THE DIELECTRIC CONSTANT

THESIS

Submitted by

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C O N T E N T S.

LIST OF TABLES AND FIGURES.

INTRODUCTION

It is known that if a piece of matter be subject to an external field, an electric moment will be induced within it.

The electric moment per unit volume, or the polarisation, at any point is related to the field at the same point by the relation

$$\underline{P}(\underline{x}) = \chi \underline{E}(\underline{x})$$

where χ is the susceptibility of the medium. The dielectric constant ε is defined by

$$\varepsilon = 1 + 4\pi\chi$$

Passing from the macroscopic to the microscopic behaviour of the matter, the electric moment is actually the average of the separate electric moments of the molecules constituting the matter. The electric moment of a single molecule depends on two parameters, namely its polarisability α and its permanent moment p. Thus one should be able to calculate the dielectric constant ε in terms of the molecular constants α and p.

Several attempts have been made to relate the dielectric constant to the molecular constants α and p; the simplest of which is the Clausius-Mosotti relation,

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} N\alpha$$

where N is the number of molecules per unit volume.

The relation is supposed to hold for non-polar molecules in the case of steady fields and for any molecules in the case of highly alternating fields. This relation which gives the same value α in the liquid state as that in the vapor state, is used for the calculation of the polarisability of molecules.

A simple relation, including the permanent moment p as well, is that given by Debye

$$\frac{\varepsilon-1}{\varepsilon+2} = \frac{4\pi}{3} N \left(\alpha + \frac{p^2}{3kT}\right),$$

where T is the absolute temperature and k Boltzman's constant. This relation when applied in the vapor state, is used to calculate the permanent moment p ; but when applied in the liquid state, it does not give the same value of p as given in the vapour state. For substances having highly polar molecules, the value of the permanent moment calculated in the liquid state is much lower than the actual value, namely that calculated for the substance in the vapor state.

This discrepancy was later explained by Debye[5] as due to strong interactions between the dipoles.

Onsager[17] has considered a molecule in a spherical cavity, replacing the other molecules by a homogeneous dielectric. In this way he replaced the effect of the interaction with the other molecules by the effect of the image field. His formula gives

values of the dielectric constant which are much lower than the observed ones in the case of highly polar substances.

Kirkwood[5] and then Fröhlich[11] constructed formulae which depend on the knowledge of the relative distribution of any two dipoles, or the probability that two dipoles have a certain configuration.

One object of the present paper is to construct a formula which gives the dielectric constant in terms of the molecular parameters α and p. Since this formula will depend on the knowledge of the relative distribution of any two dipoles, it will be a very useful means of checking the accuracy of the distrib:-ution function of the dipoles, calculated by other methods.

A knowledge of the distribution function of the dipoles can also be used in calculating an additional average potential energy and an additional specific heat due to dipole interaction; the effect of dipole rotation on the X-ray scattering; the hydration of salts and many other things.

In the first chapter a formula is obtained by considering a big cavity containing many molecules, and thus allowing for the effect of the dipole interactions and the structure of the crystal concerned. This formula, which depends on the knowledge of the distribution of the dipoles reduces to that given by Kirkwood (15) for cubic crystals and neglect of α, but for other crystals it has a factor depending on the structure of the crystal.

In the second chapter a method for calculating the distribution function of two dipoles is suggested by considering the two molecules in question as in a cavity (or two cavities), finding the energy and then calculating the probability for such a distribution, using Boltzman's law.

The calculation of such a distribution function will be carried out for ice in the third chapter, and it will be shown to give a satisfactory value for the dielectric constant.

The effect of thermal vibrations in crystals has not been taken into account. It is by no means clear however that the thermal motion will not materially affect the results so far obtained, and for this reason this effect will be considered in Chapter IV. A

formula applicable to liquids will also be considered in the same chapter.

It is observed experimentally that the dielectric constant decreases very rapidly, almost discontinuously, for polar substances at a lower temperature, usually coincident with or a little lower than the melting point of the substance considered. This has been explained [21] as due to a transfer from a state of free rotations of the dipoles to a state where the dipoles are in ordered configurations, that is when a small number, have a certain configur: -ation which is repeated throughout the whole crystal.

It was assumed in the formulae so far obtained that the dipoles are free to rotate, or in a state of disorder. In the last chapter the case of ordered dipoles will be considered, as well as the stability of such ordered configurations.

CHAPTER I.

A NEW FORMULA FOR THE DIELECTRIC CONSTANT.

The Effect of the Dipoles Interactions

Consider an assembly of $N^{(0)}$ molecules confined within a spherical cavity of volume V, equal to $\frac{N^{(0)}}{N}$, where N is the number of molecules per unit volume. The space outside the cavity will be treated macroscopically as a continuous medium of dielectric constant ε. If the external field in the medium at a great distance from the cavity be $\underline{E}$ then the field inside the cavity will be $\underline{E}'$ given by (1.5).

Let the components of the field of the dipole moment of a molecule j acting on a molecule i be

$$-\frac{1}{\alpha}\sum_{s'=1}^{3}\lambda_{ss'}^{ij}\mu_{s'}^{j} \quad (s=1,2,3) \qquad (1.26)$$

where $\lambda_{ss'}^{ij}$ depends on the type of axes taken and will be given in the first appendix at the end of this chapter.

The field components $F_s^{(i)}$ acting on a molecule i are

$$F_s^{(i)} = E_s' - \frac{1}{\alpha} \sum_{j \neq i} \sum_{s'} \lambda_{ss'}^{ij} \mu_{s'}^{j} \qquad (1.27)$$

In this expression the image field, created by the moments of the molecules confined within the cavity, has been omitted. In fact, since we are considering a large number of molecules in the cavity, we shall neglect the effect of the image field of the dipoles on the configuration of the confined molecules.

The components of the electric moment of a molecule i can be written, following equation (1.11) in the form

$$\mu_s^{(i)} = p_s^{(i)} + \alpha F_s^{(i)} \qquad (1.28)$$

Eliminating $F_s^{(i)}$ between equations (1.27) and (1.28) we obtain

$$\mu_s^{(i)} + \sum_{j \neq i} \sum_{s'} \lambda_{ss'}^{ij} \mu_{s'}^{j} = p_s^{(i)} + \alpha E_s'$$

or, if we define

$$\lambda_{ss'}^{ii} = \delta_{ss'} \qquad (1.29)$$

then

$$\sum_{j} \sum_{s'} \lambda_{ss'}^{ij} \mu_{s'}^{j} = p_s^{(i)} + \alpha E_s' \qquad (1.30)$$

Therefore

$$\mu_s^{(i)} = \sum_{j s'} (\lambda^{-1})_{ss'}^{ij} \left(p_{s'}^{j} + \alpha E_{s'}' \right) \qquad (1.31)$$

where the matrix λ^{-1} is the reciprocal of the matrix λ. The energy W of the dipoles in a given configuration will be defined by

$$-\frac{\partial W}{\partial \mu_s^{(i)}} = \sum_{s'} g_{ss'} \left[F_{s'}^{(i)} - \frac{1}{2\alpha} (\mu_{s'}^{(i)} - p_{s'}^{(i)}) \right] \qquad (1.32)$$

where

$$g_{ss'} = \underline{e}_s \cdot \underline{e}_{s'} \qquad (1.33)$$

$\underline{e}_s$ $(s = 1, 2, 3)$ are unit vectors along the three axes of the crystal. From equations (1.27) and (1.32) one obtains

$$-W = \sum_i \sum_{ss'} \mu_s^{(i)} g_{ss'} E_{s'}' - \frac{1}{2\alpha} \sum_{ij}' \sum_{ss'} (\lambda g)_{ss'}^{ij} \mu_s^{(i)} \mu_{s'}^{(j)} + \text{const.} \qquad (1.34)$$
$$-\frac{1}{2\alpha} \sum_i \sum_{ss'} g_{ss'} (\mu_s^{(i)} - p_s^{(i)})(\mu_{s'}^{(i)} - p_{s'}^{(i)})$$

or, extending the second summation over $i = j$.

$$-W = \sum_i \sum_{ss'} \mu_s^{(i)} g_{ss'} E_{s'}' - \frac{1}{2\alpha} \sum_{ij} \sum_{ss'} (\lambda g - g)_{ss'}^{ij} \mu_s^{(i)} \mu_{s'}^{(j)} + \text{const.} \qquad (1.34)$$
$$-\frac{1}{2\alpha} \sum_i \sum_{ss'} g_{ss'} (\mu_s^{(i)} - p_s^{(i)})(\mu_{s'}^{(i)} - p_{s'}^{(i)})$$

Substituting for the value of $\mu_s^{(i)}$ from equation (1.31) we obtain

$$-W = \sum_{ij} \sum_{ss'} p_s^{(i)} (g \lambda^{-1})_{ss'}^{ij} E_{s'}' - \frac{1}{2\alpha} \sum_{ij} \sum_{ss'} (g - g \lambda^{-1})_{ss'}^{ij} p_s^{(i)} p_{s'}^{(j)} \qquad (1.35)$$

to the first power in E'.

The probability ρ for the occurrence of a given configuration is given by (1.17). Putting

$$W = W^{(0)} - W^{(1)} \qquad (1.36)$$

where $W^{(0)}$ is the energy in the absence of external

field and $W^{(i)}$ is linear in E'. Then the probability ρ is given by

$$\rho = \rho_0 \left(1 + \frac{W^{(i)}}{kT} \right) \qquad (1.37)$$

to the first power in E', ρ_0 being the probability in the absence of an external field.

Substituting for $W^{(i)}$ from equation (1.35) we obtain

$$\rho = \rho_0 \left[1 + \frac{1}{kT} \sum_{ij} \sum_{ss'} p_s^{(i)} (g \lambda^{-1})_{ss'}^{ij} E_{s'}' \right] \qquad (1.38)$$

Because $\sum_j (g \lambda^{-1})_{ss'}^{ij} = (g \lambda^{-1})_{ss'}$, where

$$\lambda_{ss'} = \sum_j \lambda_{ss'}^{ij} \quad , \qquad (1.39)$$

(independent of i)

(See appendix II at the end of this Chapter).

equation (1.38) becomes

$$\rho = \rho_0 \left[1 + \frac{1}{kT} \sum_{ss'} \sum_i p_s^{(i)} (g \lambda^{-1})_{ss'} E_{s'}' \right] \qquad (1.40)$$

So far we have neglected the effect of the image field which is not represented in the expression for the probability of a given configuration specified by equation (1.38). But when we pass on to find the average total electric moment of the confined molecules, namely the average of $\sum_i \mu_s^{(i)}$, we shall

not use the expression for $\mu_s^{(i)}$ given by equation (1.31), but instead, we shall use an expression containing an extra term resulting from the image field; this will be shown in the following.

If $\xi_s^{(i)}$ are the components of the image field acting on a molecule (i) which is created by the presence of the molecules inside the cavity, then the total field acting on a molecule i will be given, instead of (1.27), by

$$F_s^{(i)} = E_s' + \xi_s^{(i)} - \frac{1}{\alpha} \sum_{j' \neq i} \sum_{s'} \lambda_{ss'}^{ij'} \mu_{s'}^{j'} \qquad (1.41)$$

Eliminating $F_s^{(i)}$ between (1.41) and (1.28) one obtains

$$\sum_{j's'} \lambda_{ss'}^{ij'} \mu_{s'}^{j'} = \alpha E_s' + \alpha \xi_s^{(i)} + p_s^{(i)} \qquad (1.42)$$

and therefore

$$\mu_s^{(i)} = \sum_{j's'} (\lambda^{-1})_{ss'}^{ij'} \left(p_{s'}^{j'} + \alpha E_{s'}' + \alpha \xi_{s'}^{j'} \right) \qquad (1.43)$$

This differs from equation (1.31) by the addition of an extra term due to the image field. Summing (1.43) over i, one finds

$$\sum_i \mu_s^{(i)} = \sum_{j's'} (\lambda^{-1})_{ss'} \left(p_{s'}^{j'} + \alpha E_{s'}' + \alpha \xi_{s'}^{j'} \right) \qquad (1.44)$$

By a limiting procedure $\frac{1}{N^{(i)}} \sum_{j'} \xi_{s'}^{j'}$ can be shown to be equivalent to the space average of the

image field inside the cavity. This space average of the image field is shown in the third appendix to be equal to $\frac{f}{N'a^3}\sum_{j'}\mu_{s'}^{j'}$ and therefore

$$\sum_{j'}\mathcal{E}_{s'}^{j'} = \frac{f}{a^3}\sum_{j'}\mu_{s'}^{j'} \qquad (1.45)$$

Using equations (1.45), equation (1.44) becomes

$$\sum_{j'}\mu_{s'}^{j'} = \sum_{j's'}(\mathcal{A}^{-1})_{ss'}\left(p_{s'}^{j'} + \alpha E_{s'}'\right) + \beta f \sum_{j's'}(\mathcal{A}^{-1})_{ss'}\mu_{s'}^{j'}$$

that is

$$\sum_{j'}\mu_{s}^{j'} = \sum_{j's'}\left(\frac{\mathcal{A}^{-1}}{1-\beta f\mathcal{A}^{-1}}\right)_{ss'}\left(p_{s'}^{j'} + \alpha E_{s'}'\right) \qquad (1.46)$$

For a cubic crystal one has the tensor equation $\mathcal{A} = 1$ and therefore equation (1.46) will be similar to equation (1.12) when only one molecule was supposed to be inside the cavity.

From equations (1.40), (1.46) one obtains for the product $\rho\sum_{j'}\mu_{s}^{j'}$ the following expression

$$\rho\sum_{j'}\mu_{s}^{j'} = \rho_0\sum_{s'}\left(\frac{\mathcal{A}^{-1}}{1-\beta f\mathcal{A}^{-1}}\right)_{ss'}\left\{\sum_{j'}\left(p_{s'}^{j'} + \alpha E_{s'}'\right) + \frac{1}{kT}\sum_{ij}\sum_{\sigma\sigma'}p_{\sigma}^{i}p_{s'}^{j'}(g\mathcal{A}^{-1})_{\sigma\sigma'}E_{\sigma'}'\right\} \qquad (1.47)$$

to the first power in E'.

The average value $\sum_{j'}\bar{\mu}_{s}^{j'}$ is the sum of $\rho\sum_{j'}\mu_{s}^{j'}$ over all the orientations of the molecules.

Putting

$$\overline{p_{s}^{i1}p_{s'}^{j'}} = \sum_{p_1\cdots p_N}\rho_0\, p_{s}^{i1}p_{s'}^{j'} \qquad (1.48)$$

the summation being taken over all the orientations of the molecules, and since $\sum_{p_1 \cdots p_N} \rho_0 \sum_{\alpha} p_s^{\alpha} = 0$ we obtain

$$\frac{1}{N\omega} \sum_{\alpha} \bar{\mu}_s^{\alpha} = \sum_{s'} \left(\frac{\Lambda^{-1}}{1-\beta f \Lambda^{-1}} \right)_{ss'} \left\{ \alpha E'_{s'} + \frac{p^2}{kT} \sum_{\sigma'} (Qg\Lambda^{-1})_{s\sigma'} E'_{\sigma'} \right\} \quad (1.49)$$

where

$$p^2 Q_{ss'} = \sum_{\alpha} \overline{p_s^{\alpha} p_{s'}^{\alpha}} \quad (1.50)$$

Since

$$\frac{1}{N\omega} \sum_{\alpha} \bar{\mu}_s^{\alpha} = \frac{1}{N} P_s ,$$

where $\underline{P}$ is the polarisation ,

then equation (1.49) becomes

$$\frac{1}{N} P_s = \sum_{s'} \left[\frac{\Lambda^{-1}}{1-\beta f \Lambda^{-1}} \left\{ \alpha + \frac{p^2}{kT} (Qg\Lambda^{-1}) \right\} \right]_{ss'} E'_{s'} \quad (1.51)$$

But by definition

$$P_s = \sum_{s'} \left(\frac{\varepsilon - 1}{4\pi} \right)_{ss'} E_{s'} , \quad (1.52)$$

then we obtain

$$\frac{\varepsilon - 1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0 + 1} \left[\beta \frac{\Lambda^{-1}}{1-\beta f \Lambda^{-1}} + \frac{p^2}{\alpha^3 kT} \frac{\Lambda^{-2} g Q}{1-\beta f \Lambda^{-1}} \right] \quad (1.53)$$

In this equation the symbol ε represents a tensor though the suffixes are not explicitly shown while ε_0 is a number taken to be $\frac{1}{3}\sum_s (\varepsilon g)_{ss}$ also f is a number given by $\frac{2(\varepsilon_0-1)}{2\varepsilon_0+1}$.

For a cubic crystal $\lambda = 1$, i.e. $\lambda_{ss'} = \delta_{ss'}$ also $Q_{ss'} = Q_0 \delta_{ss'}$ and therefore $\varepsilon_{ss'} = \varepsilon_0 \delta_{ss'}$.

Hence equation (1.53) becomes for this special case

$$\frac{\varepsilon_0-1}{3} = \frac{\varepsilon_0+2}{3}\beta + \frac{3\varepsilon_0}{2\varepsilon_0+1}\frac{P^2}{a^3kT} Q_0 \qquad (1.54)$$

The evaluation of Q as will be seen in the next chapter, will again depend on an image field, and so on the dielectric constant. Therefore equation (1.54) can only be considered as a verification of the calculation of Q_0 , or of the calculation of the configurational probability of the dipoles, and it cannot be used directly to calculate ε_0 . Naturally there must be a value of ε_0 which satisfies (1.54) but to find such a value is a very lengthy and impracticable problem.

APPENDIX I

The Tensor λ

This tensor was defined by equations (1.26) and (1.29) for $i \neq j$ and $i = j$ respectively. It is required now to find an expression for it for any type of crystal.

Let $\phi^{(i)}$ be the value of the potential at the position occupied by the molecule i due to the moment of the molecule j, then

$$-\frac{\partial \phi^{(i)}}{\partial x_s^{ij}} = \sum_{s'} g_{ss'} F_{s'}^{(i)} \qquad (1.55)$$

where the $g_{ss'}$ are defined by (1.33).
If R_{ij} is the distance between the two molecules considered, then

$$\phi^{(i)} = -\sum_{s'} \frac{\partial}{\partial x_{s'}^{ij}} \left(\frac{1}{R_{ij}}\right) \mu_{s'}^{j} \qquad (1.56)$$

Substituting for $F_s^{(i)}$ from equation (1.26) and for $\phi^{(i)}$ from (1.56), the equation (1.55) becomes

$$-\frac{1}{\alpha}\sum_{s'} (g\lambda)_{ss'}^{ij} \mu_{s'}^{j} = \sum_{s'} \frac{\partial^2}{\partial x_s^{ij} \partial x_{s'}^{ij}} \left(\frac{1}{R_{ij}}\right) \mu_{s'}^{j},$$

then

$$(g\lambda)_{ss'}^{ij} = -\frac{\partial^2}{\partial x_s^{ij} \partial x_{s'}^{ij}} \left(\frac{\alpha}{R_{ij}}\right) \qquad (1.57)$$

Since

$$R_{ij}^2 = \sum_{ss'} g_{ss'} x_s^{ij} x_{s'}^{ij}, \quad \text{and}$$

$$R_{ij} \frac{\partial R_{ij}}{\partial x_s^{ij}} = \sum_{s'} g_{ss'} x_{s'}^{ij} = y_s^{ij} \quad (\text{say})$$

then

$$(g\lambda)^{ij}_{ss'} = \frac{\alpha}{R_{ij}^3} g_{ss'} - \frac{3\alpha}{R_{ij}^5} y_s^{ij} y_{s'}^{ij} \qquad (1.58)$$

or

$$(\bar{g}^{-1}\lambda^{-1})^{ij}_{ss'} = \frac{\alpha}{R_{ij}^3} \bar{g}^{-1}_{ss'} - \frac{3\alpha}{R_{ij}^5} x_s^{ij} x_{s'}^{ij} \qquad (1.59)$$

APPENDIX II

The Tensor $\mathcal{A}$

This tensor was defined by equation (1.39) namely

$$\mathcal{A}_{ss'} = \sum_{i} \lambda^{ii}_{ss'}$$

which is assumed to be independent of i.

It is required to prove that

$$\sum_{i} [f(\lambda)]^{ii}_{ss'} = [f(\mathcal{A})]_{ss'} \qquad (1.60)$$

where $f(\lambda)$ is any tensor function of λ.

$f(\mathcal{A})$ is the same function of $\mathcal{A}$

To do this we start by considering $f(\lambda) = \lambda^2$,

$$\sum_{i} (\lambda^2)^{ii}_{ss'} = \sum_{i} \sum_{l\sigma} \lambda^{il}_{s\sigma} \lambda^{li}_{\sigma s'} = \sum_{l\sigma} \lambda^{il}_{s\sigma} \mathcal{A}_{\sigma s'} = \sum_{\sigma} \mathcal{A}_{s\sigma} \mathcal{A}_{\sigma s'}$$

$$= (\mathcal{A}^2)_{ss'} \,, \qquad \text{using equation (1.39)}$$

By successive pre-multiplication by λ one obtains

$$\sum_{i} (\lambda^n)^{ij}_{ss'} = (\mathcal{A}^n)_{ss'}$$

and hence the required formula (1.60) follows.

APPENDIX III.

The Image Field inside the Cavity.

To find the image field due to the moment of a molecule situated at any point inside the spherical cavity, we start by considering a charge e situated at a point distant $c_0 < a_0$ from the centre of the spherical cavity whose radius is a_0.

