alpha_3$
5	$4\cos\alpha_1(\cos 3\alpha_2+\cos 3\alpha_3)$ $+36\cos 3\alpha_1(\cos\alpha_2+\cos\alpha_3)$	$-12\sin\alpha_2\sin 3\alpha_3$ $-12\sin\alpha_3\sin 3\alpha_2$
6	$32\cos 2\alpha_1\cos 2\alpha_2\cos 2\alpha_3$	$-32\cos 2\alpha_1\sin 2\alpha_2\sin 2\alpha_3$
7	$8\cos\alpha_1(\cos 2\alpha_2\cos 3\alpha_3+\cos 3\alpha_2\cos 2\alpha_3)$ $+32\cos 2\alpha_1(\cos\alpha_2\cos 3\alpha_3+\cos\alpha_3\cos 3\alpha_2)$ $+72\cos 3\alpha_1(\cos\alpha_2\cos 2\alpha_3+\cos 2\alpha_2\cos\alpha_3)$	$-48\cos\alpha_1(\sin 2\alpha_2\sin 3\alpha_3+\sin 3\alpha_2\sin 2\alpha_3)$ $-24\cos 2\alpha_1(\sin\alpha_2\sin 3\alpha_3+\sin 3\alpha_2\sin\alpha_3)$ $-16\cos 3\alpha_1(\sin\alpha_2\sin 2\alpha_3+\sin 2\alpha_2\sin\alpha_3)$
8	$32\cos 4\alpha_1$	0

TABLE II

where v_a is the volume of a cell

$$v_a = |\underline{a}_1\ \underline{a}_2\ \underline{a}_3| \tag{8.2}$$

Ewald's transformation formula is

$$\sum_l e^{-\pi(\underline{a}_l - \underline{r})^2 \mu} = \frac{1}{v_a \mu^{3/2}} \sum_l e^{-(\pi \underline{b}_l^2/\mu + 2\pi i(\underline{b}_l \cdot \underline{r}))} . \tag{8.3}$$

This may be written in the form

$$\sum_l e^{-(\pi \underline{a}_l^2/\mu + 2\pi i(\underline{a}_l \cdot \underline{r}))} = v_b/\mu^{3/2} \sum_l e^{-\pi(\underline{b}_l - \underline{r})^2/\mu} . \tag{8.4}$$

Using equation (6.1) as before we get

$$\sum_l{}' \frac{e^{-2\pi i(\underline{a}_l \cdot \underline{r})}}{(\underline{a}_l^2)^{n/2}} = \frac{\pi^{n/2}}{\Gamma(n/2)} \int_0^\infty \beta^{n/2-1} \sum_l{}' e^{-\pi \underline{a}_l^2 \beta - 2\pi i(\underline{a}_l \cdot \underline{r})} d\beta . \tag{8.5}$$

Divide the integral into two parts by taking the limits 0 to γ and γ to ∞, and using (8.4) we find

$$\sum_l{}' \frac{e^{-2\pi i(\underline{a}_l \cdot \underline{r})}}{(\underline{a}_l^2)^{n/2}} = \frac{\pi^{n/2}}{\Gamma(n/2)} \sum_l{}' e^{-2\pi i(\underline{a}_l \cdot \underline{r})} \int_\gamma^\infty \beta^{n/2-1} e^{-\pi \underline{a}_l^2 \beta} d\beta \tag{8.6}$$

$$+ \frac{\pi^{n/2} v_b}{\Gamma(n/2)} \sum_l \left[\int_0^\gamma \beta^{n/2-5/2} e^{-\pi(\underline{b}_l - \underline{r})^2/\beta} d\beta \right]$$

$$- \frac{2\pi^{n/2} \gamma^{n/2}}{n\,\Gamma(n/2)}$$

$$= \frac{\gamma^{n/2} \pi^{n/2}}{\Gamma(n/2)} \left\{ \sum_l{}' \left[e^{-2\pi i(\underline{a}_l \cdot \underline{r})} \int_1^\infty \nu^{n} e^{-\pi \underline{a}_l^2 \gamma \nu} d\nu \right] \right. \tag{8.7}$$

$$\left. + v_b \gamma^{-3/2} \sum_l \left[\int_1^\infty \nu^{-\eta-1/2} e^{-\pi \nu/\gamma (\underline{b}_l - \underline{r})^2} d\nu \right] - \frac{1}{\eta+1} \right\} .$$

Because of (6.13) the sum may now be written in the form

$$(8.8)\qquad \sum_{\ell}{}' \frac{e^{-2\pi i(\underline{a}_\ell \cdot \underline{x})}}{(\underline{a}_\ell^2)^{\nu/2}} = \frac{\tau^{\nu/2}\pi^{\nu/2}}{\Gamma(\nu/2)} \left\{ \sum_{\ell}{}' e^{-2\pi i(\underline{a}_\ell \cdot \underline{x})} \varphi_\eta(\tau \underline{a}_\ell^2 \pi) + \nu_b \tau^{-3/2} \sum_{\ell} \left[\varphi_{-\eta-1/2}\tfrac{\pi}{\tau}(\underline{b}_\ell - \underline{x})^2\right] - \frac{1}{\eta+1} \right\}$$

For a face-centred lattice, the lattice vectors are

$$\underline{a}_1 = (0, b, c) \qquad \underline{a}_2 = (a, 0, c) \qquad \underline{a}_3 = (a, b, 0),$$

hence $\underline{a}_\ell$ has components

$$a(\ell_2 + \ell_3), \quad b(\ell_3 + \ell_1), \quad c(\ell_1 + \ell_2)$$

or

$$(8.9)\qquad a\ell_1, \quad b\ell_2, \quad c\ell_3$$

where $\ell_1 + \ell_2 + \ell_3$ is even.

The reciprocal lattice vectors are

$$\underline{b}_1 = \left(-\tfrac{1}{2a}, \tfrac{1}{2b}, \tfrac{1}{2c}\right) \quad \underline{b}_2 = \left(\tfrac{1}{2a}, -\tfrac{1}{2b}, \tfrac{1}{2c}\right) \quad \underline{b}_3 = \left(\tfrac{1}{2a}, \tfrac{1}{2b}, -\tfrac{1}{2c}\right)$$

hence $\underline{b}_\ell$ has components

$$\tfrac{1}{2a}(-\ell_1 + \ell_2 + \ell_3), \quad \tfrac{1}{2b}(\ell_1 - \ell_2 + \ell_3), \quad \tfrac{1}{2c}(\ell_1 + \ell_2 - \ell_3),$$

or

$$(8.10)\qquad \ell_1/2a, \quad \ell_2/2b, \quad \ell_3/2c,$$

where ℓ_1, ℓ_2, ℓ_3 are all even or all odd as in the case of a body-centred lattice.