If the potential inside the cavity is ϕ_1, and that in the dielectric is ϕ_2 then

$$\nabla^2\phi_1 = 0 \qquad \nabla^2\phi_2 = 0 \tag{1.61}$$

and at the boundary of the cavity

$$\phi_1 = \phi_2 \qquad \frac{\partial\phi_1}{\partial n} = \varepsilon\frac{\partial\phi_2}{\partial n} \tag{1.62}$$

From (1.61) ϕ_1 . ϕ_2 can be written in the form

$$\phi_1 = \frac{e}{r}\sum_{n=0}^{\infty}\left(\frac{c_0}{r}\right)^n P_n(\cos\theta) + \sum_{n=0}^{\infty} A_n r^n P_n(\cos\theta)$$

$$\phi_2 = \sum_{n=0}^{\infty}\frac{B_n}{r^{n+1}} P_n(\cos\theta)$$

Applying the boundary conditions (1.62) one obtains

$$A_n = -\frac{e c_0^n}{a_0^{2n+1}}\left(\frac{\varepsilon-1}{\varepsilon+1}\right)\frac{n+1}{n+\sigma}$$

where

$$\sigma = \frac{\varepsilon}{\varepsilon+1}$$

Fig. (2)

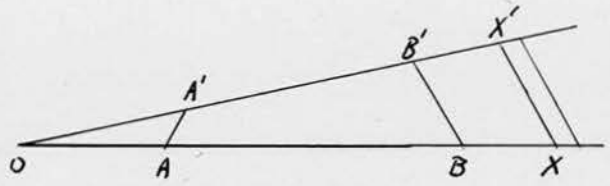


Fig. (3)

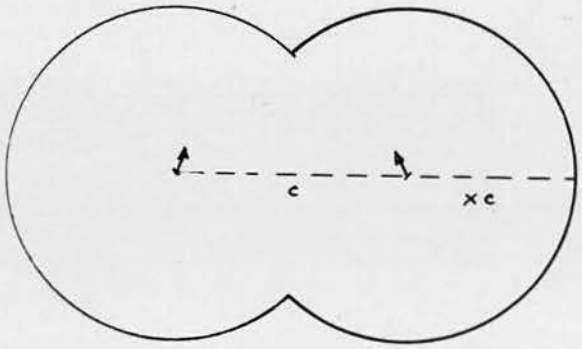


Fig. (4)

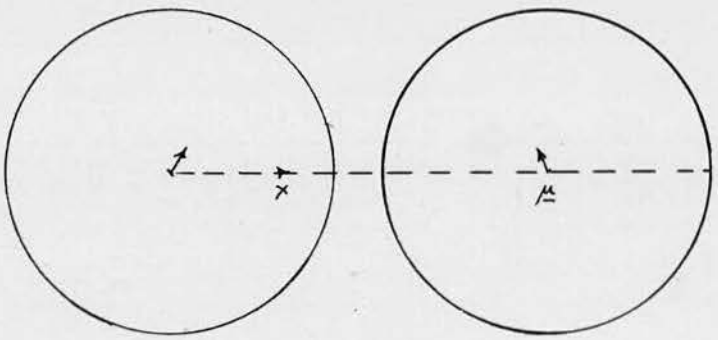
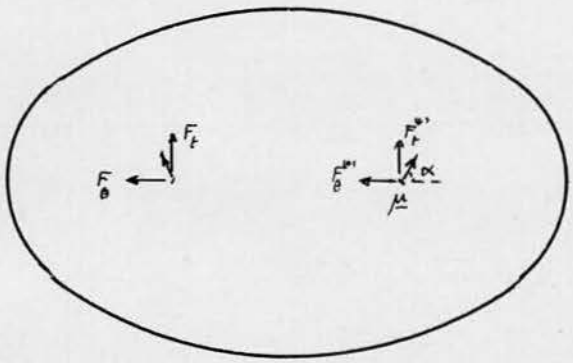


Fig. (5)



Therefore the image potential inside the cavity is

$$\phi = -\frac{e}{a_0}\frac{\xi-1}{\xi+1}\sum_{m=0}^{\infty}\left(\frac{c_0 r}{a_0^2}\right)^m \frac{m+1}{m+\sigma} P_m(\cos\theta)$$

$$= -\frac{e a_0}{c_0}\frac{\xi-1}{\xi+1}\sum_{m=0}^{\infty}\frac{r^m P_m(\cos\theta)}{\left(\frac{a_0^2}{c_0}\right)^{m+1}} - \frac{e}{a_0}\frac{\xi-1}{(\xi+1)^2}\sum_{m=0}^{\infty}\left(\frac{c_0 r}{a_0^2}\right)^m \frac{1}{m+\sigma} P_m(\cos\theta) \qquad (1.63)$$

Since

$$\left(\frac{c_0}{a_0^2}\right)^m \frac{1}{m+\sigma} = \int_{\frac{a_0^2}{c_0}}^{\infty} \frac{dx}{x^{m+1}}\left(\frac{a_0^2}{c_0 x}\right)^{\sigma} ,$$

then the image field inside the cavity is due to

(i) a charge $-\frac{e a_0}{c_0}\frac{\xi-1}{\xi+1}$ at the inverse point $x = \frac{a_0^2}{c_0}$

(ii) a line charge of density $-\frac{e}{a_0}\frac{\xi-1}{(\xi+1)^2}\left(\frac{a_0^2}{c_0 x}\right)^{\sigma}$ from $x = \frac{a_0^2}{c_0}$ to $x = \infty$. (1.64)

We now consider a dipole $\underline{\mu}$ at $x = c_0$. This is equivalent to a charge $-e$ at $\underline{c}_0$ and a charge $+e$ at $\underline{c}_0' = \underline{c}_0 + \frac{1}{e}\underline{\mu}$.

In Fig. (2) $\overrightarrow{OA}$ represents $\underline{c}_0$ and $\overrightarrow{OA'}$ represents $\underline{c}_0'$. B . B' are the inverse points of A , A' respectively with respect to the hollow sphere. If $\underline{c}_0 = c_0 \underline{k}$ then $c_0' = c_0 + \frac{1}{e}(\underline{\mu}\cdot\underline{k})$

The image system due to a charge $+e$ at A' is (i) a charge $-\frac{e a_0}{c_0'}\frac{\xi-1}{\xi+1}$

$$= -\frac{e a_0}{c_0}\frac{\xi-1}{\xi+1} + \frac{a_0}{c_0^2}\frac{\xi-1}{\xi+1}(\underline{\mu}\cdot\underline{k}) \quad \text{at } B'$$

(ii) a line charge from B' to infinity. The charge between x' and $x'+dx'$ is $-\frac{e}{a_0}\frac{\xi-1}{(\xi+1)^2}\left(\frac{a_0^2}{c_0' x'}\right)^{\sigma} dx'$ where OX' in the figure represents x' .

Since $c'x' = cx$ then the latter is

$$-\frac{e}{a_0}\frac{\xi-1}{(\xi+1)^2}\left(\frac{a_0^2}{c_0 x}\right)^{\sigma} dx + \frac{1}{a_0 c_0}\frac{\xi-1}{(\xi+1)^2}\left(\frac{a_0^2}{c_0 x}\right)^{\sigma}(\underline{\mu}\cdot\underline{k})\, dx$$

Combining this image system of $+e$ with the image system of $-e$ at A we obtain for the image system due to the dipole, remembering that $(BB') = \frac{a_0^2}{c_0^2}(AA')$ and $(XX') = \frac{x}{c_0}(AA')$.

(i) a charge $\frac{a_0}{c_0^2}\left(\frac{\xi-1}{\xi+1}\right)(\underline{\mu}\cdot\underline{k})$ at $x = \frac{a_0^2}{c_0}$

(ii) a line charge of density $\frac{1}{a_0 c_0}\frac{\xi-1}{(\xi+1)^2}\left(\frac{a_0^2}{c_0 x}\right)^{\sigma}(\underline{\mu}\cdot\underline{k})$

from $x = \frac{a_0^2}{c_0}$ to $x = \infty$

(iii) a dipole $-\frac{a_0^3}{c_0^3}\left(\frac{\xi-1}{\xi+1}\right)[\underline{\mu} - 2(\underline{\mu}\cdot\underline{k})\underline{k}]$ at $x = \frac{a_0^2}{c_0}$

(iv) a line dipole of density $-\frac{a_0}{c_0^2}\frac{\xi-1}{(\xi+1)^2}\left(\frac{c_0 x}{a_0^2}\right)^{1-\sigma}[\underline{\mu} - 2(\underline{\mu}\cdot\underline{k})\underline{k}]$

from $x = \frac{a_0^2}{c_0}$ to $x = \infty$ (1.65)

The image field of the dipole inside the cavity is thus given by the field of the image system (1.65) which lies outside the cavity.

The space average value of the image field created by the dipole $\underline{\mu}$ (at distance $c_0 < a_0$ from the centre) inside the cavity is equal to the field of the image system (1.65) at the centre of the cavity.

The field, at the centre of the cavity, of the system given by (1.65) can easily be found to be

$$\underline{\psi} = \frac{1}{a_0^3}\,\frac{2(\xi-1)}{2\xi+1}\,\underline{\mu} \qquad (1.66)$$

Now if there are $N^{(j)}$ molecules inside the cavity, then the average image field of all the molecules inside the cavity is

$$\frac{f}{a^3}\sum_i \underline{\mu}^{(j)} = \frac{f}{N^{(j)}a^3}\sum_i \underline{\mu}^{(j)} \qquad (1.67)$$

CHAPTER II

THE CONFIGURATIONAL PROBABILITY

In the last chapter the dielectric constant was shown to depend on a factor Q given by equations (1.48) and (1.50). In this chapter a direct evaluation of Q from those equations will be carried out.

Since the configurational probability ρ_0 depends on the energy $W^{(0)}$ of the dipoles in the given configuration, the evaluation of Q will depend on a knowledge of $W^{(0)}$.

The energy in a given configuration $W^{(0)}$ is, according to equations (1.35), (1.36) expressed by

$$W^{(0)} = \frac{1}{2} \sum_{ij} \sum_{ss'} \mathcal{U}^{ij}_{ss'} p^i_s p^j_{s'} \tag{2.1}$$

where

$$\mathcal{U}^{ij}_{ss'} = \frac{1}{\alpha} (g - g\lambda^{-1})^{ij}_{ss'} \tag{2.2}$$

The sum over states Z is defined by

$$Z = \sum_{p_1 \cdots p_N} \exp \left\{ -\frac{1}{2kT} \sum_{ij} \sum_{ss'} \mathcal{U}^{ij}_{ss'} p^i_s p^j_{s'} \right\} \tag{2.3}$$

where the summation is over all orientations of the dipoles. The tensor $\mathcal{U}$ as defined by (2.2) is clearly $\frac{1}{a^3}$ multiplied by a function of β (See (1.59)(1.13))

Then Z as defined by (2.3) is a function of $\frac{p^2}{a^3 kT}$ and β. The tensor $\frac{\partial Z}{\partial \mathcal{U}}$ is given by

$$\frac{\partial Z}{\partial \mathcal{U}^{ij}_{ss'}} = -\frac{1}{2kT} \sum_{p_1 \cdots p_N} p^i_s p^j_{s'} \exp \left\{ -W^{(0)}/kT \right\} \tag{2.4}$$

By using equation (1.48) one obtains

$$-\frac{2kT}{Z}\frac{\partial Z}{\partial \mathcal{U}^{ij}_{ss'}} = \overline{p^{(i)}_s p^{(j)}_{s'}} \qquad (2.5)$$

and therefore by use of (1.50)

$$Q_{ss'} = -\frac{2kT}{p^2}\sum_{i}\frac{\partial}{\partial \mathcal{U}^{ij}_{ss'}}(\log Z) \qquad (2.6)$$

which is clearly a function of $\frac{p^2}{a^3 kT}$ and β. There is no way of finding $\overline{p^{(i)}_s p^{(j)}_{s'}}$ from equation (2.5) or (1.48) by evaluating the sums given. These sums, however, can be evaluated in the case of thermal vibrations, with which we shall deal in the fourth chapter.

We therefore have to use some other approximate method to find $\overline{p^{(i)}_s p^{(j)}_{s'}}$.

The expression $\overline{p^{(i)}_s p^{(j)}_{s'}}$ does not, however, require a knowledge of the probability of a config: -uration of the whole set of dipoles, but can be evaluated if the probability of only the two mole: -cules concerned is known for any configuration. This is clear since

$$\sum_{p_1 \cdots p_N} p^{(i)}_s p^{(j)}_{s'} \varrho_0(p_1 \cdots p_N) = \sum_{p_i p_j} p^{(i)}_s p^{(j)}_{s'} \varrho^{ij}_0(p_i p_j) \qquad (2.7)$$

To evaluate the probability ϱ^{ij}_0 of the two molecules i, j, we adopt the approximate method of replacing the rest of the molecules macroscopically by a homogeneous dielectric. The most convenient shape of the internal boundary of this dielectric will be considered later. The steps required for the evaulation of ϱ^{ij}_0 are as follows.

We first calculate the field acting on the two molecules in a given configuration. This field will depend on the dielectric constant, since the two molecules concerned lie in the neighbourhood of a homogeneous dielectric. We then formulate the mutual potential energy in the same configuration, which will depend on the induced moment as well as on the permanent moment. The probability ρ_0^{ψ} is then found by Boltzman's law. In this method, as well as in the exact method shown at the beginning of this chapter, Q will depend on p and α through the quantities $\frac{p^2}{a^3 kT}$ and β. The factor Q in this method will also depend on the dielectric constant.

<u>The field acting on the two molecules.</u>

The two events when the two molecules concerned are not first neighbours, and when they are first neighbours, will be treated separately. When the two molecules are not first neighbours, the internal boundary of the dielectric will be chosen to be two separate spheres with the two molecules concerned at their centres. The volume of each sphere is taken to be equal $\frac{1}{N} = \frac{4\pi}{3} a^3$. A method of successive images will be explained in the first appendix to find the field at the centres of the two

spheres of a dipole $\underline{\mu}$ at the centre of one of them. The field inside the sphere in which the dipole lies is found to be equal to

$$\frac{f}{a^3}\underline{\mu}, \tag{2.8}$$

and the field at the centre of the other sphere is the same as the field of a dipole,

$$\frac{q\xi}{(2\xi+1)^2}\underline{\mu} \tag{2.9}$$

at the centre of the first sphere.

There are other terms due to further successive image fields and containing the parameter $\frac{a^2}{c^2}$ where c is the distance between the two molecules. These terms were found small, even in the case when the two molecules are second neighbours, and therefore are neglected. Now if the molecule at the centre of one of the two spherical cavities has the moment $\underline{\mu}^{(1)}$ and the molecule at the centre of the other spherical cavity has the moment $\underline{\mu}^{(2)}$ then the field acting on the first molecule, following equations (2.8) and (2.9) is given by

$$\underline{F}^{(1)} = \frac{f}{a^3}\underline{\mu}^{(1)} - \frac{q\xi}{(2\xi+1)^2}\frac{1}{c^3}\{\underline{\mu}^{(2)} - 3(\underline{\mu}^{(2)}\cdot\underline{k})\underline{k}\} \tag{2.10}$$

If we write the field in the form

$$-\alpha\underline{F}^{(1)} = (A_0-1)\underline{\mu}^{(1)} + (B_0-A_0)(\underline{\mu}^{(1)}\cdot\underline{k})\underline{k} + A\underline{\mu}^{(2)} + (B-A)(\underline{\mu}^{(2)}\cdot\underline{k})\underline{k} \tag{2.11}$$

then from (2.10)

$$A_0 = B_0 = 1 - \beta f \qquad (2.12)$$

$$A = \frac{9\xi}{(2\xi+1)^2}\frac{\alpha}{c^3} \qquad B = -2A \qquad (2.13)$$

When the molecules are first neighbours, the two spherical cavities surrounding the two molecules will overlap; and thus form a single cavity of volume less than the required volume, i.e. $\frac{2}{N}$. We might therefore consider the radius of each of the over: -lapping spheres to be xc where c is the distance between first neighbours, as shown in figure(3). In this case the volume of the cavity would be

$$\frac{\pi c^3}{12}(2x+1)^2(4x-1)$$

Equating this to $\frac{8\pi}{3}a^3$ we obtain

$$\frac{1}{x^3} - \frac{12}{\left(1+\frac{32a^3}{c^3}\right)}\frac{1}{x} - \frac{16}{\left(1+32\frac{a^3}{c^3}\right)} = 0 \qquad (2.14)$$

which is a cubic equation to determine $\frac{1}{x}$ and hence the radius xc of each of the overlapping spheres.

The evaluation of the field inside such a cavity is, however, found to be very difficult and therefore a cavity in the form of an ellipsoid of revolution, with its axis of revolution passing through the two molecules, will actually be considered. The

equation (2.14) will be used to fix the dimensions of the cavity. If the distance between the foci is $2b$ and the major axis is $2b\cosh t$ then the volume of the cavity is

$$\frac{4\pi}{3} b^3[(\cosh t)^3 - (\cosh t)]$$

Equating this to $\frac{8\pi}{3} a^3$ one obtains

$$(\cosh t)^3 - (\cosh t) - \frac{2a^3}{b^3} = 0 \qquad (2.15)$$

This equation, although it has fixed the volume of the cavity, has not fixed the form of the ellipsoid of revolution, since it connects two parameters b and $\cosh t$.

We choose the form of the ellipsoid to coincide as much as possible with the cavity of the two over-laping spheres whose dimensions are given by equation (2.14).

This method of choosing the form of the ellipsoid may be criticized as not precise; but bearing in mind that the image field inside the cavity does not change appreciably in changing the shape of the ellipsoid, this method will be accurate enough.

The additional or the image field inside the cavity created by the presence of a dipole $\underline{\mu}$, on the line between the foci and at a distance $\frac{1}{2}c < b$ from the centre, will be given in the second appendix.

The field at the position of the dipole (due to the image field of this dipole alone) is found to be

$$C_0 \underline{\mu} + D_0 (\underline{\mu} \cdot \underline{k}) \underline{k} , \qquad (2.16)$$

and the image field at the position of the other dipole (which was not taken into account) is

$$C \underline{\mu} + D (\underline{\mu} \cdot \underline{k}) \underline{k} \qquad (2.17)$$

where

$$\left.\begin{aligned} C_0 &= \frac{-1}{b^3} \sum_{n=0}^{\infty} (n+\tfrac{1}{2}) \left\{ P_n'\left(\frac{c}{2b}\right) \right\}^2 \frac{Q_n'(\cosh t)}{P_n'(\cosh t)} \frac{1}{(1 - X_n^{(1)})} \\ C_0 + D_0 &= \frac{2}{b^3} \sum_{n=0}^{\infty} (n+\tfrac{1}{2}) \left\{ P_n'\left(\frac{c}{2b}\right) \right\}^2 \frac{Q_n(\cosh t)}{P_n(\cosh t)} \frac{1}{1 - X_n} \end{aligned}\right\} \qquad (2.18)$$

$$\left.\begin{aligned} C &= \frac{1}{b^3} \sum_{n=0}^{\infty} (-)^n (n+\tfrac{1}{2}) \left\{ P_n'\left(\frac{c}{2b}\right) \right\}^2 \frac{Q_n'(\cosh t)}{P_n'(\cosh t)} \cdot \frac{1}{1 - X_n^{(1)}} \\ C + D &= -\frac{2}{b^3} \sum_{n=0}^{\infty} (-)^n (n+\tfrac{1}{2}) \left\{ P_n'\left(\frac{c}{2b}\right) \right\}^2 \frac{Q_n(\cosh t)}{P_n(\cosh t)} \cdot \frac{1}{1 - X_n} \end{aligned}\right\} \qquad (2.19)$$

where X_n , $X_n^{(1)}$ are given by the equations

$$\left.\begin{aligned} (\xi - 1) X_n &= \frac{Q_n(\cosh t) P_n'(\cosh t) - Q_n'(\cosh t) P_n(\cosh t)}{P_n(\cosh t) Q_n'(\cosh t)} \\ (\xi - 1) X_n^{(1)} &= \frac{\sinh^2 t}{P_n'(\cosh t)} \cdot \frac{Q_n'(\cosh t) P_n''(\cosh t) - Q_n''(\cosh t) P_n'(\cosh t)}{\cosh t\, Q_n'(\cosh t) + \sinh^2 t\, Q_n''(\cosh t)} \end{aligned}\right\} \qquad (2.20)$$

$2b$ is the distance between the foci and $2b \cosh t$ is the major axis, both being determined by equation (2.15) and the choice of the form of the ellipsoid with the help of (2.14).

P_m . Q_m are Legendre functions and Legendre associated functions respectively. The evaluation of the field thus depends on the computation of infinite series. The numerical calculation, as will be found in the next chapter, is not very difficult, since only a few terms in the series given by (2.18) and (2.19) will be needed.

Now let the two molecules, on the axis of the ellipsoidal cavity and at distances $\frac{1}{2}c$ on both sides from the centre, have moments $\underline{\mu}^{(1)}$ and $\underline{\mu}^{(2)}$. Writing the field acting on the dipole $\underline{\mu}^{(1)}$ in the form (2.11), then the constants A_0 . B_0 . A and B in that equation will be given (using equations (2.16), (2.17), (218) and (2.19) and taking into account the field of $\underline{\mu}^{(2)}$ at $\underline{\mu}^{(1)}$) by

$$\left.\begin{aligned} A_0 - 1 &= \frac{\alpha}{b^3}\sum_{n=0}^{\infty}(n+\tfrac{1}{2})\left\{P_n'\left(\tfrac{c}{2b}\right)\right\}^2 \frac{Q_n'(\cosh t)}{P_n'(\cosh t)} \cdot \frac{1}{1-\chi_n^{(1)}} \\ B_0 - 1 &= -\frac{2\alpha}{b^3}\sum_{n=0}^{\infty}(n+\tfrac{1}{2})\left\{P_n'\left(\tfrac{c}{2b}\right)\right\}^2 \frac{Q_n(\cosh t)}{P_n(\cosh t)} \cdot \frac{1}{1-\chi_n} \end{aligned}\right\} \qquad (2.21)$$

$$\left.\begin{aligned} A &= \frac{\alpha}{c^3} - \frac{\alpha}{b^3}\sum_{n=0}^{\infty}(-)^n(n+\tfrac{1}{2})\left\{P_n'\left(\tfrac{c}{2b}\right)\right\}^2 \frac{Q_n'(\cosh t)}{P_n'(\cosh t)} \cdot \frac{1}{1-\chi_n^{(1)}} \\ B &= -\frac{2\alpha}{c^3} + \frac{2\alpha}{b^3}\sum_{n=0}^{\infty}(-)^n(n+\tfrac{1}{2})\left\{P_n'\left(\tfrac{c}{2b}\right)\right\}^2 \frac{Q_n(\cosh t)}{P_n(\cosh t)} \cdot \frac{1}{1-\chi_n} \end{aligned}\right\} \qquad (2.22)$$

The Mutual Potential Energy.