Taking

$$(8.11)\qquad a = b = c = 1$$

and

$$2\pi \underline{x} = (\alpha_1, \alpha_2, \alpha_3)$$

we get the following expression for the sum

$$(8.12)\quad S_n^{\circ}(\alpha) = \frac{\tau^{n/2}\pi^{n/2}}{\Gamma(n/2)}\left\{\left[2\sum_{\ell>0}\cos(\ell,\alpha)\,\varphi_\eta(\tau\pi\ell^2)\right]_f - \frac{1}{\eta+1} + \frac{\tau^{-3/2}}{2}\left[\sum_{\ell}\varphi_{-\eta-1/2}\frac{(\alpha+\ell\pi)^2}{4\tau\pi}\right]_b\right\}$$

where $[\ ]_f$, $[\ ]_b$ and $\sum_{\ell>0}$ have the same meaning as before.

Finally we choose $\tau = 1/4$ and we get an expression for $S_n^{\circ}(\alpha)$ which is identical with that found in (6.27) by the use of ϑ -functions.

$$(8.13)\quad S_n^{\circ}(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{\ell>0}\cos(\ell,\alpha)\,\varphi_\eta\left(\frac{\pi\ell^2}{4}\right)\right]_f - \frac{1}{\eta+1} + 4\left[\sum_{\ell}\varphi_{-\eta-1/2}\frac{(\alpha+\ell\pi)^2}{\pi}\right]_b\right\}.$$

The sums of higher order are found by partial differentiation and will give the same results as (7.7) and (7.8)

If we had used a different substitution (6.5) or had taken a different value for τ we should have obtained expressions for the sums in another form involving more terms of the first type and fewer of the second, or vice versa. The formulae given are however more suitable for practical purposes.

9.

Sums for the Other Cubic Lattices

Corresponding expressions for the lattice sums in the cases of the simple and body-centred lattices may be found by the methods used above for the face-centred lattice. I shall however only quote the results.

a) The simple lattice. In this case the sum is taken over all positive and negative integers l_1, l_2 and l_3. The zero order and second order sums are :-

$$(9.1)\quad S_n^0(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0}\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_S - \frac{1}{\eta+1} + 8\left[\sum_l \varphi_{-\eta-1/2}\frac{(\alpha+2l\pi)^2}{\pi}\right]_S\right\}$$

$$(9.2)\quad S_n^2(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0} l_1^2\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_S + 16/\pi\left[\sum_l \varphi_{-\eta+1/2}\frac{(\alpha+2l\pi)^2}{\pi}\right]_S - 32/\pi^2\left[\sum_l (\alpha_1+2l_1\pi)^2\varphi_{-\eta+3/2}\frac{(\alpha+2l\pi)^2}{\pi}\right]_S\right\}$$

$$(9.3)\quad S_n''(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0} l_2 l_3\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_S - \frac{32}{\pi^2}\left[\sum_l (\alpha_2+2l_2\pi)(\alpha_3+2l_3\pi)\varphi_{-\eta+3/2}\frac{(\alpha+2l\pi)^2}{\pi}\right]_S\right\}$$

where $[\ ]_s$ means the sum over the values of $l_1\ l_2\ l_3$ for the simple lattice.

b) The body-centred lattice. For this lattice we consider only those values of l_1, l_2, l_3 which are either all odd or all even. Then :-

$$(9.4)\quad S_n^0(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0}\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_b - \frac{1}{\eta+1} + 2\left[\sum_l \varphi_{-\eta-1/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_f\right\}$$

$$(9.5)\quad S_n^2(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0} l_1^2\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_b + \frac{4}{\pi}\left[\sum_l \varphi_{-\eta+1/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_f - \frac{8}{\pi^2}\left[\sum_l (\alpha_1+l_1\pi)^2\,\varphi_{-\eta+3/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_f\right\}$$

$$(9.6)\quad S_n^{11}(\alpha) = \frac{\pi^{n/2}}{4^{n/2}\Gamma(n/2)}\left\{\left[2\sum_{l>0} l_2 l_3\cos(l,\alpha)\,\varphi_\eta\left(\frac{\pi l^2}{4}\right)\right]_b - \frac{8}{\pi^2}\left[\sum_l (\alpha_2+l_2\pi)(\alpha_3+l_3\pi)\,\varphi_{-\eta+3/2}\frac{(\alpha+l\pi)^2}{\pi}\right]_f\right\}$$

where $[\ ]_b$ and $[\ ]_f$ mean the sum over a body-centred and a face-centred lattice respectively.

10.

The Numerical Calculation of the Energy

Before we can proceed with the numerical

calculation of the energy, we must choose values for m and n which occur in the potential energy (3.2)

WE SHALL ASSUME THAT $n = 2m$

AND CONSIDER IN PARTICULAR THE CASE $m = 6$

We have calculated the sums $\sigma^{(m)}_{pq}$ and $\sigma^{(n)}_{pq}$ for these values in the case of a face-centred lattice, in which the effect of all neighbours is taken into account, by means of the expressions derived in (6.28), (7.7) and (7.8). These are tabulated for our set of $\alpha = p\frac{\pi}{8}$ in Tables III and IV.

In the case $n = 2m = 12$

(10.1) $$\gamma = \frac{S^{\circ}_{m}}{S^{\circ}_{n}} = 9{\cdot}5310 .$$

We now calculate the determinants Δ_k corresponding to these elements, and from the symmetry considerations (4.1) the determinants are symmetrical about the planes

$$p_1 = 0, \quad p_2 = 0, \quad p_3 = 0$$
$$p_1 = p_2, \quad p_2 = p_3, \quad p_3 = p_1$$

TABLE III

$p_1 p_2 p_3$	$\rho_{11}^{(6)}$	$\rho_{22}^{(6)}$	$\rho_{33}^{(6)}$	$\rho_{12}^{(6)}$	$\rho_{23}^{(6)}$	$\rho_{31}^{(6)}$
840	2·0280	1·1333	2·0280	0	0	0
822	2·4541	1·3187	1·3187	0	0·4862	0
820	2·7277	1·0994	1·3443	0	0	0
800	3·0223	1·0655	1·0655	0	0	0
731	2·2819	1·1569	1·5786	0·3467	0·3443	0·1445
711	2·7856	1·1057	1·1057	0·1459	0·1408	0·1459
660	1·3187	1·3187	2·4541	0·4862	0	0
642	1·6990	1·2504	1·6990	0·6960	0·6960	0·4936
640	1·8604	1·2032	1·8039	0·6968	0	0
622	2·2059	1·2088	1·2088	0·4908	0·4941	0·4908
620	2·4210	1·2112	1·1673	0·5006	0	0
600	2·6658	0·9129	0·9129	0	0	0
551	1·4967	1·4967	1·9166	0·8404	0·3482	0·3482
533	1·6163	1·3202	1·3202	0·8419	0·8418	0·8419
531	1·8383	1·1230	1·2533	0·8555	0·3473	0·3526
511	2·1426	0·8392	0·8392	0·3594	0·1438	0·3594
444	1·3683	1·3683	1·3683	0·9906	0·9906	0·9906
442	1·3774	1·3774	1·3189	0·9982	0·7016	0·7016
440	1·3866	1·3866	1·2694	1·0264	0	0
422	1·5255	0·9529	0·9529	0·7180	0·5039	0·7180
420	1·5939	0·8047	0·7439	0·7288	0	0
400	1·6846	0·5288	0·5288	0	0	0
333	1·1811	1·1811	1·1811	0·8547	0·8547	0·8547
331	1·0939	1·0939	0·7909	0·8793	0·3593	0·3593
311	1·0907	0·4705	0·4705	0·3731	0·1514	0·3731
222	0·7107	0·7107	0·7107	0·5217	0·5217	0·5217
220	0·6157	0·6157	0·3258	0·5351	0	0
200	0·5443	0·1541	0·1541	0	0	0
111	0·2158	0·2158	0·2158	0·1604	0·1604	0·1604