The field acting on one of the two molecules given by equation (2.11) in vector form, can be re-written in the tensor form

$$-\alpha F_s^{(i)} = \sum_{j s'} (\lambda - 1)^{ij}_{ss'} \mu_{s'}^{j} \qquad (2.23)$$

(not to be confused with λ defined by (1.59))

If the axes considered are orthogonal then λ will be given by

$$\lambda''_{ss'} = \lambda^{22}_{ss'} = A_0 \delta_{ss'} + (B_0 - A_0) k_s k_{s'} = \gamma^{(0)}_{ss'} \quad \text{say}$$

$$\lambda^{12}_{ss'} = \lambda^{21}_{ss'} = A \delta_{ss'} + (B - A) k_s k_{s'} = \gamma_{ss'} \quad \text{say}$$

where $\underline{k}$ is a unit vector along the line joining the two molecules. Omitting the suffixes s, s' then

$$\lambda \equiv \begin{pmatrix} \gamma_0 & \gamma \\ \gamma & \gamma_0 \end{pmatrix} \qquad (2.24)$$

where

$$\left.\begin{aligned} \gamma_0 &= A_0 + (B_0 - A_0)(kk) \\ \gamma &= A + (B - A)(kk) \end{aligned}\right\} \qquad (2.25)$$

It was already explained in the first chapter that if the field acting on a molecule i is given by the expression (2.23) then the mutual potential energy is given by

$$W = \frac{1}{2\alpha} \sum_{ij'} \sum_{ss'} (1 - \lambda^{-1})^{ij}_{ss'} p_s^i p_{s'}^{j} \qquad (2.26)$$

In this case i, j have only the two values one and two and so (2.26) can be written in the form

$$W = \frac{1}{2\alpha}\sum_{ss'}(1-\lambda^{-1})^{11}_{ss'}\left(p^{(0)}_s p^{(1)}_{s'} + p^{(2)}_s p^{(2)}_{s'}\right) + \frac{1}{\alpha}\sum_{ss'}(1-\lambda^{-1})^{12}_{ss'} p^{(0)}_s p^{(2)}_{s'} \qquad (2.27)$$

It is proved in the third appendix that if λ is given by (2.24) and $f(\lambda)$ is any tensor function of λ then

$$\left.\begin{aligned} [f(\lambda)]^{11} &= [f(\lambda)]^{22} = \tfrac{1}{2} f(\gamma_0+\gamma) + \tfrac{1}{2} f(\gamma_0-\gamma) \\ [f(\lambda)]^{12} &= [f(\lambda)]^{21} = \tfrac{1}{2} f(\gamma_0+\gamma) - \tfrac{1}{2} f(\gamma_0-\gamma) \end{aligned}\right\} \qquad (2.28)$$

In particular taking $f(\lambda) = 1 - \lambda^{-1}$ then omitting suffixes s, s'

$$\left.\begin{aligned} (1-\lambda^{-1})^{11} &= \frac{-\gamma_0}{\gamma_0^2-\gamma^2} + 1 = F_0(\gamma_0\gamma) \text{ say} \\ (1-\lambda^{-1})^{12} &= \frac{\pm\gamma}{\gamma_0^2-\gamma^2} = F(\gamma_0\gamma) \text{ say} \end{aligned}\right\} \qquad (2.29)$$

The expression (2.27) can then be written, using (2.29), in the form

$$W = \frac{1}{2\alpha}\sum_{ss'}\{F_0(\gamma_0\gamma)\}_{ss'}\left(p^{(1)}_s p^{(1)}_{s'} + p^{(2)}_s p^{(2)}_{s'}\right) + \frac{1}{\alpha}\sum_{ss'}\{F(\gamma_0\gamma)\}_{ss'} p^{(1)}_s p^{(2)}_{s'} \qquad (2.30)$$

where γ_0 , γ are given by equation (2.25). It is proved in the fourth appendix that if $F(\gamma_0\gamma)$ is a tensor function of the two tensors γ_0 and γ given by (2.25), then

$$F(\gamma_0\gamma) = F(A_0A) + \{F(B_0B) - F(A_0A)\}(kk) \qquad (2.31)$$

A similar equation holds for $F_0(\gamma_0\gamma)$. Substituting in (2.30) the values of $F_0(\gamma_0\gamma)$ and $F(\gamma_0\gamma)$ given by (2.31) and remembering that

$$\sum_{ss'} p_s^{(1)} p_{s'}^{(2)} k_s k_{s'} = (\underline{p}^{(1)} \cdot \underline{k})(\underline{p}^{(2)} \cdot \underline{k}) \qquad \text{and}$$

$$\sum_{ss'} p_s^{(1)} p_{s'}^{(2)} \delta_{ss'} = (\underline{p}^{(1)} \cdot \underline{p}^{(2)}) \qquad \text{we obtain for}$$

the final formula for W

$$W = \frac{1}{2\alpha}\left\{F_0(A_0A)(\underline{p}^{(1)2} + \underline{p}^{(2)2}) + \left(F_0(B_0B) - F_0(A_0A)\right)\left((\underline{p}^{(1)} \cdot \underline{k})^2 + (\underline{p}^{(2)} \cdot \underline{k})^2\right)\right\}$$
$$+ \frac{1}{\alpha}\left\{F(A_0A)(\underline{p}^{(1)} \cdot \underline{p}^{(2)}) + \left(F(B_0B) - F(A_0A)\right)(\underline{p}^{(1)} \cdot \underline{k})(\underline{p}^{(2)} \cdot \underline{k})\right\} \qquad (2.32)$$

The functions F and F_0 are given by (2.29) on replacing γ_0, γ by the constants A_0, A or B_0, B. For first neighbours A_0, A, B_0 and B are given by equations (2.21) and (2.22); and for other neighbours they are given by equations (2.12) and (2.13).

The Tensor Q.

The tensor Q, given by equation (1.50), depends on the average $\overline{p_s^{(i)} p_{s'}^{\alpha}}$ for any two molecules i, α. Let $\underline{k}(\alpha)$ be a unit vector, having components $k_s(\alpha)$, along the line joining the molecule i to the molecule α.

To evaluate the tensor $\overline{p_s^{(i)} p_{s'}^{\alpha}}$ we may first determine it for three orthogonal axes, one along the line joining the two molecules and the other two perpendicular to it. We can then find it with respect to the crystal axes by a tensor transformation.

Let l_s^σ $(s = 1,2,3)$ be the components of a unit vector along the axis σ of the orthogonal set referred to the crystal axes. If we choose the axes $\sigma = 1,2$ to be perpendicular to the line joining the two molecules and the axis $\sigma = 3$ along it, then $l_s^{(3)} = k_s$. The components of a unit vector along a crystal axis s referred to the orthogonal set of axes will then be

$$h_s^\sigma = \sum_{s'} g_{ss'} l_{s'}^\sigma \quad (\sigma = 1,2,3) \tag{2.33}$$

$g_{ss'}$ was given by equation (1.33).

The angle between two crystal axes s, s' is then $\sum_\sigma h_s^\sigma h_{s'}^\sigma$ and therefore

$$g_{ss'} = \sum_\sigma h_s^\sigma h_{s'}^\sigma \tag{2.34}$$

Using equation (2.33) one then obtains

$$\bar{g}_{ss'}^{-1} = \sum_\sigma l_s^\sigma l_{s'}^\sigma \tag{2.35}$$

where $\bar{g}^{-1}$ is the reciprocal of g .

If $p_\sigma^{(i)}$ are the components of $p^{(i)}$ along the orthogonal axes and $p_s^{(i)}$ are those along the crystal axes then

$$p_s^{(i)} = \sum_{\sigma=1}^{3} l_s^\sigma p_\sigma^{(i)} \tag{2.36}$$

and therefore

$$\overline{p_s^{(i)}} p_{s'}^{(k)} = \sum_{\sigma\sigma'} l_s^\sigma l_{s'}^{\sigma'} \overline{p_\sigma^{(i)}} p_{\sigma'}^{(k)} \tag{2.37}$$

This equation gives the tensor $\overline{p_s^{(i)} p_{s'}^{(j)}}$ referred to the crystal axes in terms of the tensor $\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}}$ referred to the orthogonal axes, namely the one along the line joining the two molecules and the other two perpendicular to it. In the calculation of the tensor $p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}$ we use polar co-ordinates.

$$\left.\begin{aligned} p_\sigma^{\prime(i)} &\equiv p(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \quad (\sigma = 1,2,3) \\ p_\sigma^{\prime(j)} &\equiv p(\sin\theta'\cos\phi', \sin\theta'\sin\phi', \cos\theta') \quad (\sigma = 1,2,3) \end{aligned}\right\} \qquad (2.38)$$

The expression for W given by (2.32) can then be written in the form

$$-\frac{W}{kT} = \mathcal{G}(\cos^2\theta + \cos^2\theta') + L\cos\theta\cos\theta' + M\sin\theta\sin\theta'\cos(\phi - \phi') \qquad (2.39)$$

where

$$\left.\begin{aligned} \mathcal{G} &= \frac{-1}{2\alpha}\left[F_0(B_0B) - F_0(A_0A)\right]\frac{p^2}{kT} \\ L &= -\frac{1}{\alpha}F(B_0B)\frac{p^2}{kT} \\ M &= -\frac{1}{\alpha}F(A_0A)\frac{p^2}{kT} \end{aligned}\right\} \qquad (2.40)$$

Now $\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}}$ is given by

$$\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}} = \sum_{p^{\prime(i)}, p^{\prime(j)}} p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)} \delta(p^{\prime(i)} p^{\prime(j)}) = \frac{1}{(4\pi)^2 K_0}\iiiint p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)} e^{-\frac{W}{kT}} \sin\theta\sin\theta' d\theta d\theta' d\phi d\phi' \qquad (2.41)$$

where $K_0 = \frac{1}{(4\pi)^2}\iiiint e^{x} f_x\left(-\frac{W}{kT}\right)\sin\theta\sin\theta' d\theta d\theta' d\phi d\phi'$ (2.42)

W is given by (2.39) and $p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}$ by (2.38).

Putting $\phi - \phi' = \phi_0$ and integrating over ϕ' one obtains

$$\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}} = \delta_{\sigma\sigma'} \overline{p_\sigma^{\prime(i)} p_\sigma^{\prime(j)}} \qquad (2.43)$$

$$\overline{p_1^{\prime(i)} p_1^{\prime(j)}} = \overline{p_2^{\prime(i)} p_2^{\prime(j)}} = \tfrac{1}{2} p^2 \overline{\sin\theta \sin\theta' \cos\phi_0} = \tfrac{1}{2} p^2 \frac{K_2}{K_0} \quad \text{(say)} \qquad (2.44)$$

$$\overline{p_3^{\prime(i)} p_3^{\prime(j)}} = p^2 \overline{\cos\theta \cos\theta'} = p^2 \frac{K_1}{K_0} \quad \text{(say)} \qquad (2.45)$$

where

$$K_2 = \frac{2\pi}{(4\pi)^2} \iiint \sin\theta \sin\theta' \cos\phi_0 \exp\{\mathcal{G}(\cos^2\theta + \cos^2\theta') + L\cos\theta\cos\theta' + M\sin\theta\sin\theta'\cos\phi_0\} \sin\theta \sin\theta' \, d\theta \, d\theta' \, d\phi_0 \qquad (2.46)$$

$$K_1 = \frac{2\pi}{(4\pi)^2} \iiint \cos\theta\cos\theta' \exp\{\mathcal{G}(\cos^2\theta + \cos^2\theta') + L\cos\theta\cos\theta' + M\sin\theta\sin\theta'\cos\phi_0\} \sin\theta \sin\theta' \, d\theta \, d\theta' \, d\phi_0 \qquad (2.47)$$

Also from (2.42)

$$K_0 = \frac{2\pi}{(4\pi)^2} \iiint \exp\{\mathcal{G}(\cos^2\theta + \cos^2\theta') + L\cos\theta\cos\theta' + M\sin\theta\sin\theta'\cos\phi_0\} \sin\theta \sin\theta' \, d\theta \, d\theta' \, d\phi_0 \qquad (2.48)$$

Performing the integration over ϕ_0 by use of the formula

$$\int_0^{2\pi} \cos n\phi \; e^{x\cos\phi} \, d\phi = 2\pi i^n J_n(ix) = 2\pi I_n(x)$$

where $J_n(x)$ is a Bessel function of order n Afterwards for the integrals over θ , θ' , we use the formula

$$\int_0^{\pi}\int_0^{\pi} F(\theta,\theta') \, d\theta \, d\theta' = \int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} \left[F(\theta,\theta') + F(\theta,\pi-\theta') + F(\pi-\theta,\theta') + F(\pi-\theta,\pi-\theta')\right] d\theta \, d\theta'$$

one then obtains the following expression for

K_0 , K_1 , and K_2

$$K_0 = \int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} \cosh(L\cos\theta\cos\theta')\, e^{\gamma(\cos^2\theta+\cos^2\theta')}\, I_0(M\sin\theta\sin\theta')\sin\theta\sin\theta' d\theta d\theta' \tag{2.49}$$

$$K_1 = \int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} \sinh(L\cos\theta\cos\theta')\, e^{\gamma(\cos^2\theta+\cos^2\theta')}\, I_0(M\sin\theta\sin\theta')\sin\theta\sin\theta'\cos\theta\cos\theta' d\theta d\theta' \tag{2.50}$$

$$K_2 = \int_0^{\frac{\pi}{2}}\int_0^{\frac{\pi}{2}} \cosh(L\cos\theta\cos\theta')\, e^{\gamma(\cos^2\theta+\cos^2\theta')}\, I_1(M\sin\theta\sin\theta')\sin^2\theta\sin^2\theta' d\theta d\theta' \tag{2.51}$$

Returning to the object of finding $\overline{p_s^{(i)} p_{s'}^{j}}$ referred to the crystal axes, equation (2.37) becomes, by use of equations (2.43), (2.44) and (2.45)

$$\overline{p_s^{(i)} p_{s'}^{j}} = \left(\ell_s^{(1)}\ell_{s'}^{(1)} + \ell_s^{(2)}\ell_{s'}^{(2)}\right)\tfrac{1}{2}p^2\frac{K_2}{K_0} + \ell_s^{(3)}\ell_{s'}^{(3)}p^2\frac{K_1}{K_0} \tag{2.52}$$

Finally using equation (2.35) one obtains the formula

$$\overline{p_s^{(i)} p_{s'}^{j}} = \tfrac{1}{2}p^2\frac{K_2}{K_0}\bar{g}^{-1}_{ss'} + p^2\frac{K_1-\frac{1}{2}K_2}{K_0}k_s^{ij}k_{s'}^{ij} \tag{2.53}$$

In this expression K_0 , K_1 , K_2 depend on the distance between the two molecules but not on the direction, while $k_s^{ij}k_{s'}^{ij}$ depends on the direction of the line joining the two molecules concerned.

If $i=j$ then $\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}}$ referred to any orthogonal axes is given

$$\overline{p_\sigma^{\prime(i)} p_{\sigma'}^{\prime(j)}} = \tfrac{1}{3}p^2\delta_{\sigma\sigma'} \tag{2.54}$$

Then by use of (2.37) and (2.35), $\overline{p_s^{(i)} p_{s'}^{(i)}}$ referred to the crystal axes is given by

$$\overline{p_s^{(i)} p_{s'}^{(i)}} = \tfrac{1}{3}p^2\bar{g}^{-1}_{ss'} \tag{2.55}$$

From (2.53), (2.55) one can then easily evaluate Q by use of (1.50).

APPENDIX I.

The internal boundary of the dielectric is two separate spheres each of radius a and the distance between their centres is c .(See fig.(4)).

It is required to find the field at the centres of the two spheres created by the presence of a dipole $\underline{\mu}$ at the centre of one of them.

We may first find the field of a dipole $\underline{\mu}'$. at distance c from the centre, inside and outside the hollow sphere of radius a in the following way.

If there is a charge e at distance $c > a$ in the dielectric, let ϕ_1 be the potential inside the cavity and ϕ_2 the potential outside. Following the procedure in the third appendix of the first chapter one obtains

$$\phi_1 = \sum_{m=0}^{\infty} A_m r^m P_m \qquad \phi_2 = \sum_{m=0}^{\infty} \frac{B_m}{r^{m+1}} P_m + \frac{e}{c} \sum_{m=0}^{\infty} \left(\frac{r}{c}\right)^m P_m$$

where

$$A_m = \frac{e\sigma}{c^{m+1}} \left[2 - \frac{\varepsilon-1}{\varepsilon+1}\right] \qquad B_m = \frac{e a^{2m+1}}{c^{m+1}} \left(\frac{\varepsilon-1}{\varepsilon+1}\right) \left[1 - \frac{\sigma}{m+\sigma}\right], \quad \sigma = \frac{\varepsilon}{\varepsilon+1}$$

showing that the field inside the cavity is due to

(i) a charge $2e\sigma$ at $x = c$

(ii) a line charge of density $-\frac{e\sigma}{c} \frac{\varepsilon-1}{\varepsilon+1} \left(\frac{c}{x}\right)^{\sigma}$ from $x = c$ to $x = \infty$ and the field outside the cavity is due to (besides the field of the charge)

(i) a charge $\frac{ea}{c} \frac{\varepsilon-1}{\varepsilon+1}$ at $x = \frac{a^2}{c}$

(ii) a line charge $-\frac{e\sigma}{a}\frac{\varepsilon-1}{\varepsilon+1}\left(\frac{a^2}{cx}\right)^{1-\sigma}$
from $x=0$ to $x=a^2/c$ (2.57)

The field at the centre of the sphere can be easily shown to be the same as the field of a charge

$$\frac{3\varepsilon}{2\varepsilon+1}e \qquad \text{at } x=c \tag{2.58}$$

If there is a dipole $\underline{\mu}'$ at distance c from the centre, one finds by the same method in the third appendix of Chapter I that the field outside the cavity is due to

(i) a dipole $\frac{a^3}{c^3}\frac{\varepsilon-1}{\varepsilon+1}\left[\underline{\mu}'-2(\underline{\mu}'\cdot\underline{k})\underline{k}\right]$ at $x=a^2/c$

(ii) a charge $-\frac{a}{c^2}\frac{\varepsilon-1}{\varepsilon+1}(\underline{\mu}'\cdot\underline{k})$ at $x=a^2/c$

(iii) a line dipole of density $\frac{a}{c^2}\sigma\left(\frac{\varepsilon-1}{\varepsilon+1}\right)\left(\frac{cx}{a^2}\right)^{\sigma}\left[-\underline{\mu}'+2(\underline{\mu}'\cdot\underline{k})\underline{k}\right]$
from $x=0$ to $x=a^2/c$

(iv) a line charge of density $\frac{\sigma}{ac}\frac{\varepsilon-1}{\varepsilon+1}(\underline{\mu}'\cdot\underline{k})\left(\frac{xc}{a^2}\right)^{\sigma-1}$
from $x=0$ to $x=a^2/c$ (2.59)

The field at the centre of the sphere, following (2.58) is the same as the field of a dipole

$$\frac{3\varepsilon}{2\varepsilon+1}\underline{\mu}' \qquad \text{at } x=c \tag{2.60}$$

$\underline{k}$ is a unit vector from the centre of the sphere towards the dipole.

If one now considers only the sphere in which the dipole lies, then the field inside is

$$\frac{f}{a^3}\underline{\mu} \qquad \text{(See(1.6))} \tag{2.61}$$

and the field outside is the same as the field of a dipole

$$\frac{3}{2\sigma+1}\,\underline{\mu} \qquad (2.62)$$

at the position of $\underline{\mu}$ $(x = c)$

Taking into account the second hollow sphere, then the field at its centre, according to (2.60), (2.62), will be the same as the field of a dipole

$$\frac{3\sigma}{2\sigma+1}\cdot\frac{3}{2\sigma+1}\,\underline{\mu} = \frac{9\sigma}{(2\sigma+1)^2}\,\underline{\mu} \qquad (2.63)$$

at $x = c$

and there will be an additional field outside, due to the following system. (Using (2.59), (2.62))

(i) a dipole $\frac{a^3}{c^3}\frac{\sigma-1}{\sigma+1}\cdot\frac{3}{(2\sigma+1)}\left(\underline{\mu} - 2(\underline{\mu}\cdot\underline{k})\,\underline{k}\right)$ at $x = \frac{a^2}{c}$

(ii) a charge $-\frac{a}{c^2}\frac{\sigma-1}{\sigma+1}\cdot\frac{3}{2\sigma+1}\,(\underline{\mu}\cdot\underline{k})$ at $x = \frac{a^2}{c}$

(iii) a line dipole of density $\frac{a}{c^2}\sigma\frac{\sigma-1}{\sigma+1}\cdot\frac{3}{2\sigma+1}\left(\frac{cx}{a^2}\right)^{\sigma}\left[-\underline{\mu} + 2(\underline{\mu}\cdot\underline{k})\,\underline{k}\right]$ from $x = 0$ to $x = \frac{a^2}{c}$

(iv) a line charge of density $\frac{\sigma}{ac}\left(\frac{\sigma-1}{\sigma+1}\right)\cdot\frac{3}{2\sigma+1}\,(\underline{\mu}\cdot\underline{k})\left(\frac{xc}{a^2}\right)^{\sigma-1}$ from $x = 0$ to $x = \frac{a^2}{c}$ (2.64)

Taking into account the first sphere again (in which the dipole lies), then owing to the image system given by (2.64), there will be an additional field at the centre of the first sphere given by (Using (2.60), (2.62))

$$-\frac{9\sigma(\sigma-1)}{(2\sigma+1)^2(\sigma+1)}\cdot\frac{a^3}{c^6}\left[\frac{1}{\left(1-\frac{a^2}{c^2}\right)^3} - \sigma\int_0^1\frac{\xi^{\sigma}\,d\xi}{\left(1-\frac{a^2}{c^2}\xi\right)^3}\right]\underline{\mu} - \frac{9\sigma(\sigma-1)}{(2\sigma+1)^2(\sigma+1)}\,\frac{a}{c^4}$$
$$\left[\frac{1}{\left(1-\frac{a^2}{c^2}\right)^2} - \sigma\int_0^1\frac{\xi^{\sigma-1}\,d\xi}{\left(1-\frac{a^2}{c^2}\xi\right)^2}\right](\underline{\mu}\cdot\underline{k})\,\underline{k} \qquad (2.65)$$

We can keep on in this way indefinitely to find the fields inside the two spheres. For the Ice crystal at $T = 273$, $\varepsilon = 74 \cdot 6$, the expression (2.65) was found to be, when the two molecules are second neighbours

$$-\frac{1}{a^3}(\cdot 00024)\underline{\mu} - \frac{1}{a^3}(\cdot 00032)(\underline{\mu}\cdot\underline{k})\underline{k} \qquad (2.66)$$

which is very small compared with the expression (2.61). For further neighbours it is clear that it will be much smaller. We therefore neglect the fields of further successive image systems and take the expression (2.61) for the field at the centre of the first cavity, and the field at the centre of the other cavity to be the same as the field of the dipole given by (2.63) at the centre of the first sphere.

APPENDIX II.

The internal boundary of the dielectric is an ellipsoid of revolution of major axis (along the axis of revolution) $2b\cosh t$ and the distance between the foci is $2b$. A dipole $\underline{\mu}$ lies at distance $\frac{c}{2} < b$ from the centre of the ellipsoid and on the line joining the two foci. It is required to find the field at the position of the dipole and at a point on the line joining the two foci at distance c from the dipole $\underline{\mu}$. (See Fig. (5))

We take then orthogonal axes $x_1\, x_2\, x_3$ the first along the axis of revolution, the second in the plane of the dipole $\underline{\mu}$ and the first axis. The co-ordinates of the dipole are then $(\frac{c}{2}, 0, 0)$ and the co-ordinates of the other point at which we want to find the field is $(-\frac{c}{2}, 0, 0)$.