TABLE IV

$p_1\ p_2\ p_3$	$\rho_{11}^{(12)}$	$\rho_{22}^{(12)}$	$\rho_{33}^{(12)}$	$\rho_{12}^{(12)}$	$\rho_{23}^{(12)}$	$\rho_{13}^{(12)}$
8 4 0	0·5313	0·3157	0·5313	0	0	0
8 2 2	0·6245	0·3623	0·3623	0	0·1092	0
8 2 0	0·6860	0·3144	0·3769	0	0	0
8 0 0	0·7502	0·3131	0·3131	0	0	0
7 3 1	0·5816	0·3199	0·4240	0·0773	0·0772	0·0320
7 1 1	0·6912	0·3180	0·3180	0·0320	0·0320	0·0320
6 6 0	0·3623	0·3623	0·6245	0·1092	0	0
6 4 2	0·4390	0·3312	0·4390	0·1546	0·1546	0·1094
6 4 0	0·4780	0·3248	0·4762	0·1546	0	0
6 2 2	0·5485	0·3298	0·3298	0·1092	0·1094	0·1092
6 2 0	0·5940	0·3299	0·3283	0·1093	0	0
6 0 0	0·6421	0·2671	0·2671	0	0	0
5 5 1	0·3743	0·3743	0·4989	0·1866	0·0773	0·0773
5 3 3	0·4059	0·3417	0·3417	0·1866	0·1866	0·1866
5 3 1	0·4513	0·2966	0·3395	0·1868	0·0773	0·0773
5 1 1	0·5062	0·2396	0·2396	0·0774	0·0320	0·0320
4 4 4	0·3467	0·3467	0·3467	0·2187	0·2187	0·2187
4 4 2	0·3469	0·3469	0·3452	0·2188	0·1546	0·1546
4 4 0	0·3470	0·3470	0·3436	0·2188	0	0
4 2 2	0·3627	0·2515	0·2515	0·1548	0·1093	0·1548
4 2 0	0·3694	0·2128	0·2111	0·1549	0	0
4 0 0	0·3788	0·1592	0·1592	0	0	0
3 3 3	0·2960	0·2960	0·2960	0·1868	0·1868	0·1868
3 3 1	0·2638	0·2638	0·2161	0·1869	0·0773	0·0773
3 1 1	0·2409	0·1290	0·1290	0·0775	0·0321	0·0775
2 2 2	0·1735	0·1735	0·1735	0·1095	0·1095	0·1095
2 2 0	0·1413	0·1413	0·09418	0·1096	0	0
2 0 0	0·1117	0·04580	0·04580	0	0	0
1 1 1	0·05087	0·05087	0·05087	0·03212	0·03212	0·03212

and about the point

$$(p_1, p_2, p_3) = (4, 4, 4)$$

The space bounded by these planes, as illustrated in Figure I, is $1/96$ of the whole cube, so that points lying wholely within the space have a weight 96. Points lying on the faces have in general a weight 48 and the weights attached to points on the different edges and corners are given in the figure. All weights can be found as follows :-

(i) For points not on the planes

$$p_3 = 0, \quad p_1 = 8$$

the weight is equal to the number of different permutations P_1 of $\pm p_1, \pm p_2, \pm p_3$ and P_2 of $\pm (8-p_1), \pm (8-p_2), \pm (8-p_3)$ since these are the number of times the determinants take a particular value. In general this equals $2P_1$ since $P_1 = P_2$, but for points on $p_1 + p_2 + p_3 = 12$, (p_1, p_2, p_3) is a permutation of $8-p_1, 8-p_2, 8-p_3$, so the actual number of different permutations is P_1.

(ii) For points in the plane $p_3 = 0$ but not in $p_1 = 8$ or $p_2 = 0$, those with the same determinants as $(p_1, p_2, 0)$

are the P_1 permutations of $(\pm p_1, \pm p_2, 0)$ and the P_2 permutations of $\pm(8-p_1)$, $\pm(8-p_2)$, ± 8, when these are distinct. The latter lie on the faces of the cube and so have a weight $1/2$; but $P_2 = 2P_1$, so the weight of $p_1, p_2, 0$ is again $2P_1$ when $p_1 + p_2 + p_3 \neq 12$ and P_1 when $p_1 + p_2 + p_3 = 12$.

(iii) For points on $p_2 = 0$, $p_3 = 0$ but not on $p_1 = 8$, we have $P_1 = 6$ points on the axes and $P_2 = 24$ points on the edges of the cube with the same determinants as $(p_1, 0, 0)$. The weight of a point on the edge of the cube is $1/4$ so the total weight of points $(p_1, 0, 0)$ is $2P_1 = 12$.

(iv) Finally for points on the face $p_1 = 8$; we have P_1 permutations of $\pm 8, \pm p_2, \pm p_3$ and $P_2 = P_{1/2}$ permutations of $0, \pm(8-p_2), \pm(8-p_3)$, the former have a weight $1/2$ so the total weight is P_1 if $p_1 + p_2 + p_3 \neq 12$ and $P_{1/2}$ if $p_1 + p_2 + p_3 = 12$.

The calculated values of Δ_k are given in Table V and the coefficients A_k in Table VI. The complete table of weights is given in the last column of Table VI.

The averaged coefficients are in the last row of this Table.

TABLE V

p_1 p_2 p_3	Δ_0	Δ_1	Δ_2	Δ_3
8 4 0	14·29	85·40	140·6	77·16
8 2 2	14·85	72·81	118·8	64·53
8 2 0	16·25	79·52	129·6	70·38
8 0 0	15·20	73·59	118·6	63·67
7 3 1	14·49	71·24	116·7	63·62
7 1 1	13·89	67·72	109·8	59·35
6 6 0	14·85	72·81	118·8	64·53
6 4 2	8·859	43·35	70·54	38·19
6 4 0	12·30	60·56	99·25	54·16
6 2 2	9·561	46·84	78·35	41·42
6 2 0	~~11·72~~ 9·736	~~57·94~~ 48·57	~~95·39~~ 80·70	~~52·31~~ 44·654
6 0 0	9·209	45·03	73·26	39·66
5 5 1	9·328	46·81	78·46	43·52
5 3 3	4·713	22·75	36·47	19·44
5 3 1	6·247	30·76	50·11	27·45
5 1 1	5·158	25·37	41·49	22·56
4 4 4	2·926	13·78	21·50	11·12
4 4 2	4·004	19·28	30·82	16·36
4 4 0	5·149	25·03	40·35	21·58
4 2 2	2·429	11·81	19·06	10·21
4 2 0	2·281	11·24	18·38	9·980
4 0 0	1·882	9·304	15·26	8·310
3 3 3	1·788	8·475	13·30	6·912
3 3 1	1·380	6·692	10·73	5·690
3 1 1	0·5043	2·505	4·121	2·247
2 2 2	0·3519	1·682	2·659	1·392
2 2 0	0·1572	0·7639	1·225	0·6480
2 0 0	0·04150	0·2131	0·3616	0·2028
1 1 1	0·008551	0·04149	0·06642	0·03490

TABLE VI

$p_1 p_2 p_3$	A_1	A_2	A_3	A_4	A_5	Weight
8 4 0	4·94	−4·06	4·43	−5·50	7·21	12
8 2 2	4·90	−4·00	4·37	−5·34	6·99	12
8 2 0	4·89	−3·98	4·29	−5·29	6·84	24
8 0 0	4·84	−3·90	4·18	−5·06	6·54	6
7 3 1	4·91	−4·00	4·29	−5·35	6·87	96
7 1 1	4·88	−4·01	4·42	−5·30	7·10	48
6 6 0	4·90	−4·00	4·37	−5·34	6·99	12
6 4 2	4·89	−4·00	4·36	−5·31	6·98	48
6 4 0	4·92	−4·04	4·40	−5·43	7·11	48
6 2 2	4·90	−4·02	4·43	−5·36	7·12	48
6 2 0	4·94	−4·09 (16)	4·61 (4)	−5·54	7·54	48
6 0 0	4·89	−4·00	4·36	−5·31	6·98	12
5 5 1	5·02	−4·19	4·62	−5·84	7·77	48
5 3 3	4·83	−3·92	4·27	−5·08	6·71	48
5 3 1	4·90	−4·03	4·42	−5·38	7·12	96
5 1 1	4·92	−4·06	4·47	−5·46	7·24	48
4 4 4	4·71	−3·74	3·99	−4·61	5·98	8
4 4 2	4·81	−3·87	4·14	−4·97	6·43	48
4 4 0	4·86	−3·97	4·34	−5·26	6·88	24
4 2 2	4·86	−3·96	4·30	−5·25	6·82	48
4 2 0	4·93	−4·09	4·58	−5·52	7·51	48
4 0 0	4·94	−4·09	4·64	−5·54	7·59	12
3 3 3	4·74	−3·79	4·12	−4·71	6·26	16
3 3 1	4·85	−3·98	4·42	−5·20	7·04	48
3 1 1	4·97	−4·18	4·75	−5·74	7·95	48
2 2 2	4·78	−3·86	4·25	−4·86	6·66	16
2 2 0	4·86	−4·02	4·51	−5·32	7·26	24
2 0 0	5·13	−4·45	5·22	−6·50	9·26	12
1 1 1	4·85	−3·99	4·42	−5·22	7·03	16
$\langle A_k \rangle_{Av}$	4·90	−4·04	4·42	−5·36	7·12	

The variations of the A_k with the different phases are small, e.g.

$$4 \cdot 71 \leq A_1 \leq 5 \cdot 13$$

so that the A_k seem to be almost independent of the phases of the waves for our particular m and n. Further in calculating the coefficients A_k it was found numerically that the relations

$$(10.2) \qquad \Delta_1^2/\Delta_0^2 - 3\Delta_2/\Delta_0 = 0 \;, \quad \Delta_2^2/\Delta_0^2 - 3\Delta_1\Delta_3/\Delta_0\Delta_0 = 0$$

held to within about 1% for every point in the phase space. This means that to within possible numerical error

$$(10.3) \qquad \Delta_0 + \Delta_1\zeta + \Delta_2\zeta^2 + \Delta_3\zeta^3 = \Delta_0\left[1 + \frac{\Delta_1}{3\Delta_0}\zeta\right]^3 .$$

I did not use this simplification in the numerical calculation of the expansion of $\log(\Delta_0 + \Delta_1\zeta + \Delta_2\zeta^2 + \Delta_3\zeta^3)$ but obtained the A_k from direct calculation.

The determinants Δ_k, Table V vary with the phase but their quotients are practically constant, so that the A_k which are functions of these quotients also vary only slightly. This invariance appears to arise from the connections between corresponding $\rho_{pq}^{(m)}$ and $\rho_{pq}^{(n)}$. From Tables III and IV we can see numerically that

$$(10.4) \qquad \rho_{pq}^{(m)} = k\rho_{pq}^{(n)} - \sigma_{pq}$$

where k is a constant, in the neighbourhood of 4. and σ_{pq} is a quantity which varies with the phase, but which is small compared with $k\rho_{pq}^{(n)}$.

A similar connection with $k = 4$ can be found from the general expressions for $\rho_{pq}^{(n)}$ and $\rho_{pq}^{(n)}$, but σ_{pq} is a complicated function of α and I have not been able to show that in general it is small compared with $k\rho_{pq}^{(n)}$.

For first neighbours only it can be shown that

$$\rho_{11}^{(n)} = \tfrac{1}{2}^{n/2}\left\{n\left[2 - \cos\alpha_1\cos\alpha_2 - \cos\alpha_1\cos\alpha_3\right] - 2\left(1 - \cos\alpha_2\cos\alpha_3\right)\right\} \tag{10.5}$$

$$\rho_{23}^{(n)} = \tfrac{1}{2}^{n/2}(n+2)\sin\alpha_2\sin\alpha_3 .$$

Therefore

$$2^{m/2}n\rho_{11}^{(m)} - 2^{n/2}m\rho_{11}^{(n)} = -2(n-m)(1-\cos\alpha_2\cos\alpha_3). \tag{10.6}$$

When $n = 2m$ this gives

$$\rho_{11}^{(m)} = 2^{m/2-1}\rho_{11}^{(2m)} - \tfrac{1}{2}^{m/2}\left(1 - \cos\alpha_2\cos\alpha_3\right), \tag{10.7}$$

so that for first neighbours only

$$\sigma_{11} = \tfrac{1}{2}^{m/2}\left(1 - \cos\alpha_2\cos\alpha_3\right). \tag{10.8}$$

The maximum value of $\dfrac{\sigma_{11}}{2^{m/2-1}\rho_{11}^{(2m)}}$ is $\dfrac{1}{m-1}$ so for $m = 6$

$$0 \leq \sigma_{pq} \leq \tfrac{1}{5}\left(4\rho_{pq}^{(n)}\right) \quad \text{when} \quad p = q. \tag{10.9}$$