Using orthogonal co-ordinates (t, θ, ϕ) given by

$$x_1 = b\cosh t\cos\theta \qquad x_2 = b\sinh t\sin\theta\cos\phi \qquad x_3 = b\sinh t\sin\theta\sin\phi$$

then the general potential V satisfying $\nabla^2 V = 0$ can be written in terms of these new co-ordinates

$$V(t\theta\phi) = \sum_{n=0}^{\infty}\sum_{m=0}^{n}\left[A_n^m P_n^m(\cosh t) + B_n^m Q_n^m(\cosh t)\right] T_n^m(\cos\theta)\cos m\phi \qquad (2.67)$$

where

$$T_n^m(x) = (1-x^2)^{\frac{m}{2}}(-)^m \frac{d^m}{dx^m} P_n \quad , \quad P_n^m(x) = (x^2-1)^{\frac{m}{2}} \frac{d^m}{dx^m} P_n$$

$$Q_n^m(x) = (x^2-1)^{\frac{m}{2}} \frac{d^m}{dx^m} Q_n$$

The co-ordinates of the dipole μ in the new system are $(0, \theta_0, 0)$ and those of the other point $(-\frac{c}{2}, 0, 0)$ are $(\infty, \pi-\theta_0, 0)$ where $\cos\theta_0 = \frac{c}{2b}$. If R is the distance between $(t\,\theta\,\phi)$ and $(t'\theta'\phi')$ then

$$\frac{1}{R} = \frac{1}{b}\sum_{n=0}^{\infty}(2n+1)\left[Q_n(\cosh t)P_n(\cosh t')P_n(\cos\theta)P_n(\cos\theta') + 2\sum_{m=1}^{n}\left\{\frac{(n-m)!}{(n+m)!}\right\}^2 Q_n^m(\cosh t)P_n^m(\cosh\mu)(-)^m T_n^m(\cos\theta)T_n^m(\cos\theta')\cos m(\phi-\phi')\right] \tag{2.68}$$

Taking a charge $-e$ at $t=0$ $\theta=\theta_0$ and a charge $+e$ at $t=t'$ $\theta=\theta'$ then if the dipole makes an angle α with the direction of the axis x_1, then

$$\frac{\mu}{be}\cos\alpha = \cosh t'\cos\theta' - \cos\theta_0$$

$$\frac{\mu}{be}\sin\alpha = \sinh t'\sin\theta' \,, \qquad \text{and to first power in } \frac{\mu}{e} \text{ we have}$$

$$\begin{aligned}\sinh t'\sin\theta_0 &= \frac{\mu}{be}\sin\alpha \\ \cos\theta' &= \cos\theta_0 + \frac{\mu}{be}\cos\alpha\end{aligned} \tag{2.69}$$

The potential of the dipole μ at $(0, \theta_0, 0)$ is then, by use of equations (2.68) (2.69) given by

$$V = \frac{\mu}{b^2}\sum_{n=0}^{\infty}(2n+1)P_n'(\cos\theta_0)\left\{\cos\alpha\, Q_n(\cosh t)P_n(\cos\theta) + \frac{\sin\alpha}{n(n+1)}Q_n^1(\cosh t)T_n^{(1)}(\cos\theta)\cos\phi\right\} \tag{2.70}$$

To find the image field inside the cavity, let the potentials outside and inside the cavity be (following (2.67))

$$\left.\begin{aligned}V_0 &= \sum_{n=0}^{\infty}\sum_{m=0}^{n} C_n^m Q_n^m(\cosh t)T_n^m(\cos\theta)\cos m\phi \\ V_1 &= \sum_{n=0}^{\infty}\sum_{m=0}^{n}\left\{A_n^m P_n^m(\cosh t) + B_n^m Q_n^m(\cosh t)\right\}T_n^m(\cos\theta)\cos m\phi\end{aligned}\right\} \tag{2.71}$$

The second part in the expression for V_1 is due to the dipole $\underline{\mu}$ at (o, θ_o, o) and is given by (2.70); the first part is the additional or image potential inside the cavity. Applying the boundary conditions

$$V_o = V_1 \quad , \quad \varepsilon \frac{\partial V_o}{\partial t} = \frac{\partial V_1}{\partial t} \qquad \text{at the boundary } t = t_1,$$

one obtains

$$A_n^m = - \frac{Q_n^m(\cosh t_1)}{P_n^m(\cosh t_1)} \cdot \frac{1}{(1 - \chi_n^{(m)})} \; B_n^m \tag{2.72}$$

where

$$(\varepsilon - 1)\, \chi_n^{(m)} = \left[\frac{Q_n^m \frac{\partial P_n^m}{\partial t} - P_n^m \frac{\partial Q_n^m}{\partial t}}{P_n^m \frac{\partial Q_n^m}{\partial t}} \right]_{t = t_1} \tag{2.73}$$

Using the expression for B_n^m from (2.70) we obtain

$$\left.\begin{aligned} A_n^{(o)} &= - \frac{Q_n(\cosh t_1)}{P_n(\cosh t_1)} \frac{1}{1 - \chi_n^{(o)}} \frac{\mu \cos\alpha}{b^2} (2n+1)\, P_n'(\cos\theta_o) \\ A_n^{(1)} &= - \frac{Q_n'(\cosh t_1)}{P_n'(\cosh t_1)} \frac{1}{1 - \chi_n^{(1)}} \frac{\mu \sin\alpha}{b^2} \frac{(2n+1)}{n(n+1)} P_n'(\cos\theta_o) \end{aligned}\right\} \tag{2.74}$$

where

$$\left.\begin{aligned} (\varepsilon - 1)\, \chi_n^{(o)} &= \left(\frac{Q_n P_n' - P_n Q_n'}{P_n Q_n'} \right)_{t = t_1} \\ (\varepsilon - 1)\, \chi_n^{(1)} &= \frac{\sinh^2 t_1}{P_n'(\cosh t_1)} \left(\frac{Q_n' P_n'' - P_n' Q_n''}{\cosh t\, Q_n' + \sinh^2 t\, Q_n''} \right)_{t = t_1} \end{aligned}\right\} \tag{2.75}$$

The field components are given by

$$\frac{-1}{b\sqrt{\cosh^2 t - \cos^2\theta}} \frac{\partial V}{\partial t} \quad , \quad \frac{-1}{b\sqrt{\cosh^2 t - \cos^2\theta}} \frac{\partial V}{\partial \theta}$$

and at $\theta = \pi - \theta_o$ $t = o$ the image field inside is given by

$$\left.\begin{aligned} F_t &= \frac{-1}{b} \sum_{n=o}^{\infty} (-)^n A_n^{(1)} P_n'(\cos\theta_o) \frac{n(n+1)}{2} \cos\phi \\ F_\theta &= \frac{-1}{b} \sum_{n=o}^{\infty} (-)^n A_n^{(o)} P_n'(\cos\theta_o) \quad , \end{aligned}\right\} \tag{2.76}$$

(See Fig. 5)

and at $\theta = \theta_o$ $t = o$

$$\left.\begin{aligned} F_t^{(1)} &= \frac{1}{b}\sum_{n=0}^{\infty} A_n^{(1)} P_n'(\cos\theta_0)\,\frac{n(n+1)}{2}\cos\phi \\ F_\theta^{(1)} &= \frac{1}{b}\sum_{n=0}^{\infty} A_n^{(1)} P_n'(\cos\theta_0) \end{aligned}\right\} \qquad (2.77)$$

Putting the fields at $x_1 = \frac{\epsilon}{2}$, $x_1 = -\frac{\epsilon}{2}$ as

$$\underline{F}^{(1)} = C_0 \underline{\mu} + D_0(\underline{\mu}\cdot\underline{k})\underline{k} \qquad \text{and} \qquad \underline{F} = C\underline{\mu} + D(\underline{\mu}\cdot\underline{k})\underline{k} \qquad (2.78)$$

respectively,

then

$$F_t = C\mu\sin\alpha\cos\phi \qquad F_\theta = -(C+D)\mu\cos\alpha \qquad (2.79)$$

$$F_t^{(1)} = C_0\mu\sin\alpha\cos\phi \qquad F_\theta^{(1)} = -(C_0+D_0)\mu\cos\alpha \qquad (2.80)$$

Using equations (2.74), (2.76), (2.77), (2.79) and (2.80) we finally obtain

$$C_0 = \frac{-1}{b^3}\sum_{n=0}^{\infty} \frac{Q_n'(\cosh t_1)}{P_n'(\cosh t_1)}\cdot\frac{1}{1-X_n^{(1)}}(n+\tfrac{1}{2})\{P_n'(\cos\theta_0)\}^2$$

$$C = \frac{1}{b^3}\sum_{n=0}^{\infty} \frac{Q_n'(\cosh t_1)}{P_n'(\cosh t_1)}\frac{(-)^n}{1-X_n^{(1)}}(n+\tfrac{1}{2})\{P_n'(\cos\theta_0)\}^2$$

$$C_0+D_0 = \frac{2}{b^3}\sum_{n=0}^{\infty} \frac{Q_n(\cosh t_1)}{P_n(\cosh t_1)}\frac{1}{1-X_n^{(1)}}(n+\tfrac{1}{2})\{P_n'(\cos\theta_0)\}^2$$

$$C+D = \frac{-2}{b^3}\sum_{n=0}^{\infty} \frac{Q_n(\cosh t_1)}{P_n(\cosh t_1)}\frac{(-)^n}{1-X_n^{(1)}}(n+\tfrac{1}{2})\{P_n'(\cos\theta_0)\}^2 \qquad (2.81)$$

APPENDIX III.

If λ is a tensor given by

$$\lambda \equiv \begin{pmatrix} \gamma_0 & \gamma \\ \gamma & \gamma_0 \end{pmatrix} , \qquad (2.82)$$

to prove that if $f(\lambda)$ is any tensor function of λ, then

$$[f(\lambda)]^{11} = [f(\lambda)]^{22} = \tfrac{1}{2} f(\gamma_0+\gamma) + \tfrac{1}{2} f(\gamma_0-\gamma)$$
$$[f(\lambda)]^{12} = [f(\lambda)]^{21} = \tfrac{1}{2} f(\gamma_0+\gamma) - \tfrac{1}{2} f(\gamma_0-\gamma)$$

Suppose that $$\lambda^n \equiv \begin{pmatrix} \gamma_0(n) & \gamma(n) \\ \gamma(n) & \gamma_0(n) \end{pmatrix} \qquad (2.83)$$

Multiplying the tensor λ given by (2.82) by the tensor λ^n given by (2.83) we obtain

$$\left.\begin{aligned} \gamma_0(n+1) &= \gamma_0\gamma_0(n) + \gamma\gamma(n) \\ \gamma(n+1) &= \gamma_0\gamma(n) + \gamma\gamma_0(n) \end{aligned}\right\} \qquad (2.84)$$

Eliminating $\gamma(n)$ from equations (2.84) one obtains

$$\gamma_0(n+2) - 2\gamma_0\gamma_0(n+1) + (\gamma_0^2 - \gamma^2)\gamma_0(n) = 0 \qquad (2.85)$$

By eliminating $\gamma_0(n)$ we obtain a similar equation for $\gamma(n)$.

Putting $\gamma_0(n) \propto x^n$ we obtain from (2.85)

$$x^2 - 2\gamma_0 x + \gamma_0^2 - \gamma^2 = 0 , \qquad (2.86)$$

giving $$x = \gamma_0 \pm \gamma$$

The general expression for $\gamma_0(n)$ is therefore

$$\gamma_0(n) = A_0(\gamma_0+\gamma)^n + B_0(\gamma_0-\gamma)^n \quad , \text{ similarly}$$

$$\gamma(n) = A(\gamma_0+\gamma)^n + B(\gamma_0-\gamma)^n \qquad (2.87)$$

where A_0 , B_0 , A , B are arbitrary constants.

Since the determinant of λ is $\gamma_0^2 - \gamma^2$ and that of λ^n is $[\gamma_0(n)]^2 - [\gamma(n)]^2$ then

$$[\gamma_0(n)]^2 - [\gamma(n)]^2 = (\gamma_0^2 - \gamma^2)^n \qquad (2.88)$$

Also $$\gamma_0(n) + \gamma(n) = (\gamma_0+\gamma)^n \qquad (2.89)$$

then from (2.88) and (2.89)

$$\gamma_0(n) - \gamma(n) = (\gamma_0-\gamma)^n \qquad (2.90)$$

By use of (2.89) (2.90) equation (2.87) becomes

$$\gamma_0(n) = \tfrac{1}{2}(\gamma_0+\gamma)^n + \tfrac{1}{2}(\gamma_0-\gamma)^n = (\lambda^n)'' = (\lambda^n)^{22}$$
$$\gamma(n) = \tfrac{1}{2}(\gamma_0+\gamma)^n - \tfrac{1}{2}(\gamma_0-\gamma)^n = (\lambda^n)'^2 = (\lambda^n)^{21} \qquad (2.91)$$

Hence the required formula follows.

APPENDIX IV.

The tensors γ_0 , γ are given by

$$\left.\begin{aligned} \gamma^{(0)}_{ss'} &= A_0\,\delta_{ss'} + (B_0 - A_0)\,k_s\,k_{s'} \\ \gamma_{ss'} &= A\,\delta_{ss'} + (B - A)\,k_s\,k_{s'} \end{aligned}\right\} \qquad (2.92)$$

where A_0 , B_0 , A and B are constants and $\underline{k}$ is a unit vector. It is required to prove that if $F(\gamma^{(0)}\gamma)$ is any tensor function of $\gamma^{(0)}$, γ then

$$\{F(\gamma^{(0)}\gamma)\}_{ss'} = F(A_0 A)\,\delta_{ss'} + \{F(B_0 B) - F(A_0 A)\}\,k_s\,k_{s'} \qquad (2.93)$$

We first consider the tensor $(\gamma^n)_{ss'}$;

omitting the suffixes s, s' we have

$$\gamma = A + (B - A)(kk)$$

$$\gamma^n = \sum_{\lambda=0}^{n} A^{n-\lambda}(B-A)^{\lambda}\binom{n}{\lambda}(kk)^{\lambda} \qquad (2.94)$$

We also have

$$[(kk)^2]_{ss'} = \sum_{s''} k_s k_{s''} k_{s''} k_{s'} = k_s k_{s'} = (kk)_{ss'}$$

by successive pre multiplication by (kk) we obtain

$$(kk)^{\lambda} = (kk) \qquad \lambda \geq 1 \qquad (2.95)$$

Substituting from (2.95) into (2.94) we obtain

$$\gamma^n = A^n + (kk)\sum_{\lambda=1}^{n} A^{n-\lambda}(B-A)^{\lambda}\binom{n}{\lambda}$$

$$= A^n + (B^n - A^n)(kk) \qquad (2.96)$$

Similarly

$$\gamma_0^n = A_0^n + (B_0^n - A_0^n)(kk) \qquad (2.97)$$

From (2.95), (2.96) and (2.97)

$$\gamma_0^m \gamma^n = A_0^m A^n + (B_0^m B^n - A_0^m A^n)(kk) \qquad (2.98)$$

Hence the required formula (2.93) follows.

CHAPTER III

APPLICATION TO ICE.

The Structure of the Crystal.

The positions of the oxygen atoms in the crystal are known from X-ray diffraction experiments. They form a hexagonal crystal with four oxygen atoms in a unit cell. The oxygen atoms lie in planes, normal to the axis of the crystal; the distances between successive planes are c and $\frac{c}{3}$ alternately as shown in Fig. 6; c being the distance between first neighbours.

The positions of the atoms in the planes drawn in black in Fig. 6 are shown in black in Fig. 7, while the positions of the atoms in the planes drawn in red in Fig. 6 are shown in red in Fig. 7.

If $\underline{k}_s$ $(s=1,2,3,4)$ are unit vectors along the lines joining an atom and its four first neighbours then

$$\underline{k}_s \cdot \underline{k}_{s'} = -\frac{1}{3} \qquad (s \neq s') \tag{3.1}$$

which means that each oxygen atom is symmetrically surrounded by four oxygen atoms.

If $(a_1\ a_2\ a_3)$ are the fundamental translations of the unit cell then it is clear from Figs. 6 and 7 that

$$a_1 = a_2 = \sqrt{\frac{8}{3}}\, c \qquad a_3 = \frac{8}{3}\, c \tag{3.2}$$

Fig. (6)

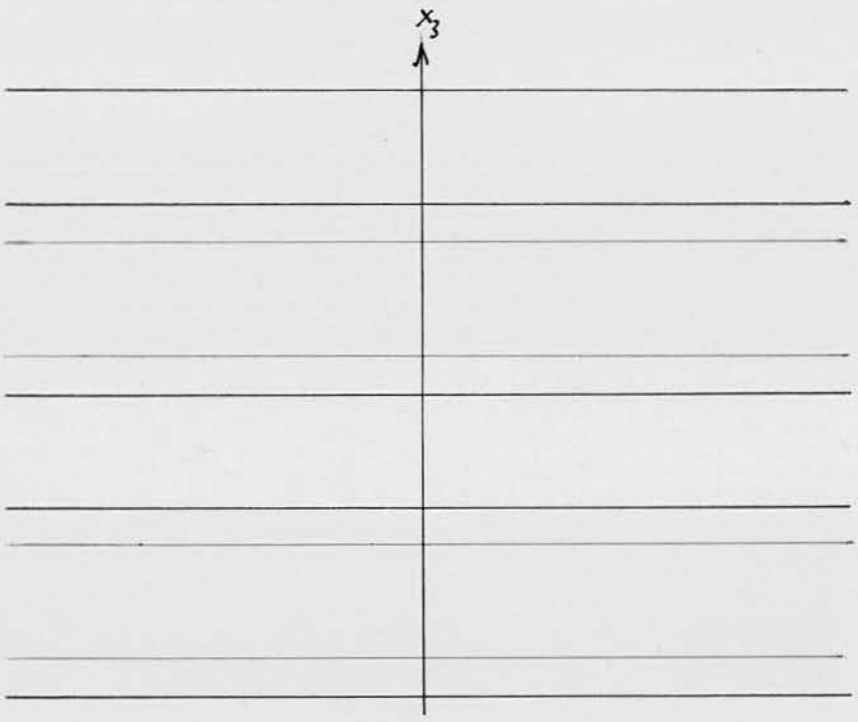
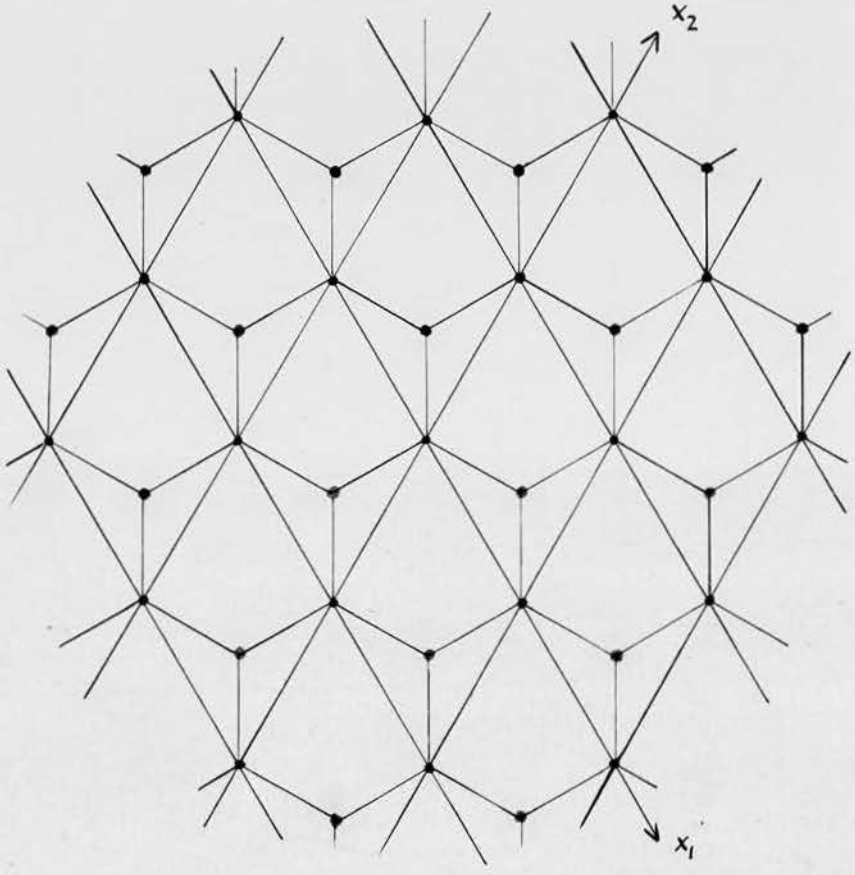


Fig. (7)



giving the dimensions of a unit cell in terms of the distance between first neighbours.

Also the tensor g defined by (1.33) is given, for the Ice crystal, by

$$g \equiv \begin{pmatrix} 1 & -\frac{1}{2} & 0 \\ -\frac{1}{2} & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (3.3)$$

If v is the volume of a unit cell then v^2 is given by the determinant

$$v^2 = \begin{vmatrix} \frac{8}{3}c^2 & -\frac{4}{3}c^2 & 0 \\ -\frac{4}{3}c^2 & \frac{8}{3}c^2 & 0 \\ 0 & 0 & \frac{64}{9}c^2 \end{vmatrix} = 3\left(\frac{32}{9}\right)^2 c^6 \quad , \qquad \text{or}$$

$$v = \frac{32}{9}\sqrt{3}\, c^3 \qquad (3.4)$$

Since there are four molecules in each unit cell then

$$\frac{1}{N} = \frac{8\sqrt{3}}{9} c^3 = \frac{4\pi}{3} a^3 \qquad (3.5)$$

where N, a are defined by (1.4).

The distance $O-H$ in the steam molecule is $.95\,A^{(4)}$ while the angle $H-O-H$ is about 109^0. It has been assumed that the hydrogen atoms will retain the same relative positions in Ice [1][20][18].

Since the angle between the two lines joining an oxygen atom and any two of the four first neighbours is $\cos^{-1}(-\frac{1}{3}) = 109^\circ\ 32'$ i.e. nearly the same as the angle $H-O-H$ in the steam molecule, then it is possible geometrically for the molecule to have a

configuration similar to that in the gas with the two hydrogen atoms lying on two lines joining the oxygen atom of the same molecule and two of its first neighbours.

There are $(\frac{4}{2}) = 6$ such orientations for the molecule. The question now is whether the molecule rotates freely in the solid or assumes such definite restricted orientations. It will be shown that the high dielectric constant of ice near the melting point can only be explained if the dipolar molecules are free, or nearly free to rotate. At lower temperatures when the dielectric constant drops to a small value, it may happen that the dipoles restrict their rotations to between the six orientations mentioned before. The distribution of the dipoles at any instant is then very probably regular, i.e., the dipoles are divided into groups, or unit cells, which are similar in their configurations.

Experimental values of the Dielectric Constant.

Curves for the dielectric constant of ice, for the lower frequencies, are shown on the same scale in Figs. (8), (9), (10) and (11), showing values of ε due to Errera [7] (1924), the International Critical Tables [14] (1929), Wintch [28] (1932), and Smyth and Hitchcock [22] (1932), respectively.