For the non-diagonal elements however

$$(10.10)\qquad \rho_{pq}^{(m)} = 2^{m/2-1}\,\rho_{pq}^{(2m)}\left[1+\frac{1}{m+1}\right]$$

so that $\sigma_{pq} = -1/4\,(4\rho_{pq}^{(2m)})$ when $m=6$, $p\neq q$.
Hence since $\rho_{pq}^{(m)}$ is always positive

$$(10.11)\qquad -\tfrac{1}{4} \leqslant \frac{\sigma_{pq}}{4\rho_{pq}^{(m)}} \leqslant \tfrac{1}{5}.$$

If we substitute (10.4) for $\rho_{pq}^{(m)}$ in the determinants Δ_k (3.23), we find, writing

$$\beta = \gamma - k = 9\cdot 53 - 4 = 5\cdot 53,$$

$$\Delta_0 = \left|\beta\rho_1^{(m)}+\sigma_1 \quad \beta\rho_2^{(m)}+\sigma_2 \quad \beta\rho_3^{(m)}+\sigma_3\right|$$

$$\Delta_1 = \gamma\left|\beta\rho_1^{(m)}+\sigma_1 \quad \beta\rho_2^{(m)}+\sigma_2 \quad \rho_3^{(m)}\right| + \gamma\left|\rho_1^{(m)} \quad \beta\rho_2^{(m)}+\sigma_2 \quad \beta\rho_3^{(m)}+\sigma_3\right| + \gamma\left|\beta\rho_1^{(m)}+\sigma_1 \quad \rho_2^{(m)} \quad \beta\rho_3^{(m)}+\sigma_3\right|$$

$$(10.12)\qquad \Delta_2 = \gamma^2\left|\beta\rho_1^{(m)}+\sigma_1 \quad \rho_2^{(m)} \quad \rho_3^{(m)}\right| + \gamma^2\left|\rho_1^{(m)} \quad \beta\rho_2^{(m)}+\sigma_2 \quad \rho_3^{(m)}\right| + \gamma^2\left|\rho_1^{(m)} \quad \rho_2^{(m)} \quad \beta\rho_3^{(m)}+\sigma_3\right|$$

$$\Delta_3 = \gamma^3\left|\rho_1^{(m)} \quad \rho_2^{(m)} \quad \rho_3^{(m)}\right| = \gamma^3 D_3.$$

Now if we let

$$3\varepsilon_1 = \frac{1}{\beta D_3}\left\{ |\sigma_1 \rho_2^{(n)} \rho_3^{(n)}| + |\rho_1^{(n)} \sigma_2 \rho_3^{(n)}| + |\rho_1^{(n)} \rho_2^{(n)} \sigma_3| \right\}$$

$$(10.13)\quad 3\varepsilon_2^2 = \frac{1}{\beta^2 D_3}\left\{ |\rho_1^{(n)} \sigma_2 \sigma_3| + |\sigma_1 \rho_2^{(n)} \sigma_3| + |\sigma_1 \sigma_2 \rho_3^{(n)}| \right\}$$

$$\varepsilon_3^3 = \frac{1}{\beta^3 D_3} |\sigma_1 \sigma_2 \sigma_3|$$

from (10.11) for first neighbours only,

$$(10.14)\ (i)\qquad -\frac{4}{7\beta} \leq \varepsilon_1 \leq \frac{4}{5\beta}$$

i.e. approximately

$$-1/10 \leq \varepsilon_1 \leq 1/4$$

and

$$(10.14)\ (ii)\qquad 0 \leq \varepsilon_2^2 \leq 1/49$$

$$(iii)\qquad -1/1000 \leq \varepsilon_3^3 \leq 1/343.$$

Then we can express the determinants in terms of ε

$$\Delta_0 = \beta^3 D_3 \left\{ 1 + 3\varepsilon_1 + 3\varepsilon_2^2 + \varepsilon_3^3 \right\}$$

$$\Delta_1 = 3\beta^2 \gamma D_3 \left\{ 1 + 2\varepsilon_1 + \varepsilon_2^2 \right\}$$

$$(10.15)$$

$$\Delta_2 = 3\beta\gamma^2 D_3 \left\{ 1 + \varepsilon_1 \right\}$$

$$\Delta_3 = \gamma^3 D_3 .$$

Therefore

$$\Delta_1/\Delta_0 = \frac{3\gamma}{\beta}\left[1 + 2\varepsilon_1 + \varepsilon_2^2\right]\left[1 - 3\varepsilon_1 - 3\varepsilon_2^2 + 9\varepsilon_1^2 + \cdots\right]$$

$$= \frac{3\gamma}{\beta}\left[1 - \varepsilon_1 + 3\varepsilon_1^2 - 2\varepsilon_2^2 + \cdots\right]$$

(10.16)

$$\Delta_2/\Delta_0 = 3\gamma^2/\beta^2\left[1 - 2\varepsilon_1 + 6\varepsilon_1^2 - 3\varepsilon_2^2 + \cdots\right]$$

$$\Delta_3/\Delta_0 = \gamma^3/\beta^3\left[1 - 3\varepsilon_1 + 9\varepsilon_1^2 - 3\varepsilon_2^2 + \cdots\right].$$

Using these results we can find an accurate expression for the functions (10.2), which were numerically zero.

$$\frac{\Delta_1^2}{\Delta_0^2} - \frac{3\Delta_2}{\Delta_0} = 9\gamma^2/\beta^2\left\{\varepsilon_1^2 - \varepsilon_2^2 + \cdots\right\}$$

(10.17)

$$\Delta_2^2/\Delta_0^2 - \frac{3\Delta_1\Delta_2}{\Delta_0^2} = -9\gamma^4/\beta^4\left\{\varepsilon_1^2 + \varepsilon_2^2 + \cdots\right\}.$$

These are both zero if we neglect second and higher order quantities, such as ε_1^2, ε_2^2.

We can also find expressions for the coefficients A_k in terms of ε

(10.18) $$A_1 = \frac{3\gamma}{\beta}\left\{1 - \varepsilon_1 + 3\varepsilon_1^2 - 2\varepsilon_2^2 + \cdots\right\}, \text{ etc.}$$

Neglecting second and higher order terms and assuming ε_1 lies between the values (10.14) (i)

(10.19) $$4.42 \leq A_1 \leq 5.67.$$

The A_1 given in Table VI lie well within this range.

As these maximum and minimum values are so widely different it does not seem possible to find an averaged A_1 from this result. The lower limit depends on the diagonal elements of the determinants and the upper limits on the non-diagonal elements, and since the latter are generally small compared with the diagonal elements, the averaged A_1 must be more nearly equal to the smaller value than the larger. If it were possible to prove that $\langle \varepsilon_1 \rangle_{Av}$ was about $1/20$, equation (10.18) would give the coefficients immediately, but I have not been able to find a method for averaging the expressions (10.13).

The following approximation gives a fairly accurate result. Let us assume that $S_n^2(\alpha)$, $S_n''(\alpha)$, etc. obey the simplifications (5.7), which S_n^2, etc. obey, so that

$$S_n^{''0}(\alpha) = S_n^{'0'}(\alpha) = S_n^{0''}(\alpha) = 0$$

$$S_{n+2}^{200}(\alpha) = S_{n+2}^{020}(\alpha) = S_{n+2}^{002}(\alpha) = 1/3\, S_n^0(\alpha). \tag{10.20}$$

Then

$$\rho_{pq}^{(n)} = 0 \qquad \text{if} \quad p \neq q \tag{10.21}$$

and $\rho^{(n)}_{pq} = \frac{2(n-1)}{3} \sum_{l>0} \frac{1-\cos(l,\alpha)}{l^{n+2}}$ if $p = q$.