Fig. (8)

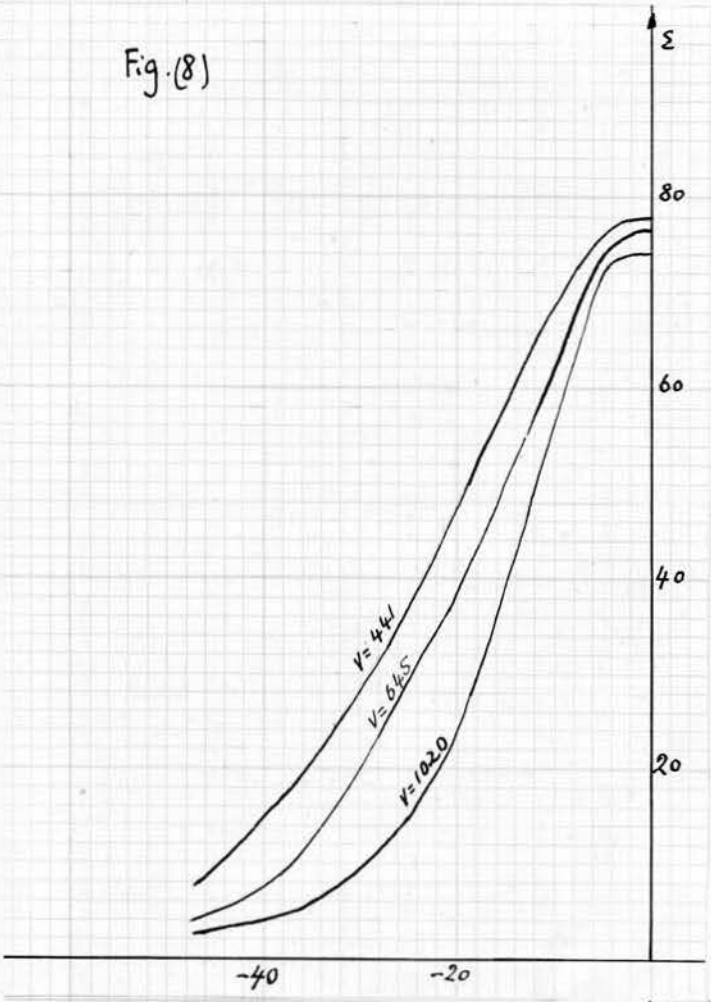


Fig. (9)

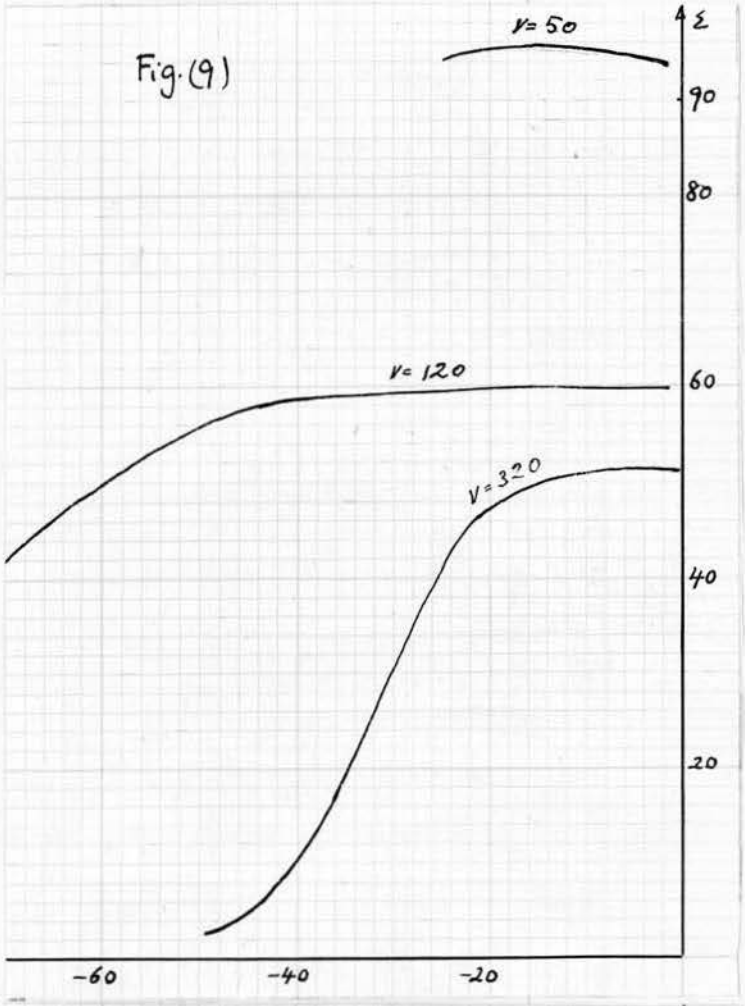


Fig. (10)

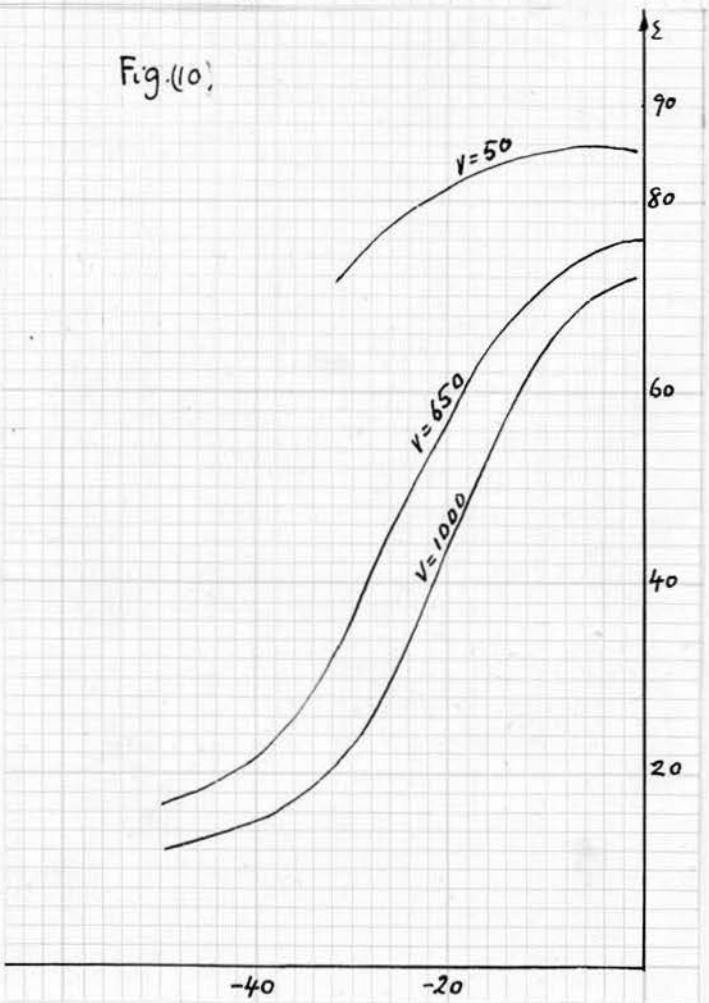
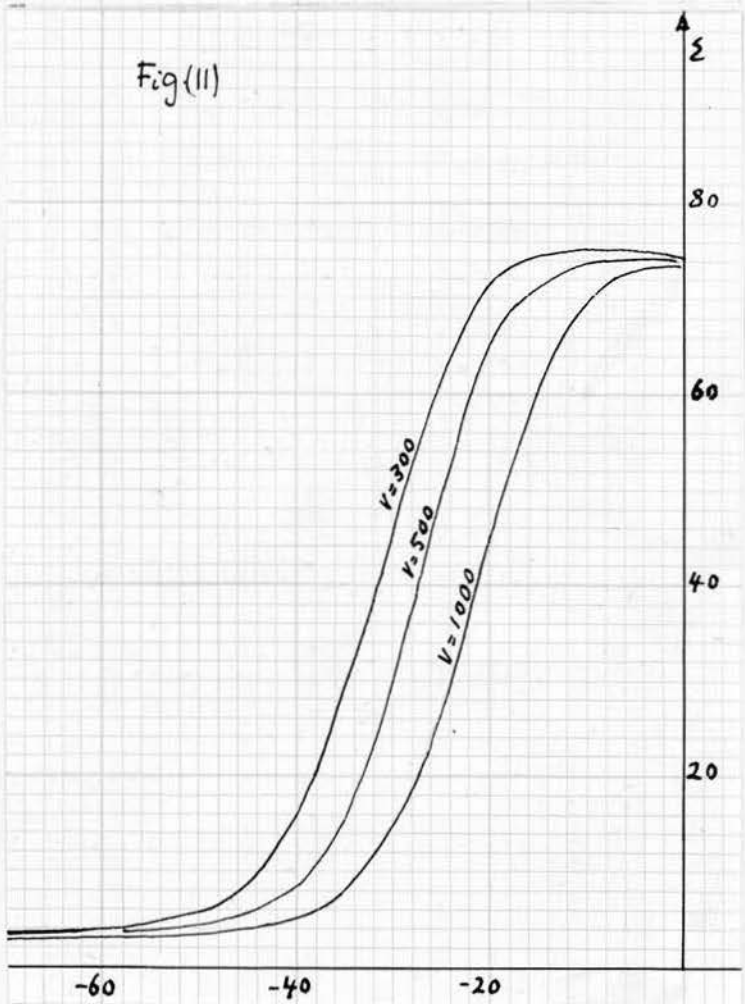


Fig. (11)



Murphy [16] (1934) has recorded, for $\nu = 1$ cycle/sec., a value of $\varepsilon = 150$ at $t = -90°$, this value decreasing gradually with rising temperatures and rapidly with falling temperatures. His values $\varepsilon = 95$ at $t = -7.1°$ for $\nu = 30$ and $\varepsilon = 99$ at $t = 0$ for $\nu = 1000$ are much higher than the corresponding values due to Smyth and Hitchcock. Drawing curves relating the dielectric constant and the frequency (at zero temperature) for different authors, one would expect by extrapolating to zero frequency, the following values for the dielectric constant at zero temperature and for a steady field.

Errera $\varepsilon = 81$, Wintch $\varepsilon = 86$, Smyth and Hitchcock $\varepsilon = 74$, Granier [12] (1924) has given the high value $\varepsilon = 153$, and Weymann [27] (1931) has given the value $\varepsilon = 88$, the same as that of water at zero degree.

It is noticed that the value given by Smyth and Hitchcock is the lowest of all. It was explained by them that the low values of the dielectric constant they recorded, were due to the purity of the sample they experimented upon. It is shown in their paper [22] that the existence of small quantities of KCl in water will raise the dielectric constant of ice near the melting point to a much higher value. The higher values of the dielectric constant recorded by others may then be due to existence of small quantities of such impurities.

Dorsey[6] (1940) has given an empirical equation which fitted the curves given by Smyth and Hitchcock for all frequencies. For $t = o$ and a steady field it gives

$$\varepsilon = 74 \cdot 6 \qquad (3.6)$$

The Tensor λ.

In order to calculate the dielectric constant of ice from equation (1.53), we start by calculating the tensor λ appearing in that equation and defined by equations (1.39) and (1.59).

Putting

$$A_{ss'} = \alpha \sum_{j \neq i} \frac{x_s^j x_{s'}^j}{R_j^5} \qquad (3.7)$$

then

$$\alpha \sum_{j \neq i} \frac{1}{R_j^3} = \sum_{ss'} g_{ss'} A_{ss'} = 2A_{11} - A_{12} + A_{33} \qquad (3.8)$$

Substituting from (3.7), (3.8) in (1.39) one obtains

$$(\lambda - 1)_{ss'} = (2A_{11} - A_{12} + A_{33})\delta_{ss'} - 3(gA)_{ss'} \qquad (3.9)$$

It is noticed, referring to Fig. (7), that in any plane there are always three molecules with co-ordinates.

$$(x_1, x_2)\ (-x_1 + x_2, -x_1)\ (-x_2, x_1 - x_2)$$

These co-ordinates are equidistant from the origin and

at an equal angular separation $\frac{2\pi}{3}$. For three such molecules

$$\sum_{i=1}^{3} x_s^{(i)} = 0 \quad , \quad \sum_{i=1}^{3} x_s^{(i)} x_{s'}^{(i)} = \begin{pmatrix} 2\lambda^2 , & \lambda^2 \\ \lambda^2 , & 2\lambda^2 \end{pmatrix} \tag{3.10}$$

where λ is the distance of any of them from the origin in the plane.

If there are m molecules in a plane at an equal distance λ from the origin, then

$$\sum_{i=1}^{m} x_s^{(i)} = 0 \quad \sum_{i=1}^{m} x_s^{(i)} x_{s'}^{(i)} = \begin{pmatrix} \frac{2m}{3}\lambda^2 , & \frac{m}{3}\lambda^2 \\ \frac{m}{3}\lambda^2 , & \frac{2m}{3}\lambda^2 \end{pmatrix} \tag{3.11}$$

The tensor A defined by (3.7) can then be written

$$\left.\begin{aligned} A_{11} = A_{22} = \tfrac{2}{3}\alpha \sum_j \frac{m_j \lambda_j^2}{R_j^5} \qquad A_{33} = \alpha \sum_j \frac{m_j \ell_j^2}{R_j^5} \\ A_{12} = A_{21} = \tfrac{1}{2} A_{11} \qquad A_{23} = A_{32} = 0 \end{aligned}\right\} \tag{3.12}$$

where m_j is the number of molecules in the plane ℓ_j at equal distances λ_j from the origin in that plane; R_j is the distance of the set of molecules from the origin of co-ordinates, i.e., $R_j^2 = \ell_j^2 + \lambda_j^2$

Since, using (3.12) and (3.3)

$$(g A)_{ss'} = \begin{pmatrix} \frac{3}{4}A_{11} & 0 & 0 \\ 0 & \frac{3}{4}A_{11} & 0 \\ 0 & 0 & A_{33} \end{pmatrix} \tag{3.13}$$

then equation (3.9) becomes

$$\left.\begin{aligned} \lambda_{11} - 1 = A_{33} - \tfrac{3}{4} A_{11} = B \ (\text{say}) \\ \lambda_{33} - 1 = -2 A_{33} + \tfrac{3}{2} A_{11} = -2 B \end{aligned}\right\} \tag{3.14}$$

and the non-diagonal elements vanish.

B can be written

$$B = \frac{\alpha}{c^3} \sum_j \frac{c^3 m_j}{R_j^5} \left(\ell_j^2 - \tfrac{1}{2} r_j^2 \right) \qquad (3.15)$$

In tables (2) and (3) the number m_j of molecules at the same distance from the origin and r_j^2, the square of their distances from the origin in their plane are tabulated for planes marked in black and red (See Fig. (7)) respectively.

In table (4) m_j, r_j^2, ℓ_j^2 and R_j^2 are tabulated for molecules in all planes up to the 184th nearest neighbours. It is found that

$$\frac{10^4}{27} \sum_j \frac{c^3 m_j}{R_j^5} \left(\ell_j^2 - \tfrac{1}{2} r_j^2 \right) \approx 14 \qquad (3.16)$$

The quantity $\frac{\alpha}{c^3}$ appearing in (3.15) is given, by use of equation (3.5), by

$$\frac{\alpha}{c^3} = \frac{8\sqrt{3}}{9} N\alpha = \frac{8\sqrt{3}}{9} \frac{\alpha d}{M} \times \frac{10^{23}}{(.166)}$$

where d is the density and M the molecular weight. For $T = 273$ we have $d = .9168$

also
$$M = 18.0156$$
$$\alpha = .16 \times 10^{-23} \qquad (3.17)$$

then

$$\frac{\alpha}{c^3} = .07575 \qquad (3.18)$$

Substituting from equations (3.18) and (3.16) into (3.15) one finally obtains

$$B = .003 \qquad (3.19)$$

to three places of decimals

Table(2)

$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n
0	I	I68	I2	384	6	648	6	888	I2
24	6	2I6	6	456	I2	672	I2	936	I2
72	6	288	6	504	I2	744	I2		
96	6	3I2	I2	600	6	864	6		

Table(3)

$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n	$9r^2/c^2$	n
8	3	I52	6	344	6	536	6	776	6
32	3	200	3	392	9	584	6	800	3
56	6	224	6	4I6	6	608	6	824	6
I04	6	248	6	488	6	632	6	872	6
I28	3	296	6	5I2	3	728	I2	896	6

Table(4)

	n	$9\frac{n^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$\frac{9m}{c^2}(l^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4 mc^3}{27R^5}(-l^2+\frac{n^2}{2})$	$\sum \frac{9m}{c^2}(-l^2+\frac{n^2}{2})$
1st	1	0	9	9	0			
	3	8	1	9				
2nd	6	24	0	24	0			
	6	8	16	24				
3rd	1	0	25	25	- 25	3.20000	-80.00000	
4th	6	24	9	33	63	1.59851	100.70613	
	3	32	1	33				
5th	6	32	16	48	0			
6th	6	24	25	49	- 78	.59499	-46.40923	
7th	3	8	49	57	27	.40767	11.00719	
	6	56	1	57				
8th	2	0	64	64	-128	.30518	-39.06250	
9th	6	72	0	72	360	.22734	81.84103	
	12	56	16	72				
10th	6	72	9	81	63	.16935	10.66904	
	3	32	49	81				
11th	12	24	64	88	-624	.13766	-85.89697	
12th	3	8	81	89	-231	.13382	-30.91270	
13th	6	96	0	96	288	.11074	31.89439	
14th	6	72	25	97	66	.10791	7.12221	
15th	6	96	9	105	414	.08852	36.64604	
	6	56	49	105				
	6	104	1	105				
16th	3	32	81	113	-195	.07367	-14.36609	
17th	12	104	16	120	432	.06339	27.38612	

	.n	$.9\frac{n^2}{c^2}$	$.9\frac{l^2}{c^2}$	$.9\frac{K^2}{c^2}$	$.9\frac{m}{c^2}(l^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(l^2+\frac{n^2}{2})$	$\sum\frac{9m}{c^2}(l^2+\frac{n^2}{2})$
18th	1	0	121	121	17	.06209	1.05556	
	6	96	25	121				
19th	3	128	1	129	189	.05291	9.99971	
20th	12	72	64	136	-336	.04636	-15.57730	
21st	6	56	81	137	-318	.04552	-14.47523	
22nd	6	128	16	144	288	.04019	11.57409	
23rd	6	24	121	145	-654	.03950	-25.83195	
24th	6	8	144	152	-840	.03511	-29.48971	
25th	6	104	49	153	468	.03454	16.16285	
	6	152	1	153				
26th	12	96	64	160	-192	.03088	- 5.92927	
27th	12	168	0	168	1728	.02734	47.23574	
	12	152	16	168				
28th	1	0	169	169	-169	.02693	- 4.55161	
29th	6	32	144	176	-768	.02433	-18.68874	
30th	12	168	9	177	945	.02399	22.67244	
	3	128	49	177				
31st	6	104	81	185	-174	.02148	- 3.73783	
32nd	6	24	169	193	-744	.01932	-14.37735	
	6	72	121	193				
	12	168	25	193				
33rd	12	56	144	200	-1392	.01768	-24.60736	
34th	6	152	49	201	459	.01746	8.01350	
	3	200	1	201				
35th	3	128	81	209	- 51	.01584	- .80762	
36th	6	216	0	216	1152	.01458	16.80031	
	6	200	16	216				

	n	$9\frac{n^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{K^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{n^2}{2})$	$(\frac{3K}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{K^5}(-l^2+\frac{n^2}{2})$	$\sum\frac{9m}{c^2}(-l^2+\frac{n^2}{2})$
37th	6	96	121	217	-438	.01442	- 6.31430	
38th	6	216	9	225	1260	.01317	16.59256	
	6	224	1	225				
39th	24	168	64	232	480	.01220	5.85494	
40th	3	8	225	233	-693	.01207	- 8.36264	
	6	152	81	233				
41st	12	224	16	240	1152	.01121	12.91000	
42nd	6	72	169	241	-300	.01109	- 3.32721	
	6	216	25	241				
43rd	12	104	144	248	-1104	.01032	-11.39825	
44th	3	200	49	249	891	.01022	9.10709	
	6	248	1	249				
45th	2	0	256	256	-512	.00954	- 4.88279	
46th	3	32	225	257	-627	.00944	- 5.92151	
47th	12	248	16	264	1296	.00883	11.44446	
48th	6	96	169	265	-726	.00875	- 6.35069	
49th	6	128	144	272	-480	.00820	- 3.93384	
50th	6	224	49	273	378	.00812	3.06962	
51st	12	24	256	280	-2400	.00762	-18.29424	
	12	216	64	280				
52nd	6	56	225	281	-1125	.00756	- 8.49938	
	3	200	81	281				
53rd	6	288	0	288	864	.00710	6.13812	
54th	12	168	121	289	-444	.00704	- 3.12709	
55th	12	152	144	296	-816	.00663	- 5.41326	
56th	6	288	9	297	1287	.00658	8.46614	
	3	8	289	297				
	6	248	49	297				
	6	296	1	297				

	n	$9\frac{\lambda^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{\lambda^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4 mc^3}{27R^5}(-l^2+\frac{\lambda^2}{2})$	$\sum 9\frac{m}{c^2}(-l^2+\frac{\lambda^2}{2})$
57th	6	224	81	305	186	.00616	1.14489	
58th	12	312	0	312	3456	.00582	20.09975	
	12	296	16	312				
59th	6	288	25	313	714	.005770	4.11942	
60th	12	312	9	321	945	.00542	5.11878	
	3	32	289	321				
61st	12	72	256	328	-2640	.00513	-13.54927	
62nd	6	104	225	329	-780	.00509	- 3.97285	
	6	248	81	329				
63rd	12	168	169	337	474	.00480	2.27354	
	6	216	121	337				
	12	312	25	337				
64th	6	200	144	344	-264	.00456	- 1.20284	
65th	6	56	289	345	54	.00452	.24426	
	6	296	49	345				
	6	344	1	345				
66th	12	96	256	352	-1536	.00430	- 6.60741	
	12	288	64	352				
67th	3	128	225	353	-483	.00427	- 2.06304	
68th	12	344	16	360	1872	.00407	7.61286	
69th	1	0	361	361	-361	.00404	- 1.45793	
70th	12	224	144	368	-384	.00385	- 1.47813	
71st	24	312	64	376	2208	.00365	8.05434	
72nd	6	152	225	377	-492	.00362	- 1.78286	
	6	296	81	377				
73rd	6	384	0	384	1152	.00346	3.98684	
74th	6	24	361	385	-2460	.00344	- 8.45822	
	6	216	169	385				

	n	$9\frac{h^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{h^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(-l^2+\frac{h^2}{2})$	$\sum \frac{9m}{c^2}(-l^2+\frac{h^2}{2})$
75th	12	248	144	392	- 240	.00329	- .78886	
76th	6	384	9	393	2169	.00327	7.08395	
	6	104	289	393				
	6	344	49	393				
	9	392	1	393				
77th	6	8	400	408	864	.00297	2.56962	
	18	392	16	408				
78th	6	288	121	409	1140	.00296	3.36973	
	6	384	25	409				
79th	3	128	289	417	567	.00282	1.59679	
	6	416	1	417				
80th	24	168	256	424	-4128	.00270	-11.15138	
81st	3	200	225	425	171	.00269	.45922	
	6	344	81	425				
82nd	6	32	400	432	0			
	12	416	16	432				
83rd	6	72	361	433	-1530	.00256	- 3.92170	
	12	312	121	433				
84th	12	296	144	440	48	.00246	.11820	
85th	1	0	441	441	- 396	.00245	- .96961	
	6	152	289	441				
	9	392	49	441				
86th	12	384	64	448	1536	.00235	3.61574	
87th	6	224	225	449	- 678	.00234	- 1.58713	
88th	12	456	0	456	-1728	.00225	- 3.89163	
	12	56	400	456				
89th	6	96	361	457	-2028	.00224	- 4.54231	
	6	288	169	457				