For first neighbours only

(10.22) $$\rho^{(m)}_{pq} = 4\rho^{(n)}_{pq}\left\{1 - \frac{1}{2m-1}\right\}.$$

Then

(10.23) $$\varepsilon_1 = \frac{4}{11\beta} \simeq 1/15$$

$$\varepsilon_2^2 = \varepsilon_1^2 , \quad \varepsilon_3^3 = \varepsilon_1^3 .$$

Therefore

(10.24) $$\frac{\Delta_1}{\Delta_0} = \frac{3\gamma}{\beta(1+\varepsilon_1)} , \quad \frac{\Delta_2}{\Delta_0} = \frac{3\gamma^2}{\beta^2(1+\varepsilon_1)^2} ,$$

giving $$\Delta_3/\Delta_0 = \gamma^3/\beta^3(1+\varepsilon_1)^3$$

(10.25) $A_1 = 4\cdot84$, $A_2 = -3\cdot92$, etc.

The error in the value of A_1 is less than 2% , and $\log\left[\Delta_0 + \Delta_1\zeta + \Delta_2\zeta^2 + \Delta_3\zeta^3\right]$ becomes exactly $\log\Delta_0 + 3\log\left[1 + 1\cdot61\zeta\right]$.

11.

The Energy and Equation of State

Considering the action of all neighbours, we find using the averaged values of A_k, that the mean frequency (3.25) is

$$(11.1)\quad \log \bar{\omega} = \tfrac{1}{2}\log \frac{c\bar{I}_0}{\mu} + \tfrac{2}{3}\log(1+\zeta) + \tfrac{1}{6}\{4.90\zeta - 4.04\zeta^2 + 4.42\zeta^3 - \cdots\}$$

where

$$(11.2)\quad \log I_0 = \tfrac{1}{3}\langle \log \Delta_0 \rangle_{AV}.$$

The potential energy $\bar{\Phi}_0$ of the whole lattice is given in (3.11). Introducing $r_0^{n-m} = \gamma a_0^{n-m}$ we get

$$(11.3)\quad \bar{\Phi}_0 = \frac{N u n m}{2(n-m)}\left\{-\tfrac{1}{m}\gamma^{m/n-m}\left(\tfrac{a_0}{a}\right)^m S_m^0 + \tfrac{1}{n}\gamma^{n/n-m}\left(\tfrac{a_0}{a}\right)^n S_n^0\right\}$$

From the value of γ (3.14), and since $\left(\tfrac{a_0}{a}\right)^{n-m} = 1+\zeta$

$$(11.4)\quad \bar{\Phi}_0 = \frac{N u S_m^0}{2(n-m)}\gamma^{\frac{m}{n-m}}(1+\zeta)^{m/n-m}(-n+m+m\zeta).$$

For $n = 2m$

$$(11.5)\quad \bar{\Phi}_0 = -\frac{N u \gamma S_m^0}{2}(1-\zeta^2)$$

Thus for $m = 6$ the potential energy is

$$(11.6)\quad \bar{\Phi}_0 = -8.62\, u(1-\zeta^2)$$

Substituting (11.1) and (11.6) in (1.2)

the free energy of a face-centred lattice, taking into account the action of all neighbours, in terms of volume change ζ , is

$$(11.7)\quad \frac{A}{N} = -8{\cdot}62\,u(1-\zeta^2) + 3kT\log\frac{k}{kT} + \frac{3kT}{2}\log\frac{cI_0}{\mu} + 2kT\log(1+\zeta) + kT\{2{\cdot}45\zeta - 2{\cdot}02\zeta^2 + 2{\cdot}21\zeta^3 - 2{\cdot}68\zeta^4 \cdots\}$$

Our law of force (3.2) contains four arbitrary constants,- u , r_0 , and the numbers m and n . We have used the particular case $n = 2m = 12$, so that our energy expression contains only two arbitrary constants u , r_0 . The arbitrary distance r_0 has been changed to a unit of volume, v_0 —equations (3.13) and (3.18) - which is the equilibrium volume of a cell. We now write the other constant u as a quantity with the dimensions of temperature, $u = k\Theta$, where Θ can be regarded as the unit of temperature.

On differentiating A/N with respect to the volume v of the cell, we obtain the equation of state for the crystal, connecting the pressure p , temperature T and volume v .

$$(11.8)\qquad p = -\frac{\partial}{\partial v}\left(A/N\right)$$

$$= \frac{2k\Theta}{v_0}(1+\zeta)^{3/2}\left\{14.24\,\zeta + T/\Theta\, F(\zeta)\right\}$$

where

$$(11.9)\qquad F(\zeta) = \left\{\frac{2}{1+\zeta} + 2.45 - 4.04\,\zeta + 6.63\,\zeta^2 - 10.72\,\zeta^3 + 17.85\,\zeta^4 - \cdots\right\}.$$

Now if we write

$$(11.10)\qquad p_0 = \frac{k\Theta}{v_0}$$

the equation of state becomes

$$(11.11)\qquad p/p_0 = 2(1+\zeta)^{3/2}\left\{14.24\,\zeta + T/\Theta\, F(\zeta)\right\}$$

where we have three constants, p_0, Θ and v_0 connected by (11.10)

We can now construct curves which give the volume in terms of either pressure or temperature. Equation (11.11) is linear in p/p_0 and T/Θ, so we can draw a system of straight lines for different values of ζ. It is only necessary to calculate two points for each line.

Figure II represents the isobars giving $v/v_0 = (1+\zeta)^{-1/2}$ as a function of T/Θ for

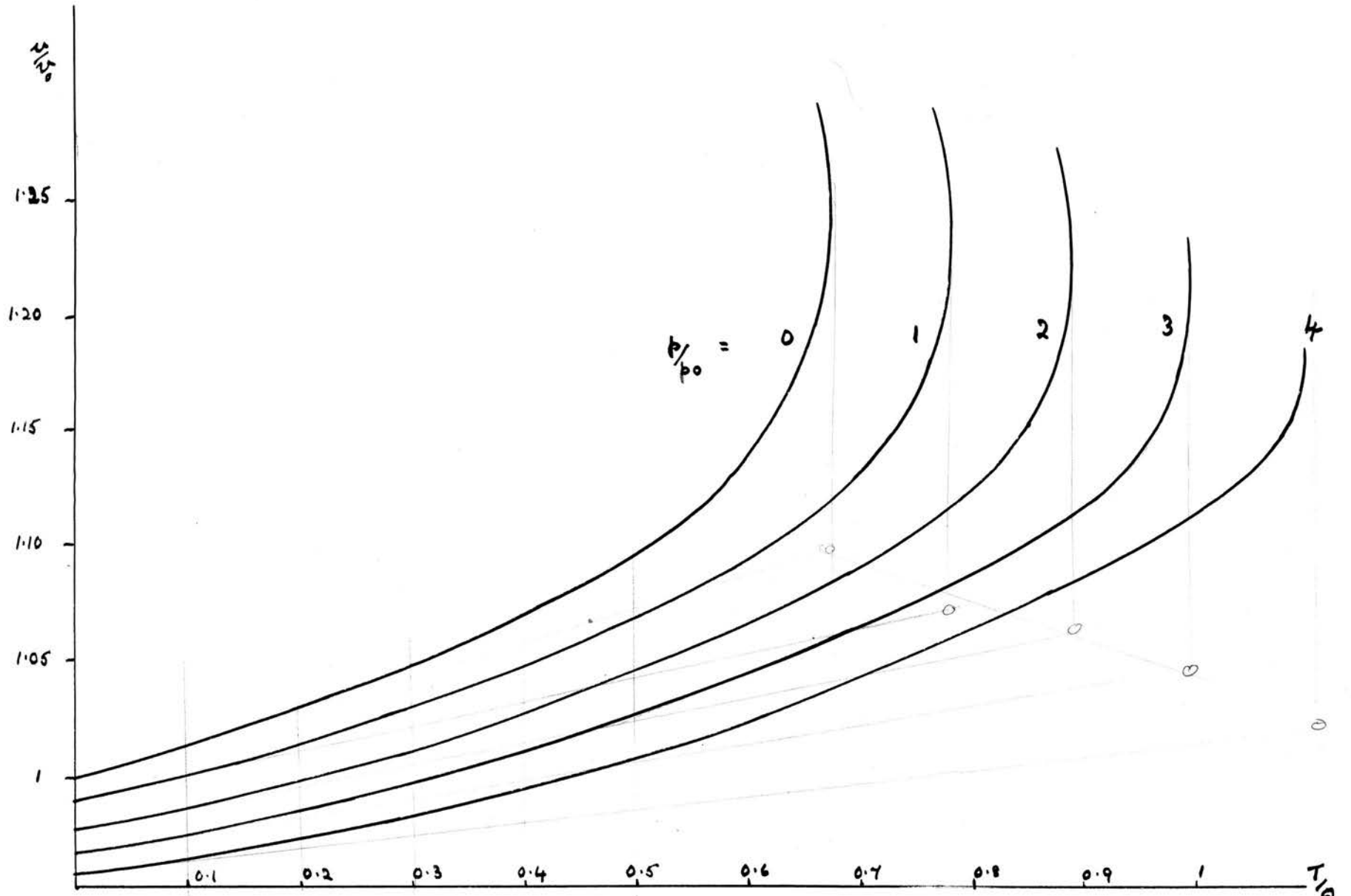

Figure II ISOBARS p/p_0 = constant

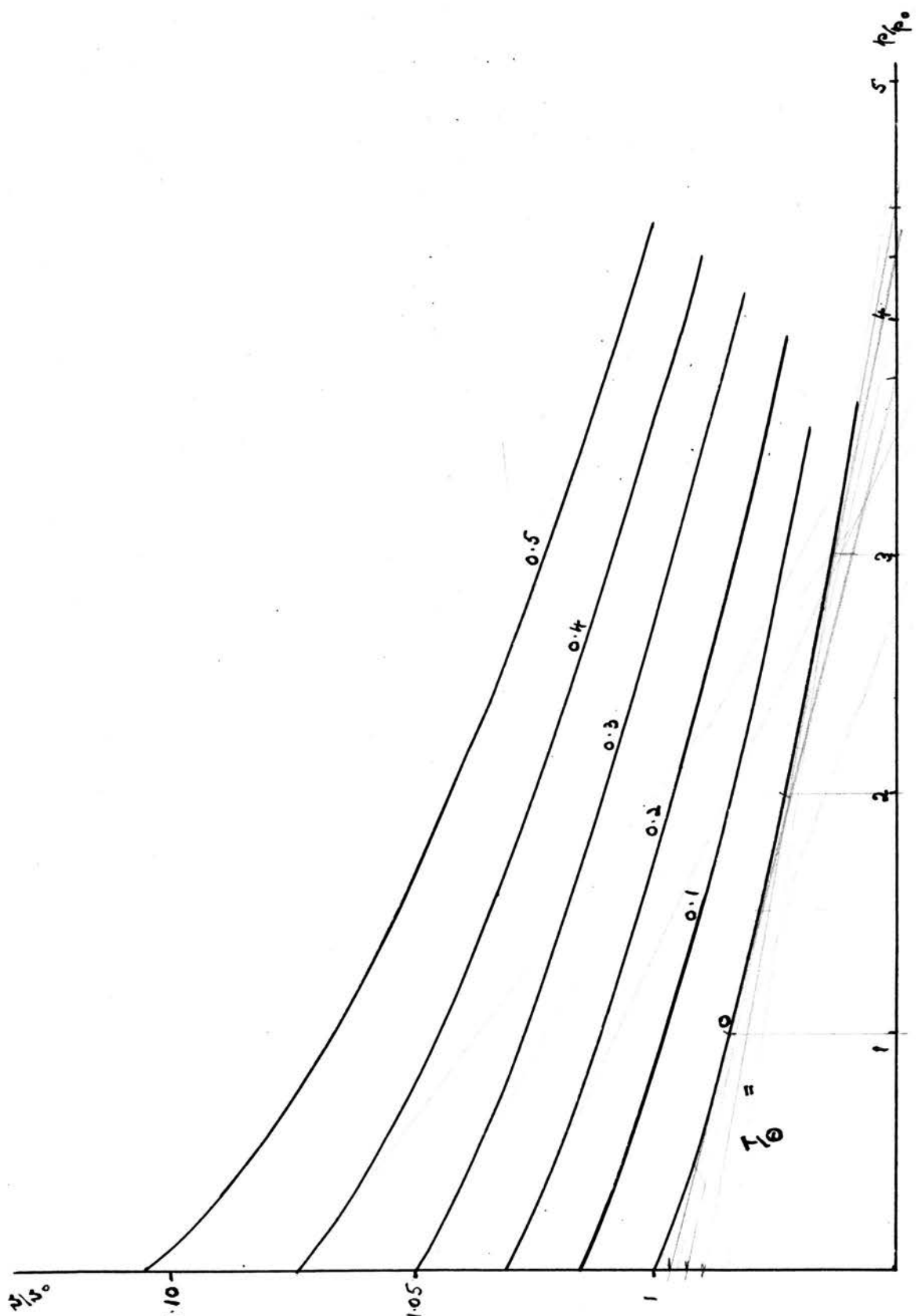

Figure III ISOTHERMS T/Θ = constant

constant pressure.

Figure III represents isotherms, v/v_0 as a function of p/p_0 for constant temperature.