	n	$.9\frac{n^2}{c^2}$	$.9\frac{l^2}{c^2}$	$.9\frac{R^2}{c^2}$	$.9\frac{m}{c^2}(-l^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(-l^2+\frac{n^2}{2})$	$\Sigma 9\frac{m}{c^2}(-l^2+\frac{n^2}{2})$
90th	6	24	441	465	1008	.00214	2.16186	
	12	456	9	465				
	6	416	49	465				
91st	12	216	256	472	-1776	.00207	- 3.66939	
92nd	6	248	225	473	431	.00206	.88579	
	9	392	81	473				
93rd	12	312	169	481	2280	.00197	4.49388	
	12	456	25	481				
94th	12	344	144	488	336	.00190	.63870	
95th	3	200	289	489	891	.00189	1.68506	
	6	488	1	489				
96th	6	416	81	497	762	.00182	1.38379	
97th	12	504	0	504	384	.00175	.67338	
	12	104	400	504				
	12	488	16	504				
98th	6	384	121	505	426	.00174	.74333	
99th	6	72	441	513	189	.00168	.31709	
	12	504	9	513				
	6	224	289	513				
	3	512	1	513				
100th	24	456	64	520	3936	.00162	6.38340	
101st	6	296	225	521	- 462	.00161	- .74567	
102nd	6	128	400	528	- 576	.00156	- .89914	
	6	512	16	528				
103rd	12	168	361	529	- 600	.00155	- .93222	
	12	504	25	529				
104th	18	392	144	536	936	.00150	1.40718	

	n	$9\frac{n^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4 mc^3}{27R^5}(-l^2+\frac{n^2}{2})$	$\sum 9\frac{m}{c^2}(-l^2+\frac{n^2}{2})$
105th	6	96	441	537	-2151	.00150	- 3.21897	
	3	8	529	537				
	6	248	289	537				
	6	488	49	537				
	6	536	1	537				
106th	12	288	256	544	-1344	.00145	- 1.94719	
107th	12	152	400	552	- 864	.00140	- 1.20692	
	12	536	16	552				
108th	6	384	169	553	138	.00139	.19190	
109th	12	416	144	560	768	.00135	1.03488	
110th	3	32	529	561	- 918	.00134	- 1.23150	
	3	512	49	561				
111th	24	312	256	568	2112	.00130	2.74687	
	24	504	64	568				
112th	6	344	225	569	660	.00129	.85457	
	6	488	81	569				
113th	2	0	576	576	-1152	.00126	- 1.44680	
114th	6	216	361	577	- 234	.00125	- .29259	
	12	456	121	577				
115th	6	56	529	585	- 792	.00121	- .95682	
	6	296	289	585				
	6	536	49	585				
	6	584	1	585				
116th	3	512	81	593	526	.00117	.61310	
117th	12	24	576	600	-3456	.00113	- 3.91910	
	6	600	0	600				
	6	200	400	600				
	12	584	16	600				

	n	$9\frac{\lambda^2}{c^2}$	$9\frac{\rho^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}\left(-l^2+\frac{\lambda^2}{2}\right)$	$\left(\frac{3R}{c}\right)^{-5}$	$\frac{10^4}{27}\frac{me^3}{R^5}\left(-l^2+\frac{\lambda^2}{2}\right)$	$\sum \frac{9m}{c^2}\left(-l^2+\frac{\lambda^2}{2}\right)$
118th	12	168	441	609	- 720	.00109	- .78667	
	6	600	9	609				
	6	608	1	609				
119th	9	392	225	617	861	.00106	.91051	
	6	536	81	617				
120th	12	224	400	624	0			
	12	608	16	624				
121st	12	456	169	625	3930	.00102	4.02432	
	12	504	121	625				
	6	600	25	625				
122nd	12	488	144	632	1200	.000996	1.19508	
123rd	3	8	625	633	-2079	.000992	-2.06237	
	6	104	529	633				
	6	344	289	633				
	6	584	49	633				
	6	632	1	633				
124th	12	384	256	640	- 768	.000965	- .74120	
125th	6	416	225	641	- 102	.000961	- .09805	
126th	12	72	576	648	-4248	.000936	-3.97400	
	6	648	0	648				
	12	248	400	648				
	12	632	16	648				
127th	6	288	361	649	-1302	.000932	-1.21333	
128th	6	512	144	656	672	.000907	.60971	
129th	6	216	441	657	-1800	.000904	-1.62684	
	6	648	9	657				
	3	32	625	657				
	3	128	529	657				

	n	$9\frac{n^2}{c^2}$	$9\frac{\ell^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-\ell^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{me^3}{R^5}(-\ell^2+\frac{n^2}{2})$	$\sum\frac{9m}{c^2}(-\ell^2+\frac{n^2}{2})$
130th	12	600	64	664	2832	.000880	2.49273	
131st	6	584	81	665	1266	.000877	1.11016	- 3390
132nd	12	96	576	672	-2304	.000854	-1.96808	
	12	672	0	672				
133rd	12	312	361	673	330	.000851	.28086	
	12	504	169	673				
	6	648	25	673				
134th	12	536	144	680	1488	.000829	1.23400	
135th	12	672	9	681	-1611	.000826	-1.33117	- 5487
	6	56	625	681				
	6	152	529	681				
	9	392	289	681				
	6	632	49	681				
136th	6	608	81	689	1338	.000803	1.07375	
137th	12	296	400	696	-3072	.000783	-2.40384	- 7221
138th	12	672	25	697	3732	.000780	2.90984	- 3489
139th	6	416	289	705	- 486	.000758	- .36829	
140th	24	456	256	712	2448	.000739	1.80981	
	12	648	64	712				
141st	6	488	225	713	1524	.000737	1.12273	- 3
	6	632	81	713				
142nd	6	600	121	721	1074	.000716	.76941	
143rd	12	584	144	728	1776	.000699	1.24196	
144th	1	0	729	729	-2880	.000697	-2.00707	- 33
	6	288	441	729				
	6	104	625	729				
	3	200	529	729				
	12	728	1	729				

	n	$9\frac{h^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{h^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(-l^2+\frac{h^2}{2})$	$\sum 9\frac{m}{c^2}(-l^2+\frac{h^2}{2})$
145th	24	672	64	736	6528	.000681	4.44230	6495
146th	3	512	225	737	93	.000678	.06307	
147th	24	168	576	744	-1728	.000662	-1.14445	4860
	12	744	0	744				
	12	344	400	744				
	24	728	16	744				
148th	6	384	361	745	-1014	.000660	- .66934	3846
149th	12	608	144	752	1920	.000645	1.23821	5766
150th	6	24	729	753	-7533	.000643	-4.84146	- 1767
	12	312	441	753				
	12	744	9	753				
	3	128	625	753				
	6	224	529	753				
151st	24	504	256	760	- 96	.000628	- .06029	
152nd	6	536	225	761	258	.000626	.16151	
153rd	6	600	169	769	6168	.000610	3.76125	4563
	6	648	121	769				
	12	744	25	769				
154th	12	632	144	776	2064	.000596	1.23035	6627
155th	6	152	625	777	108	.000594	.06417	
	6	248	529	777				
	6	488	289	777				
	12	728	49	777				
	6	776	1	777				
156th	12	216	576	792	-9504	.000567	-5.38402	- 2769
	6	8	784	792				
	18	392	400	792				
	12	776	16	792				

	n	$9\frac{h^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^3}(-l^2+\frac{h^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4 mc^3}{27R^5}(-l^2+\frac{h^2}{2})$	$\sum\frac{qm}{c^2}(-l^2+\frac{h^2}{2})$
157th	12	672	121	793	2580	.000565	1.45693	- 189
158th	6	72	729	801	-3060	.000551	-1.68514	- 3249
	3	512	289	801				
	3	800	1	801				
159th	24	744	64	808	7392	.000539	3.98355	4143
160th	6	584	225	809	3798	.000537	2.04029	7941
	12	728	81	809				
161st	6	32	784	816	-4608	.000526	-2.42243	3333
	12	416	400	816				
	6	800	16	816				
162nd	12	456	361	817	- 666	.000524	- .34905	2667
	6	648	169	817				
163rd	6	96	729	825	-5067	.000512	-2.59177	- 2400
	6	384	441	825				
	3	200	625	825				
	6	296	529	825				
	6	536	289	825				
	6	776	49	825				
	6	824	1	825				
164th	6	608	225	833	474	.000499	.23667	
165th	12	56	784	840	-4320	.000489	-2.11248	- 6246
	12	824	16	840				
166th	1	0	841	841	1163	.000488	.56696	
	12	672	169	841				
167th	6	224	625	849	-2025	.000476	- .96410	- 7108
	3	800	49	849				
168th	12	600	256	856	528	.000467	.24631	

	n	$9\frac{h^2}{c^2}$	$9\frac{l^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-l^2+\frac{h^2}{2})$	$(3\frac{R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(-l^2+\frac{h^2}{2})$	$\sum 9\frac{m}{c^2}(-l^2+\frac{h^2}{2})$
169th	6	632	225	857	2388	.000465	1.11066	- 4192
	6	776	81	857				
170th	12	288	576	864	-2592	.000456	-1.18117	- 6784
	6	864	0	864				
171st	6	24	841	865	-3270	.000454	-1.48589	-10054
	12	504	361	865				
	12	744	121	865				
172nd	24	728	144	872	5280	.000445	2.35171	- 4774
173rd	6	864	9	873	2196	.000444	.97524	
	6	248	625	873				
	6	344	529	873				
	6	584	289	873				
	6	824	49	873				
	6	872	1	873				
174th	3	800	81	881	957	.000434	.41543	- 1621
175th	24	312	576	888	-10368	.000426	-4.41262	-11989
	12	888	0	888				
	12	104	784	888				
	12	488	400	888				
	12	872	16	888				
176th	6	864	25	889	2442	.000424	1.03638	- 9547
177th	6	608	289	897	-2304	.000415	- .95616	-11851
	6	896	1	897				
	12	168	729	897				
	12	456	441	897				
	12	888	9	897				
178th	12	648	256	904	816	.000407	.33211	-11035

	n	$9\frac{n^2}{c^2}$	$9\frac{\ell^2}{c^2}$	$9\frac{R^2}{c^2}$	$9\frac{m}{c^2}(-\ell^2+\frac{n^2}{2})$	$(\frac{3R}{c})^{-5}$	$\frac{10^4}{27}\frac{mc^3}{R^5}(-\ell^2+\frac{n^2}{2})$	$\sum 9\frac{m}{c^2}(-\ell^2+\frac{n^2}{2})$
179th	6	824	81	905	1986	.000406	.80612	- 9049
180th	6	128	784	912	0			
	6	512	400	912				
	12	896	16	912				
181st	6	72	841	913	2634	.000397	1.04570	- 6415
	12	744	169	913				
	12	888	25	913				
182nd	12	776	144	920	2928	.000390	1.14046	- 3487
183rd	6	296	625	921	-3375	.000389	-1.31119	- 6862
	9	392	529	921				
	6	632	289	921				
	6	872	49	921				
184th	24 12	672 δ64	256 64	928 928	6336	.000381	2.41528	- 526

-14.63309

Extrapolating for $\sum \frac{9m}{c^2}(-\ell^2+\frac{n^2}{2}) = 0$,

we obtain

$$\sum \frac{10^4}{27}\frac{mc^3}{R^5}(-\ell^2+\frac{n^2}{2}) = -14.4326$$

The Mutual Potential Energy.

The field acting on one of the two first neighbours, included inside a cavity of the form of an ellipsoid of revolution, is given by equation (2.11) where A_0 , B_0 , A and B appearing in that equation are given by (2.21) and (2.22). The dimensions of the ellipsoid of revolution are determined by the distance between the foci $2b$ and the major axis $2b\cosh t$; these are related by equation (2.15). It is required that the ellipsoid should coincide as nearly as possible with a cavity of two overlapping spheres whose dimensions are given by (2.14)

Substituting in equation (2.14) $\frac{a^3}{c^3} = \frac{2}{\pi\sqrt{3}}$ given by (3.5), one finds that

$$x = .7333 \quad , \tag{3.20}$$

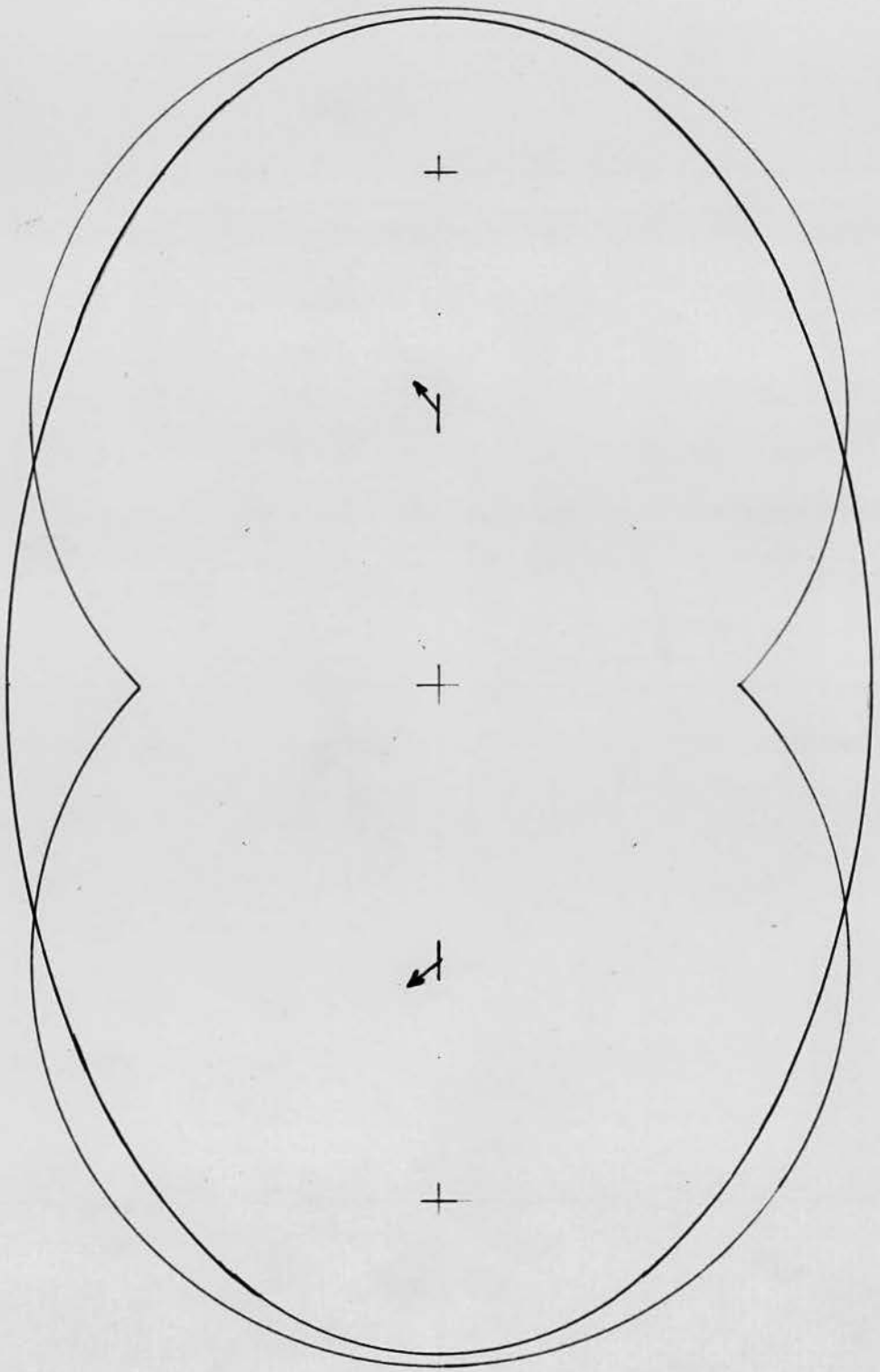
which determines the radius xc of each of the overlapping spheres.

Putting now $\cosh t = \ldots , 1.2, 1.3, 1.4, \ldots$ one obtains from (2.15) $2b\cosh t = \ldots , 2.9032c, 2.4331c, 2.1263c, \ldots$ respectively. It is found that for $\cosh t = 1.3$ the ellipsoid will coincide as nearly as possible with the cavity of the two overlapping spheres. This is clearly shown in Fig.(12).

For $\cosh t = 1.3$

$$\left.\begin{aligned} \frac{c^3}{b^3} &= 1.2202335 \\ \frac{c}{2b} &= .534299 \end{aligned}\right\} \tag{3.21}$$

Fig. (12)



In Table (5) values of $P_n(\cosh t), P_n'(\cosh t), P_n''(\cosh t)$ $Q_n(\cosh t), Q_n'(\cosh t), Q_n''(\cosh t)$ for $\cosh t = 1.3$ are tabulated for $n = 1$ to $n = 10$

In Table (6) those for $P_n'(\frac{c}{2b})$ are given [$\frac{c}{2b}$ given by (3.21)]

In table (7) the values of $(\xi - 1) X_n^{(1)}$, $(\xi - 1) X_n$ are tabulated for $\cosh t = 1.3$.

Finally in Table (8) values of

$$\frac{c^3}{b^3}(n+\tfrac{1}{2})\{P_n'(\tfrac{c}{2b})\}^2 \frac{Q_n}{P_n} \frac{1}{1-X_n} \quad \text{and}$$

$$\frac{c^3}{b^3}(n+\tfrac{1}{2})\{P_n'(\tfrac{c}{2b})\}^2 \frac{-Q_n'}{P_n'} \frac{1}{1-X_n^{(1)}}$$

are tabulated, using for ξ the value given by (3.6)

The values of A_0 . B_0 . A . B are then

$$\left.\begin{aligned} A_0 &= 1 - \frac{\alpha}{c^3}(2.6114) = .8022 \\ B_0 &= 1 - \frac{2\alpha}{c^3}(.99545) = .8492 \\ A &= \frac{\alpha}{c^3} - \frac{\alpha}{c^3}(.6405) = .0272 \\ B &= -\frac{2\alpha}{c^3} - \frac{2\alpha}{c^3}(.0045) = -.1522 \end{aligned}\right\} \qquad (3.22)$$

using the value of $\frac{\alpha}{c^3}$ given by (3.18)

The mutual potential energy is expressed by (2.39) where $\mathcal{G}$. L . M are given by (2.40) and (2.29). Using the values provided by (3.22) one obtains

$$\begin{aligned} F(B_0 B) - F(A_0 A) &= .03135 \\ F(A_0 A) &= .04232 \quad F(B_0 B) = -.21806 \end{aligned} \qquad (3.23)$$

Taking $p = 1.845 \times 10^{-18}$ (3.24)

then for $T = 273$

Table(5)

n.	$P_m(\cosh t)$	$P_m'(\cosh t)$	$P_m''(\cosh t)$	$Q_m(\cosh t)$	$-Q_m'(\cosh t)$	$Q_m''(\cosh t)$
1	1.3	1.	0.	.32397	.86562	4.20080
2	2.035	3.9	3.	.12253	.47736	2.86419
3	3.5425	11.175	19.5	.04949	.25299	1.81401
4	6.532938	28.6975	81.225	.02070	.13091	1.09329
5	12.45307	69.97144	277.7775	.00884	.06669	.635799
6	24.23571	165.6813	850.91081	.00383	.03363	.359728
7	47.83787	385.0357	2431.6345	.00166	.01692	.198605
8	95.39856	883.2493	6626.4460	.00070	.00871	.105873
9	191.7339	2006.811	17446.873	.00024	.00502	.050542
10	387.7240	4526.194	44755.858	-.00003	.00410	.010472

Table(6)

n.	$P_m'(\frac{c}{2b})$	n.	$P_m'(\frac{c}{2b})$	n.	$P_m'(\frac{c}{2b})$	n.	$P_m'(\frac{c}{2b})$
1	1.	4	-1.337981	7	1.3909474	9	1.8355375
2	1.602897	5	-2.409817	8	2.9948891	10	-1.257233
3	.641066	6	-1.227062				

Table(7)

n.	$-(\xi-1)X_m$	$-(\xi-1)X_m^{(1)}$	n.	$-(\xi-1)X_m$	$-(\xi-1)X_m^{(1)}$
1	1.287898	1.634600	6	1.778136	1.796585
2	1.491910	1.644621	7	1.790141	1.832318
3	1.617132	1.686489	8	1.744276	1.913794
4	1.694577	1.728975	9	1.505426	2.292858
5	1.745147	1.765221	10	.911113	18.614887

Table(8)

n	$1-X_m$	$1-X_m^{(1)}$	$\frac{c^3}{b^3}(m+\frac{1}{2})\{P_m'(\frac{c}{2b})\}^2$	$\frac{c^3}{b^3}(m+\frac{1}{2})\frac{\{P_m'(\frac{c}{2b})\}^2}{1-X_m^{(1)}}(-\frac{Q_m'}{P_m'})$	$\frac{c^3}{b^3}(m+\frac{1}{2})\frac{\{P_m'(\frac{c}{2b})\}^2}{1-X_m}(\frac{Q_m}{P_m})$
1	1.017499	1.022209	1.830350	1.5499598	.4482965
2	1.020271	1.022345	7.837800	.9383733	.4625345
3	1.021972	1.022914	1.755157	.0388441	.0239940
4	1.023024	1.023492	9.830040	.0438135	.0304458
5	1.023711	1.023984	38.973901	.0362747	.0270371
6	1.024159	1.024410	11.942339	.0023663	.0018418
7	1.024323	1.024896	17.706210	.00075934	.00060032
8	1.023699	1.026003	93.030073	.00089411	.00066696
9	1.020454	1.031153	39.056477	.00009477	.00004840
10	1.012379	1.252920	20.251820	.00001465	.00000161

$$\frac{p^2}{\beta a^3 kT} = 56.27518 \qquad (3.25)$$

Therfore from (3.23), (3.25) and (2.40)

$$-\mathcal{G} = .8821 \quad L = 12.2714 \quad -M = 2.3816 \qquad (3.26)$$

The Tensor $\mathcal{Q}$.

The average $\overline{p_s^{(i)} p_{s'}^{\alpha}}$ is given by (2.53), (2.55) for $i \neq \alpha$, $i = \alpha$ respectively; K_0, K_1 and K_2 appearing in equation (2.53) are expressed by (2.49) (2.50) and (2.51). The evaluation of the double integrals over θ, θ' between the limits $\theta = 0 \to 90°$, $\theta' = 0 \to 90°$ will be effected numerically by dividing the range between the two limits into $9 \times 9 = 81$ intervals; the difference between the upper and lower limit of both θ, θ' for each interval is 10 degrees.