We notice that in Figure II v/v_0 increases linearly with respect to T/Θ at first but later the increase becomes more rapid until it is eventually infinite. This is the same type of curve as that found by M.Born for a body-centred lattice, * but the values of T/Θ corresponding to the extreme points differs widely in the two cases.

Before we can compare the two sets of curves we must compare the scales used. The constant of temperature has the same meaning, but the v_0 used above is the actual equilibrium volume and is slightly smaller than the v_0 $(0.92 v_0)$, used by Born, which is the equilibrium volume if first neighbours only act. Hence our constant of pressure is slightly larger than (1.1 times) the p_0 defined by Born. These differences are slight and are not sufficient to account for the differences in the two sets of graphs.

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* Born, M., Journ. of Chem. Physics., Vol. 7.,No. 8., (1939).

To obtain a closer analogy with Born's results I have considered the equation of state under simplified assumptions. Born considered first neighbours only in the thermic term and first and second neighbours in the static term.

I have first derived $F(\xi)$ considering the action of first neighbours only in the thermic term, but I have considered the action of all neighbours in the static term, so that p_0, Θ and v_0 are the same constants as before. Since the variations in the A_k were so slight I have assumed that there will only be a small percentage error if we average over only a few points in the phase space. If we choose $\alpha_1, \alpha_2, \alpha_3$ equal to 0, $\pi/2$ or π, we get 5 distinct points in the phase space. I used this approximation to obtain $F_1(\xi)$, the value of $F(\xi)$ when the action of first neighbours only is taken into account.

$$(11.12)\quad F_1(\xi) = \frac{2}{1+\xi} + 2\cdot33 - 3\cdot65\xi + 5\cdot55\xi^2 - \cdots$$

For $v > v_0$, i.e. when ξ is negative, $F_1(\xi) < F(\xi)$, so that for a given pressure and volume, T/Θ is greater when we consider first neighbours only in the thermic term, than when we consider the action

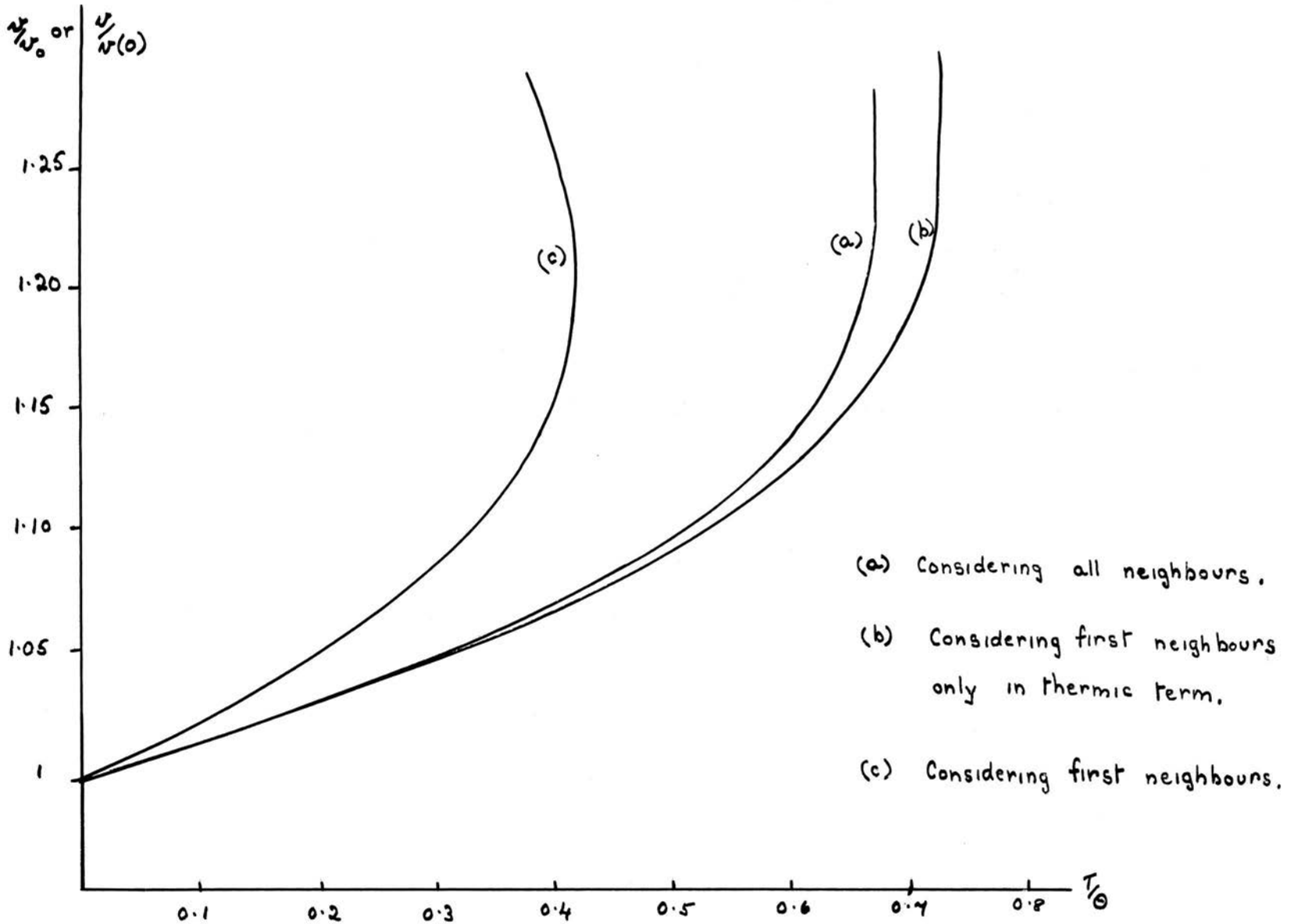

Figure IV ISOBARS $P/P_0 = 0$

of all neighbours. The differences are not great. The graphs of the isobars, $p/p_0 = 0$ are compared in Figure IV.

Secondly I considered first neighbours only in both static and thermic terms, defining $v(0)$ as the new equilibrium volume, $p(0)$ as the corresponding pressure, and $v/v(0) = (1+\zeta)^{-1/2}$ In this case $\gamma = 8$. Then

$$(11.13) \quad \frac{p}{p(0)} = 2(1+\zeta)^{3/2}\left\{12\zeta + \frac{T}{\theta}F_2(\zeta)\right\}$$

where

$$(11.14) \quad F_2(\zeta) = \frac{2}{1+\zeta} + 2\cdot61 - 4\cdot73\zeta + 8\cdot76\zeta^2 - \cdots$$

was found by averaging over a few points in the phase space as before. The isobar, $p/p(0) = 0$ corresponding to this equation is also shown in Figure IV, and this corresponds most nearly to the isobar, $p/p_0 = 0$ of Born.

The differences in the curves depend mainly on the number of neighbours considered in the static potential ; in this type of crystal lattice it seems that a consideration of the action of first neighbours only in the thermic term is a fairly good approximation, but that the static potential must be determined accurately.

I wish to express my gratitude to Professor M. Born, who suggested this problem to me, for his advice on many occasions.