The values of the integrands at the middle of each interval are tabulated in Table (9). There are 9 diagonal intervals $(\theta = \theta')$ and $2 \times 36 = 72$ non-diagonal elements $(\theta \neq \theta')$. The values of K_0, K_1, K_2 are found to be

$$\left.\begin{aligned} K_0 &= \left(\tfrac{\pi}{2}\right)^2 .6526.89 \\ K_1 &= \left(\tfrac{\pi}{2}\right)^2 .5147.15 \\ -K_2 &= \left(\tfrac{\pi}{2}\right)^2 \quad 338.29 \end{aligned}\right\} \qquad (3.27)$$

then

$$\frac{K_1 + K_2}{K_0} = .73678 \qquad (3.28)$$

In Table (4) it is noticed that $\sum_j \lambda_{ss'}^{ij}$ over

Table(9)

θ	θ'	$L\cos\theta\cos\theta'$	$-M\sin\theta\sin\theta'$	$-\frac{\mu}{2}(\cos^2\theta+\cos^2\theta')$	$\cosh(L\cos\theta\cos\theta')$	$\sinh(L\cos\theta\cos\theta')$	$e^{\frac{\mu}{2}(\cos^2\theta+\cos^2\theta')}$
5	5	12.17814	.01810	1.75080	97243.		.17364
5	15	11.80815	.05372	1.69841	67171.		.18297
5	25	11.07936	.08772	1.59995	32410.		.20191
5	35	10.01383	.11906	1.46729	11167.		.23055
5	45	8.64422	.14677	1.31645	2839.		.26808
5	55	7.01176	.17003	1.16560	555.		.31174
5	65	5.16638	.18812	1.03295	88.		.35596
5	75	3.16394	.20050	.93449	12.		.39279
5	85	1.06540	.20678	.8821	2.	1.	.41391
15	15	11.44934	.15954	1.64603	46920.		.19281
15	25	10.74275	.26050	1.54757	23147.		.21276
15	35	9.70962	.35355	1.41491	8238.		.24295
15	45	8.38149	.43586	1.26406	2183.		.28251
15	55	6.79872	.50492	1.11321	448.		.32850
15	65	5.00943	.55865	.98056	75.		.37510
15	75	3.06785	.59540	.8821	11.		.41391
15	85	1.03313	.61405	.82971	2.	1.	.43617
25	25	10.07961	.42538	1.44911	11926.		.23478
25	35	9.11029	.57730	1.31645	4524.		.26808
25	45	7.86425	.71172	1.16560	1299.		.31174
25	55	6.37916	.82449	1.01475	295.		.36250
25	65	4.70019	.91220	.8821	55.		.41391
25	75	2.87850	.97222	.78364	9.		.45674
25	85	.96932	1.00268	.73125	2.	1.	.48130

θ	θ'	$L\cos\theta\cos\theta'$	$-M\sin\theta\sin\theta'$	$-\frac{g}{2}(\cos^2\theta+\cos^2\theta')$	$\cosh^2(L\cos\theta\cos\theta)$	$\sinh^2(L\cos\theta\cos\theta)$	$e^{\frac{g}{2}(\cos^2\theta+\cos^2\theta')}$
35	35	8.23423	.78352	1.18380	1884.		.30611
35	45	7.10796	.96593	1.03295	611.		.35596
35	55	5.76572	1.11899	.8821	160.		.41391
35	65	4.24824	1.23805	.74945	35.		.47263
35	75	2.60166	1.31948	.65099	7.		.52153
35	85	.87606	1.36082	.59860	1.		.54958
45	45	6.13570	1.19080	.8821	231.		.41391
45	55	4.97703	1.37949	.73125	73.		.48130
45	65	3.66719	1.52627	.59860	20.		.54958
45	75	2.24579	1.62666	.50014	5.		.60644
45	85	.75629	1.67765	.44775	1.		.63906
55	55	4.03717	1.59808	.58040	28.		.55968
55	65	2.97459	1.76810	.44775	10.		.63906
55	75	1.82169	1.88442	.34929	3.		.70520
55	85	.61345	1.94346	.29691	1.		.74310
65	65	2.19179	1.95622	.31509	5.		.72973
65	75	1.34225	2.08492	.21663	2.		.80523
65	85	.45208	2.15025	.16425	1.		.84853
75	75	.82206	2.22206	.11818	1.		.88854
75	85	.27684	2.29169	.06579	1.	0.	.93633
85	85	.09325	2.36350	.01340	1.	0.	.98669

Table(9)cont.

θ	θ'	$I_0(M\sin\theta\sin\theta')$	$-I_1(M\sin\theta\sin\theta')$	Integrand of K_0	Integrand of K_1	Integrand of $-K_2$
5	5	1.00008	.00905	128.29	127.34	.01
5	15	1.00072	.02687	277.44	266.96	.17
5	25	1.00192	.04390	241.50	218.04	.39
5	35	1.00355	.05964	129.16	105.40	.38
5	45	1.00539	.07358	47.16	33.22	.21
5	55	1.00724	.08532	12.44	7.11	.08
5	65	1.00887	.09448	2.50	1.05	.02
5	75	1.01007	.10075	.40	.10	0.
5	85	1.01072	.10394	.07	0.	0.
15	15	1.00637	.08002	609.87	569.02	3.25
15	25	1.01704	.13136	547.86	479.61	7.74
15	35	1.03149	.17955	306.47	242.49	7.92
15	45	1.04806	.22315	118.29	80.79	4.61
15	55	1.06476	.26068	33.22	18.41	1.72
15	65	1.07956	.29036	7.12	2.91	.45
15	75	1.09061	.31109	1.24	.31	.09
15	85	1.09651	.32172	.25	.01	.02
25	25	1.04575	.21754	522.97	429.57	19.43
25	35	1.08507	.30084	319.00	236.82	21.44
25	45	1.13070	.37887	136.83	87.69	13.70
25	55	1.17730	.44828	43.58	22.66	5.75
25	65	1.21910	.50588	10.63	4.07	1.69
25	75	1.25064	.54585	2.10	.49	.37
25	85	1.26758	.56704	.51	.02	.10

θ	θ'	$I_0(M\sin\theta\sin\theta')$	$-I_1(M\sin\theta\sin\theta')$	Integrand of K_0	Integrand of K_1	Integrand of $-K_2$
35	35	1.15947	.42260	219.99	147.62	26.38
35	45	1.24721	.54152	110.02	63.72	19.37
35	55	1.33840	.65176	41.65	19.57	9.53
35	65	1.42150	.74545	12.22	4.23	3.33
35	75	1.48497	.81412	3.00	.64	.91
35	85	1.51938	.85054	.48	.03	.15
45	45	1.38718	.70736	66.32	33.16	16.91
45	55	1.53541	.86745	31.25	12.67	10.23
45	65	1.67286	1.00800	11.78	3.52	4.55
45	75	1.77929	1.11369	3.69	.67	1.58
45	85	1.83751	1.17065	.83	.05	.37
55	55	1.74790	1.08275	18.38	6.05	6.50
55	65	1.94818	1.27756	9.24	2.24	4.50
55	75	2.10534	1.42711	3.52	.52	1.89
55	85	2.19198	1.50867	1.33	.07	.75
65	65	2.21135	1.52683	6.63	1.18	3.76
65	75	2.42014	1.72130	3.41	.37	2.12
65	85	2.53606	1.82842	1.94	.07	1.26
75	75	2.67180	1.95327	2.21	.15	1.51
75	85	2.81224	2.08192	2.53	0.	1.80
85	85	2.96675	2.22298	2.91	0.	2.16

first neighbours, vanishes, i.e.

$$\sum_{\alpha=1}^{4}\left(g^{-1}_{ss'} - 3\, k_s^{ij} k_{s'}^{ij}\right) = 0 \qquad (3.29)$$

where k_s^{ij} are the components of a unit vector along the line joining the molecules i, α. Then

$$\sum_{\alpha=1}^{4} k_s^{ij} k_{s'}^{ij} = \frac{4}{3} g^{-1}_{ss'} \qquad (3.30)$$

Summing $\overline{p_s^{(i)} p_{s'}^{(\alpha)}}$ over first neighbours using equation (3.30) one obtains

$$\frac{1}{p^2}\sum_{\alpha=1}^{4}\overline{p_s^{(i)} p_{s'}^{\alpha}} = \frac{4}{2}\frac{K_2}{K_0} g^{-1}_{ss'} + \frac{4}{3}\left(\frac{K_1}{K_0} - \frac{1}{2}\frac{K_2}{K_0}\right) g^{-1}_{ss'}$$

$$= \frac{4}{3}\left(\frac{K_1 + K_2}{K_0}\right) g^{-1}_{ss'} \qquad (3.31)$$

For further neighbours A_0, B_0, A, B are given by (2.12) and (2.13). Since, for ice, A is very small we may neglect its square and higher powers, and so

$$F(A_0 A) = A, \quad F(B_0 B) = B = -2A; \text{ then}$$

$$\mathcal{G} = 0 \qquad -M = \frac{9z}{(2z+1)^2}\frac{p^2}{R^3 kT} \qquad L = -2M \qquad (3.32)$$

where R is the distance of the molecule considered from the molecule taken as origin.

Neglecting second and higher powers of M in the double integrals for K_0, K_1, K_2 we obtain

$$K_0 = 1 \qquad K_1 = \frac{L}{9} \qquad K_2 = \frac{2M}{9} \qquad (3.33)$$

Therefore $\overline{p_s^{(i)} p_{s'}^{\alpha}}$ for second and higher neighbours will be given by (from (2.53))

$$\frac{1}{p^2}\overline{p_s^{(i)} p_{s'}^{\alpha}} = -\frac{\varepsilon}{(2\Sigma+1)^2}\frac{p^2}{R_{ij}^3 kT}\left(g^{-1}_{ss'} - 3\, k_s^{ij} k_{s'}^{ij}\right) \qquad (3.34)$$

Remembering, according to (3.29) that the sum on the right hand side of (3.34) vanishes for first neighbours, it is seen that the sum of the left hand side for second and further neighbours is

$$\frac{1}{p^2}\sum_{\alpha>4}\overline{p_s^{(i)} p_{s'}^{\alpha}} = \frac{-\varepsilon}{(2\Sigma+1)^2}\frac{p^2}{\alpha kT}\left[g^{-1}(\Lambda-1)\right]_{ss'} , \qquad (3.35)$$

using the definition of Λ given by (1.39), (1.59).

Combining (3.31), (3.35) one finally obtains

$$Q_{ss'} = \frac{1}{3}\bar{g}^{-1}_{ss'} + \frac{1}{p^2}\sum_{\alpha=1}^{4}\overline{p_s^{(i)} p_{s'}^{\alpha}} + \frac{1}{p^2}\sum_{\alpha>4}\overline{p_s^{(i)} p_{s'}^{\alpha}}$$

$$= \frac{1}{3}\bar{g}^{-1}_{ss'}\left[1 + 4\,\frac{\pi_1+\pi_2}{\pi_0}\right] - \frac{\varepsilon}{(2\Sigma+1)^2}\frac{p^2}{\alpha kT}\left[\bar{g}^{-1}(\Lambda-1)\right]_{ss'} , \text{ or}$$

$$(gQ)_{ss'} = \frac{\delta_{ss'}}{3}\left[1+4\,\frac{\pi_1+\pi_2}{\pi_0}\right] - \frac{\varepsilon}{(2\Sigma+1)^2}\frac{p^2}{\alpha kT}(\Lambda-1)_{ss'} \qquad (3.36)$$

Expressing

$$Q_0 = \frac{1}{3}\left[1 + 4\,\frac{\pi_1+\pi_2}{\pi_0}\right] \qquad (3.37)$$

$$S_0 = \frac{\varepsilon}{(2\Sigma+1)^2}\,\frac{p^2}{\alpha kT} \qquad (3.38)$$

then

$$(gQ)_{ss'} = Q_0\,\delta_{ss'} - S_0\,(\Lambda-1)_{ss'} \qquad (3.39)$$

By use of (3.6), (3.25) and (3.28) one obtains

$$Q_0 = 1.31570$$
$$S_0 = .186087 \qquad (3.40)$$

To calculate the dielectric constant from equation (1.53) we express it in the form

$$\frac{\varepsilon_{ss'} - \delta_{ss'}}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1}\left[F(\lambda)\right]_{ss'} \qquad (3.41)$$

where $F(\lambda)$ is a function of the tensor λ, then

$$\frac{\varepsilon_{11}-1}{3} = \frac{\varepsilon_{22}-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1} F(\lambda_{11}) \qquad (3.42)$$
$$\frac{\varepsilon_{33}-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1} F(\lambda_{33})$$

The non diagonal elements of the tensor λ and therefore of ε vanish.

Since $\lambda_{11} = 1+\beta \qquad \lambda_{33} = 1-2\beta$ (See (3.14)

then we can express

$$\varepsilon_{11} = \varepsilon_0 + \Delta \qquad \varepsilon_{33} = \varepsilon_0 - 2\Delta \qquad (3.43)$$

where

$$\frac{\varepsilon_0-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1}\left[F(\lambda)\right]_{\lambda=1}$$
$$\frac{\Delta}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1}\left[\frac{\partial}{\partial\lambda} F(\lambda)\right]_{\lambda=1}\cdot\beta \qquad (3.44)$$

Equations (3.44) can be expressed in the form

$$\frac{\varepsilon_0-1}{3} = \frac{\varepsilon_0+2}{3}\beta + \left(\frac{3\varepsilon_0}{2\varepsilon_0+1}\right)\frac{p^2}{a^3kT} Q_0 \qquad (3.45)$$

$$A = -\frac{9\varepsilon_0}{2\varepsilon_0+1}\left[\frac{\beta}{(1-\beta f)^2}+\frac{2-\beta f}{(1-\beta f)^2}\cdot\frac{p^2}{a^3kT}Q_0+\frac{1}{(1-\beta f)}\frac{p^2}{a^3kT}S_0\right]B \quad (3.46)$$

Substituting from (3.45) into (3.46) one obtains

$$-\frac{A}{B}=\frac{1}{(1-\beta f)}\left[2(\varepsilon_0-1)-\beta(\varepsilon_0+2)\right]+\frac{1}{(1-\beta f)}\cdot\frac{p^2}{a^3kT}\cdot\frac{9\varepsilon_0}{2\varepsilon_0+1}S_0 \quad (3.47)$$

Putting

$$\beta = .2061 \qquad \frac{p^2}{a^3kT} = 11.5984 \quad (3.48)$$

and substituting for Q_0 from (3.40), equation (3.45) becomes

$$1.5878\varepsilon_0^2 - 139.3706\varepsilon_0 - 1.4122 = 0$$

giving

$$\varepsilon_0 = 87.84 \quad (3.49)$$

Also from (3.40) (3.47) (3.48) and (3.19)

$$-A = .62 \quad (3.50)$$

By use of equations (3.43) (3.49) and (3.50) we finally obtain

$$\varepsilon_{11} = \varepsilon_{22} = 87.22 \qquad \varepsilon_{33} = 89.08, \quad (3.51)$$

and the non-diagonal elements vanish.

One notices from this result obtained the following:

(i) The dielectric constant along the axis is somewhat bigger than that perpendicular to the axis; in spite of the fact that the results of all the experiments available do not distinguish between the values along

the axis and those perpendicular to the axis.
(ii) The value of the dielectric constant calculated is higher than that given by the most accurate experiments, and which we used to calculate the tensor Q. This may be explained by our assumption that the molecules in ice are free to rotate. There may be some restriction on the rotations of the molecules which will lower the dielectric constant.

Restricted Rotations.

In this section we shall consider any molecule in the ice crystal to have only 6 definite orientations. The rotation of the molecules between these orientations can either happen in an orderly way, that is, at any instant the molecules are divided into groups with similar configurations, or in a disorderly way. The former case is the more probable and will be dealt with in the last Chapter. The latter case will be treated in this Chapter, just to show that it will not give the expected high dielectric constant near the melting point.

If $\underline{k}_s$ $(s = 1, 2, 3, 4)$ are unit vectors along the four lines joining a molecule to its four first neighbours; then a unit vector along the dipole has one of the 6 values

$$\frac{\sqrt{3}}{2}(\underline{k}_s + \underline{k}_{s'}) \qquad (s \neq s') \tag{3.52}$$

The cosine of the angle between such a dipole and either $\underline{k}_3$ or $\underline{k}_{3'}$ is $\frac{1}{\sqrt{3}}$; and with the other two lines it makes an angle whose cosine is $\frac{-1}{\sqrt{3}}$

Three of the six vectors given by equation (3.52) by use of (3.1), are mutually perpendicular and opposite to the other three.

The six states of the molecule will be labelled $\sigma = (1, 2, 3, \bar{1}, \bar{2}, \bar{3})$ so that the direction $\bar{\sigma}$ is opposite to the direction σ . These states are shown in Fig. (13) for the middle molecule and one of the upper three molecules. (By upper three we mean those in red plane in Fig. 6). In Fig. (14) they are shown for the middle molecule and the lower molecule.

We consider the mutual potential energy $W_{\sigma\sigma'}$ between the middle molecule in state σ and one of the first neighbours in state σ' . It is clear that $W_{\sigma\sigma'} = - W_{\bar{\sigma},\sigma'}$ so that we need only write down the energy tensor for $\sigma, \sigma' = 1, 2, 3$. Using the expression for W given by equation (2.39), we may write

$$- \frac{W_{\sigma\sigma'}}{kT} = L(\cos\theta \cos\theta')_{\sigma\sigma'} + M(\sin\theta \sin\theta' \cos\phi)_{\sigma\sigma'} \quad (3.53)$$

The term containing $\mathcal{G}$ has been omitted since $\cos^2\theta = \frac{1}{3}$ for all orientations of the molecule.

For the middle molecule and one of the upper three

$$\cos\theta \cos\theta' = \begin{pmatrix} \frac{1}{3} & \frac{-1}{3} & \frac{-1}{3} \\ \frac{-1}{3} & \frac{1}{3} & \frac{1}{3} \\ \frac{-1}{3} & \frac{1}{3} & \frac{1}{3} \end{pmatrix} \quad (3.54)$$

Fig.(13)

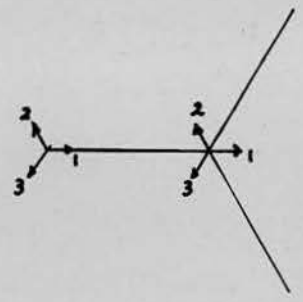


Fig.(14)

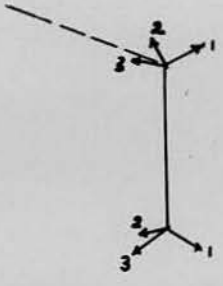
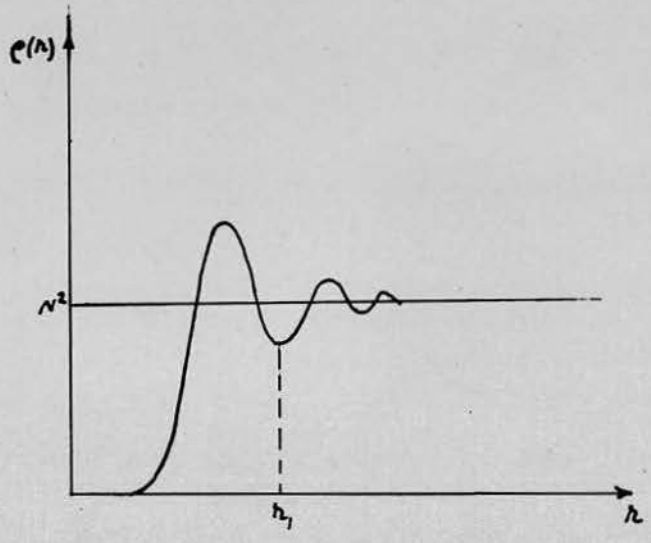


Fig.(15)



and for the middle and the lower molecules

$$\cos\theta\cos\theta' \equiv \begin{pmatrix} -\frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \\ -\frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \\ -\frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \end{pmatrix} \tag{3.55}$$

The tensors W , W' for an upper, and the lower molecules respectively can then be written, following equations (3.53) (3.54) and (3.55)

$$-\frac{W}{kT} \equiv \begin{pmatrix} \frac{1}{3}L+\frac{2}{3}M, -\frac{1}{3}L+\frac{1}{3}M, -\frac{1}{3}L+\frac{1}{3}M \\ -\frac{1}{3}L+\frac{1}{3}M, \frac{1}{3}L+\frac{2}{3}M, \frac{1}{3}L-\frac{1}{3}M \\ -\frac{1}{3}L+\frac{1}{3}M, \frac{1}{3}L-\frac{1}{3}M, \frac{1}{3}L+\frac{2}{3}M \end{pmatrix} \tag{3.56}$$

$$-\frac{W'}{kT} \equiv \begin{pmatrix} -\frac{1}{3}L+\frac{2}{3}M, -\frac{1}{3}L-\frac{1}{3}M, -\frac{1}{3}L-\frac{1}{3}M \\ -\frac{1}{3}L-\frac{1}{3}M, -\frac{1}{3}L+\frac{2}{3}M, -\frac{1}{3}L-\frac{1}{3}M \\ -\frac{1}{3}L-\frac{1}{3}M, -\frac{1}{3}L-\frac{1}{3}M, -\frac{1}{3}L+\frac{2}{3}M \end{pmatrix} \tag{3.57}$$

Using for the probability Boltzman's expression (1.17) we may write the probability tensors ρ, ρ' corresponding to the energy tensors W , W' in the form.

$$\rho \equiv \begin{pmatrix} \rho_{11} & \rho_{12} & \rho_{12} & \rho_{1\bar{1}} & \rho_{12} & \rho_{12} \\ \rho_{12} & \rho_{11} & \rho_{12} & \rho_{12} & \rho_{1\bar{1}} & \rho_{12} \\ \rho_{12} & \rho_{12} & \rho_{11} & \rho_{12} & \rho_{12} & \rho_{1\bar{1}} \\ \rho_{1\bar{1}} & \rho_{12} & \rho_{12} & \rho_{11} & \rho_{12} & \rho_{12} \\ \rho_{12} & \rho_{1\bar{1}} & \rho_{12} & \rho_{12} & \rho_{11} & \rho_{12} \\ \rho_{12} & \rho_{12} & \rho_{1\bar{1}} & \rho_{12} & \rho_{12} & \rho_{11} \end{pmatrix} \tag{3.58}$$

$$\rho' \equiv \begin{pmatrix} \rho'_{11} & \rho'_{12} & \rho'_{12} & \rho'_{1\bar{1}} & \rho'_{1\bar{2}} & \rho'_{1\bar{2}} \\ \rho'_{12} & \rho'_{11} & \rho'_{12} & \rho'_{1\bar{2}} & \rho'_{1\bar{1}} & \rho'_{1\bar{2}} \\ \rho'_{12} & \rho'_{12} & \rho'_{11} & \rho'_{1\bar{2}} & \rho'_{1\bar{2}} & \rho'_{1\bar{1}} \\ \rho'_{1\bar{1}} & \rho'_{1\bar{2}} & \rho'_{1\bar{2}} & \rho'_{11} & \rho'_{12} & \rho'_{12} \\ \rho'_{1\bar{2}} & \rho'_{1\bar{1}} & \rho'_{1\bar{2}} & \rho'_{12} & \rho'_{11} & \rho'_{12} \\ \rho'_{1\bar{2}} & \rho'_{1\bar{2}} & \rho'_{1\bar{1}} & \rho'_{12} & \rho'_{12} & \rho'_{11} \end{pmatrix} \qquad (3.59)$$

Where, using for L, M the values given by (3.26)

$$\left.\begin{aligned} 36\,\rho_{11} &= .26488 & 36\,\rho_{1\bar{1}} &= .00178 \\ 36\,\rho_{12} &= .00017 & 36\,\rho_{1\bar{2}} &= 2.86650 \end{aligned}\right\} \qquad (3.60)$$

$$\left.\begin{aligned} 36\,\rho'_{11} &= .00005 & 36\,\rho'_{1\bar{1}} &= 5.06298 \\ 36\,\rho'_{12} &= .00064 & 36\,\rho'_{1\bar{2}} &= .46784 \end{aligned}\right\} \qquad (3.61)$$

We now consider the average $\overline{p_3^{(i)} p_3^{d'}}$, where p_3 is the component along the axis of the ice crystal, for the middle molecule and one of the upper three molecules

$$\left.\begin{aligned} \overline{p_3^{(i)} p_3^{d'}} &= \tfrac{1}{3} p^2 [6\rho_{11} + 8\rho_{12} + 4\rho_{1\bar{2}} - 6\rho_{1\bar{1}} - 8\rho_{1\bar{2}} - 4\rho_{12}] \\ &= \tfrac{2}{3} p^2 [3(\rho_{11} - \rho_{1\bar{1}}) + 2(\rho_{12} - \rho_{1\bar{2}})] \end{aligned}\right\} \qquad (3.62)$$

and for the middle and lower molecules

$$\begin{aligned} \overline{p_3^{(i)} p_3^{d'}} &= \tfrac{1}{3} p^2 [-6\rho'_{11} - 12\rho'_{12} + 6\rho'_{1\bar{1}} + 12\rho'_{1\bar{2}}] \\ &= 2p^2 [(\rho'_{1\bar{1}} - \rho'_{11}) + 2(\rho'_{1\bar{2}} - \rho'_{12})] \end{aligned} \qquad (3.63)$$

Summing $\overline{p_3^{(i)} p_3^{d'}}$ over the four first neighbours then

$$\frac{1}{p^2} \sum_{d=1}^{4} \overline{p_3^{(i)} p_3^{d'}} = 6(\rho_{11} - \rho_{1\bar{1}}) + 4(\rho_{12} - \rho_{1\bar{2}}) + 2(\rho'_{1\bar{1}} - \rho'_{11}) + 4(\rho'_{1\bar{2}} - \rho'_{12}) \qquad (3.64)$$

Neglecting $\overline{p_3^{(i)} p_3^{d'}}$ for further neighbours, we obtain,

by use of equations (3.60) (3.61) and (3.64)

$$Q_0 = \frac{1}{3} + \frac{1}{\beta^2} \sum_{j=1}^{4} \overline{p_j^{(i)}} p_j^{(i')} = .391887 \qquad (3.65)$$

Substituting for this value of Q_0 in (3.45) we obtain

$$1.5878\, \varepsilon_0^2 - 2.0305\, \varepsilon_0 - 1.4122 = 40.9074\, \varepsilon_0$$

giving

$$\varepsilon_0 = 27.09 \qquad (3.66)$$

which is much lower than the value we used for the calculation of L , M , namely $\varepsilon_0 = 74.6$

CHAPTER IV.

AN EXPRESSION FOR THE CORRELATION COEFFICIENT Q. IN LIQUIDS AND THE EFFECT OF THERMAL VIBRATIONS IN SOLIDS.

An Expression of Q_0 for Liquids.

The positions of the molecules, in the liquid state, are neither fixed nor confined to certain volumes. A single molecule will be assumed to have the same probability of occupying any position throughout the liquid.

The tensor $\overline{p_s^{(i)} p_{s'}^{\alpha'}}$, defined by equation (2.53) will then depend on the simultaneous positions $\underline{x}^{(i)}$, $\underline{x}^{\alpha'}$ of the two molecules i, α' in question.

The tensor Q will then be defined by

$$N^{(\alpha)} Q_{ss'} = \tfrac{1}{3} N^{(\alpha)} \delta_{ss'} + \sum_{i\alpha}{}' \iint q_{ss'}^{i\alpha} \rho^{i\alpha}(\underline{x}\,\underline{x}')\, dx\, dx' \qquad (4.1)$$

(using orthogonal axes)

where

$$\rho^2 q_{ss'}^{i\alpha} = \overline{p_s^{(i)} p_{s'}^{\alpha'}} \qquad (4.2)$$

$N^{(\alpha)}$ is the total number of molecules and $\rho^{i\alpha}(\underline{x}\,\underline{x}')$ is the probability that two molecules i, α' occupy positions $\underline{x}, \underline{x}'$ simultaneously. Since both $\rho^{i\alpha}$ and $q_{ss'}^{i\alpha}$ depend on the difference $\underline{x} - \underline{x}'$, then, integrating over $\underline{x}'$ in (4.1), remembering that the volume occupied by $N^{(\alpha)}$ molecules is $\frac{N^{(\alpha)}}{N}$, we obtain

$$Q_{ss'} = \tfrac{1}{3} \delta_{ss'} + \frac{1}{N} \sum_{i\alpha}{}' \int q_{ss'}^{i\alpha}(x)\, \rho^{i\alpha}(x)\, dx \qquad (4.3)$$

Substituting for $q_n^{ij}(x)$ from (2.53), the integral in (4.3) becomes

$$\int \left[\frac{1}{2}\frac{K_2}{K_0}\delta_{ss'} - \left(\frac{K_1}{K_0} - \frac{1}{2}\frac{K_2}{K_0}\right) k_s k_{s'}\right] \rho^{ij}(\lambda)\, \lambda^2\, d\lambda\, d\Omega$$
$$= \frac{4\pi}{3}\delta_{ss'} \int_0^\infty \left(\frac{K_1 + K_2}{K_0}\right) \rho^{ij}(\lambda)\, \lambda^2\, d\lambda \qquad (4.4)$$

Writing

$$\rho(\lambda) = \sum_{ij}{}' \rho^{ij}(\lambda) \qquad (4.5)$$

for the probability that any two molecules be found simultaneously at distance λ apart, then by use of (4.5) and (4.4) equation (4.3) becomes

$$Q_0 = \frac{1}{3}\left[1 + \frac{1}{N}\int_0^\infty \left(\frac{K_1 + K_2}{K_0}\right) 4\pi\, \rho(\lambda)\, \lambda^2\, d\lambda\right] \qquad (4.6)$$

Since the liquid is isotropic we put $\lambda = 1$ and the dielectric constant will be given by equation (1.54) where Q_0 is given by (4.6).

K_0 , K_1 , and K_2 are functions of λ and are given for 1st neighbours by equations (2.49) (2.50) and (2.51).

For further neighbours we shall neglect $\frac{K_1 + K_2}{K_0}$ and therefore the integral in (4.6) will have the upper limit λ_1 , instead of ∞ (See Fig. (15)).

The expression $\frac{1}{N} 4\pi\, \rho(\lambda)\, \lambda^2\, d\lambda$ is the number of molecules which lie between spheres λ and $\lambda + d\lambda$ relative to the molecule at the centre of the sphere; calling this expression $m(\lambda)\, d\lambda$ then

$$Q_0 = \frac{1}{3}\left[1 + \int_0^{\lambda_1} \left(\frac{K_1 + K_2}{K_0}\right) m(\lambda)\, d\lambda\right] \qquad (4.7)$$

Let

$$z = \int_0^{r_1} n(r)\, dr \qquad (4.8)$$

be the co-ordination number, that is the number of first neighbours, then Q_0 may be given approximately by

$$Q_0 = \frac{1}{3}\left[1 + z\left(\frac{H_1 + H_2}{H_0}\right)_{r=r_0}\right] \qquad (4.9)$$

where r_0 is the value for which $n(r)$ is greatest or more correctly given by

$$r_0 = \frac{1}{z}\int_0^{r_1} r\, n(r)\, dr \qquad (4.10)$$

Thermal Vibrations in Solids

If $\underline{x}'^{(i)}$ is the undisturbed position of a molecule (i) in a crystal and $\underline{u}^{(i)}$ its thermal displacement, then its position vector will be given by

$$\underline{x}'^{(i)} = \underline{x}^{(i)} + \underline{u}^{(i)} \qquad (4.11)$$

We assume a certain thermal configuration of the whole set of molecules and proceed in the same way as we have done in the second section of Chapter I. Instead of equations (1.40) and (1.43), we have

$$\rho = \rho_0\left[1 + \frac{1}{kT}\sum_{ij}\sum_{ss'} p_s^{(i)}\left(g\lambda'^{-1}\right)_{ss'}^{ij} E'_{s'}\right] \qquad (4.12)$$

$$\sum_c \mu_s^{(i)} = \sum_j \sum_{s'} \left(\lambda'^{-1}\right)_{ss'}^{ij}\left[p_{s'}^{j} + \alpha E'_{s'} + \alpha \vartheta_{s'}^{j}\right] \qquad (4.13)$$

The tensor λ' appearing in these equations depends on the new positions $\underline{x}'$ given by (4.11).

The image field $\bar{e}_s^{\alpha'}$ will depend on the given thermal configuration, as well as on the configuration of the dipoles. Forming the product $\rho \sum_{j'} \mu_{s'}^{\alpha'}$, and averaging over all the orientations of the dipoles leaving the thermal configuration as it is, we obtain

$$\sum_{\alpha'} \bar{\mu}_s^{\alpha'} = \sum_{j's'} (\chi^{-1})_{ss'}^{\alpha\alpha'} (\alpha E_{s'}^{\alpha'} + \alpha \bar{e}_{s'}^{\alpha'}) + \frac{\beta^2}{kT} \sum_{j's'} (\chi^{-1} q' g \chi^{-1})_{ss'}^{\alpha\alpha'} E_{s'}^{\alpha'} \qquad (4.14)$$

Other terms which will vanish after thermal averaging are omitted.

The tensor q', defined by (4.2) will also depend on the new positions x' given by (4.11).

We may expand the tensors λ', q' in powers of the thermal displacements as follows

$$(\lambda')_{ss'}^{\alpha\alpha'} = \lambda_{ss'}^{\alpha\alpha'} + \sum_{\sigma} \frac{\partial \lambda_{ss'}^{\alpha\alpha'}}{\partial x_{\sigma\sigma'}^{\alpha\alpha'}} u_{\sigma}^{\alpha} + \frac{1}{2} \sum_{\sigma\sigma'} \frac{\partial^2 \lambda_{ss'}^{\alpha\alpha'}}{\partial x_{\sigma}^{\alpha} \partial x_{\sigma'}^{\alpha'}} u_{\sigma}^{\alpha} u_{\sigma'}^{\alpha'} \qquad (4.15)$$

$$(q')_{ss'}^{\alpha\alpha'} = q_{ss'}^{\alpha\alpha'} + \sum_{\sigma} \frac{\partial q_{ss'}^{\alpha\alpha'}}{\partial x_{\sigma\sigma'}^{\alpha\alpha'}} u_{\sigma}^{\alpha\alpha'} + \frac{1}{2} \sum_{\sigma\sigma'} \frac{\partial^2 q_{ss'}^{\alpha\alpha'}}{\partial x_{\sigma}^{\alpha} \partial x_{\sigma'}^{\alpha'}} u_{\sigma}^{\alpha} u_{\sigma'}^{\alpha'} \qquad (4.16)$$

where

$$u_{\sigma}^{\alpha\alpha'} = u_{\sigma}^{\alpha} - u_{\sigma}^{\alpha} \qquad (4.17)$$

and the tensors $\lambda_{ss'}^{\alpha\alpha'}$, $q_{ss'}^{\alpha\alpha'}$ are defined by equations (1.29), (1.59), (2.53) (2.55) and (4.2).

The tensors (χ^{-1}), $(\chi^{-1} q' \chi^{-1})$ appearing in equation (4.14) can be expanded, with the help of (4.15) and (4.16) in first and second powers of the thermal displacements.

If $\phi(R_{ij})$ is the mutual potential energy

between molecules i and α then the mutual potential energy of the whole crystal is

$$\Phi^{(0)} + \frac{1}{2}\sum_{ij}\sum_{ss'} \Phi^{ij}_{ss'} u^i_s u^\alpha_{s'} \qquad (4.18)$$

where

$$\Phi^{ij}_{ss'} = -\frac{\partial^2 \phi^{ij}}{\partial x^i_s \partial x^\alpha_{s'}} \qquad i \neq \alpha$$
$$\Phi^{ii}_{ss'} = \sum_{\alpha \neq i} \frac{\partial^2 \phi^{i\alpha}}{\partial x^i_s \partial x^i_{s'}} \qquad (4.19)$$

The probability of the given thermal displacement is

$$\rho = \frac{1}{Z} \exp.\left\{ -\frac{\Phi}{kT} \right\} \qquad (4.20)$$

where

$$Z = \int \cdots \int \exp.\left\{ -\frac{1}{2}\sum_{ij}\sum_{ss'} \frac{1}{kT} \Phi^{ij}_{ss'} u^i_s u^\alpha_{s'} \right\} du^{(1)} \cdots du^{(N)}$$

$$= \left(\frac{2\pi kT}{\Delta_N} \right)^{\frac{1}{2}} \qquad (4.21)$$

Δ_N is the determinant of $\Phi^{ij}_{ss'}$.

Following equations (2.3) and (2.5) we have

$$\overline{u^i_s u^\alpha_{s'}} = -2kT \frac{\partial}{\partial \Phi^{ij}_{ss'}} (\log Z) \qquad (4.22)$$

By use of equation (4.21) we obtain

$$\overline{u^i_s u^\alpha_{s'}} = \frac{kT}{\Delta_N} \frac{\partial \Delta_N}{\partial \Phi^{\alpha i}_{ss'}} = kT \left(\Phi^{-1} \right)^{\alpha i}_{ss'} \qquad (4.23)$$

where Φ^{-1} is the reciprocal of the matrix Φ.

Since the average of terms linear in the thermal displacements vanish and the averages of quadratic terms, according to (4.23) are proportional to the temperature, we may write

$$\sum_{\alpha'} (\lambda^{-1})^{\alpha\alpha'}_{ss'} = (\lambda^{-1})_{ss'} + \xi_{ss'} T \tag{4.24}$$

$$\sum_{\alpha'} (\lambda^{-1} q' g \lambda^{-1})^{\alpha\alpha'}_{ss'} = (\lambda^{-2} Q g)_{ss'} + \eta_{ss'} T \tag{4.25}$$

The tensor $\xi_{ss'}$ depends on the structure of the crystal as well as on the form of the potential field of a molecule. The tensor $\eta_{ss'}$ depends in addition on the temperature T.

Proceeding from equation (4.14) in the same way as we have done in the second section of Chapter I, we obtain, instead of (1.53),

$$\frac{\varepsilon-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1}\left[\beta \frac{\lambda^{-1}+\xi T}{1-\beta f(\lambda^{-1}+\xi T)} + \frac{p^2}{a^3 kT} \frac{\lambda^{-2} g Q + \eta T}{1-\beta f(\lambda^{-1}+\xi T)}\right] \tag{4.26}$$

For an isotropic crystal, putting $\lambda = 1$

$$\frac{\varepsilon_0-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1} \cdot \frac{1}{1-\beta f-\beta f \xi_0 T}\left[\beta + \frac{p^2}{a^3 kT} Q_0 + \xi_0 T\beta + \eta_0 T \frac{p^2}{a^3 kT}\right] \tag{4.27}$$

Neglecting second and higher powers of ξ_0, η_0 one obtains

$$\left[\frac{\varepsilon_0-1}{3} - \beta\frac{\varepsilon_0+2}{3} - \frac{3\varepsilon_0}{2\varepsilon_0+1}\frac{p^2 Q_0}{a^3 kT}\right] = \frac{3\varepsilon_0 T}{2\varepsilon_0+1}\left[\frac{\beta f \xi_0}{1-\beta f}\left(\beta + \frac{p^2 Q_0}{a^3 kT}\right) + \xi_0\beta + \eta_0 \frac{p^2}{a^3 kT}\right] \tag{4.28}$$

Putting

$$\varepsilon_0 = \varepsilon_0^{(0)} + \varepsilon_0^{(1)} \tag{4.29}$$

where $\xi_0^{(1)}$ is the excess due to the thermal motion, then

$$\frac{\xi_0^{(1)}-1}{3} - \beta\frac{\xi_0^{(1)}+2}{3} - \frac{3\xi_0^{(1)}}{2\xi_0^{(1)}+1}\cdot\frac{p^2\alpha_0}{a^3kT} = 0$$

$$\frac{\xi_0^{(1)}}{3\xi_0^{(1)}(2\xi_0^{(1)}+1)}\left[2\xi_0^{(1)2}(1-\beta)+(1+2\beta)\right] = T\left[\zeta_0\beta\frac{\xi_0^{(1)}+2}{3}+\zeta_0\frac{p^2}{a^3kT}\cdot\frac{3\xi_0^{(1)}}{2\xi_0^{(1)}+1}\right] \quad (4.30)$$

In the particular case when $p = 0$

$$\xi_0^{(1)} - 1 - \beta(\xi_0^{(1)}+2) = 0$$

$$\xi_0^{(1)} = \frac{3\beta}{(1-\beta)^2}\zeta_0 T \quad (4.31)$$

Since ζ_0 is independent of T, the last equation is in agreement with the experimental results of the slightly linear increase of ε with the temperature.

CHAPTER V.

THE TRANSITION FROM FREE ROTATIONS TO FIXED ORIENTATIONS OF POLAR MOLECULES IN THE SOLID STATE.

Experimental Evidence.

The dependence of the dielectric constant on temperature for nitrobenzine [22], as shown in Fig.(16) shows a discontinuity at the melting point. The difference between the dielectric constant of the liquid and the solid at the melting point is so high that it cannot be explained by the slight change of volume on the transition from the liquid to the solid state. Substances which show similar behaviour are ammonia [14][24], acetone [14] and nitromethane [26].

The discontinuity in the dielectric constant may occur in the solid state as for hydrochloride acid [23] (Fig. (18)) and methyl alcohol [14],[25].

There is more than one discontinuity in the case of hydrogen sulphide [24] (Fig.(19)), and finally in the case of water [6],[22] (Fig. (17)), there is no discontinuity in the dielectric constant but it decreases rapidly to a much lower value.

The specific heats of HCl and H_2S [4] show corresponding transitions at a transition temperature the same as that of the dielectric constant. For phosphine [4]

Fig.(16)

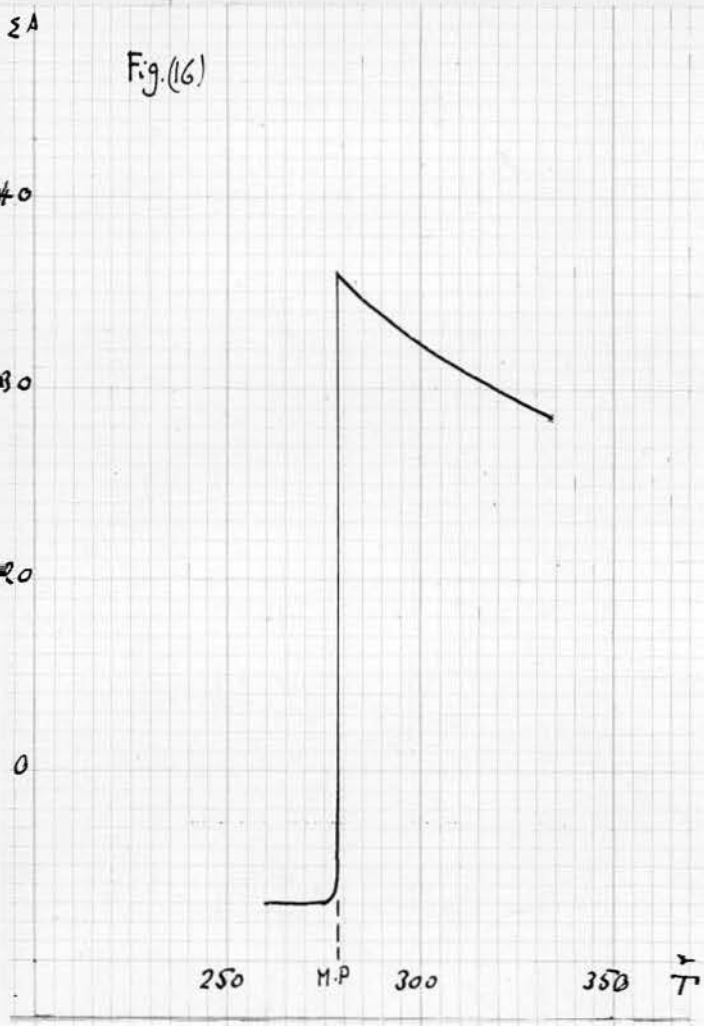


Fig.(17)

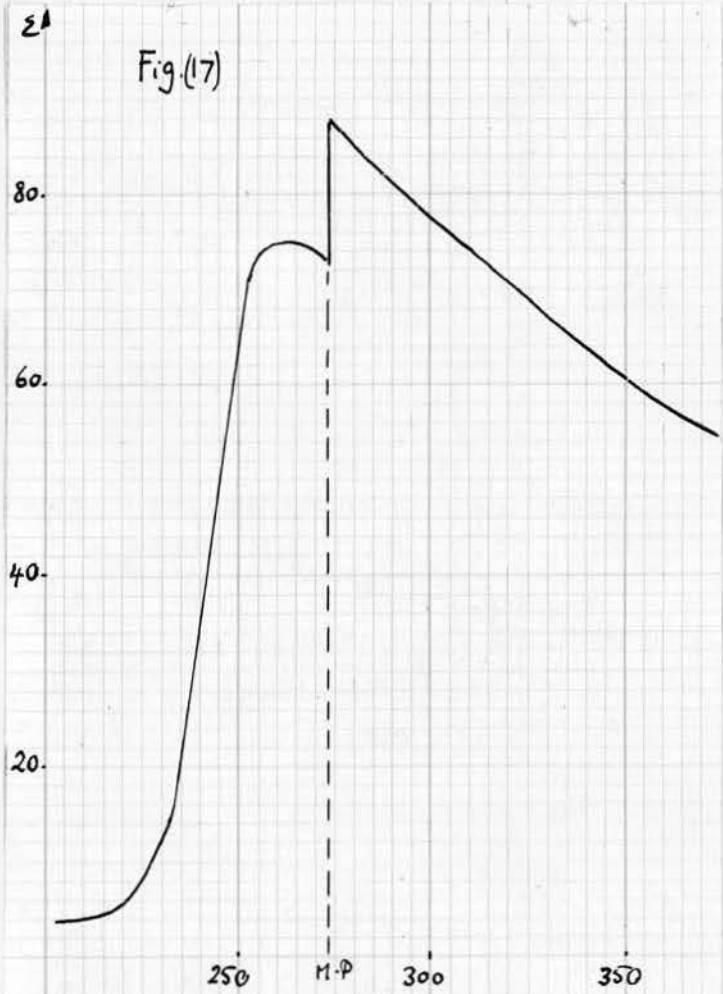


Fig.(18)

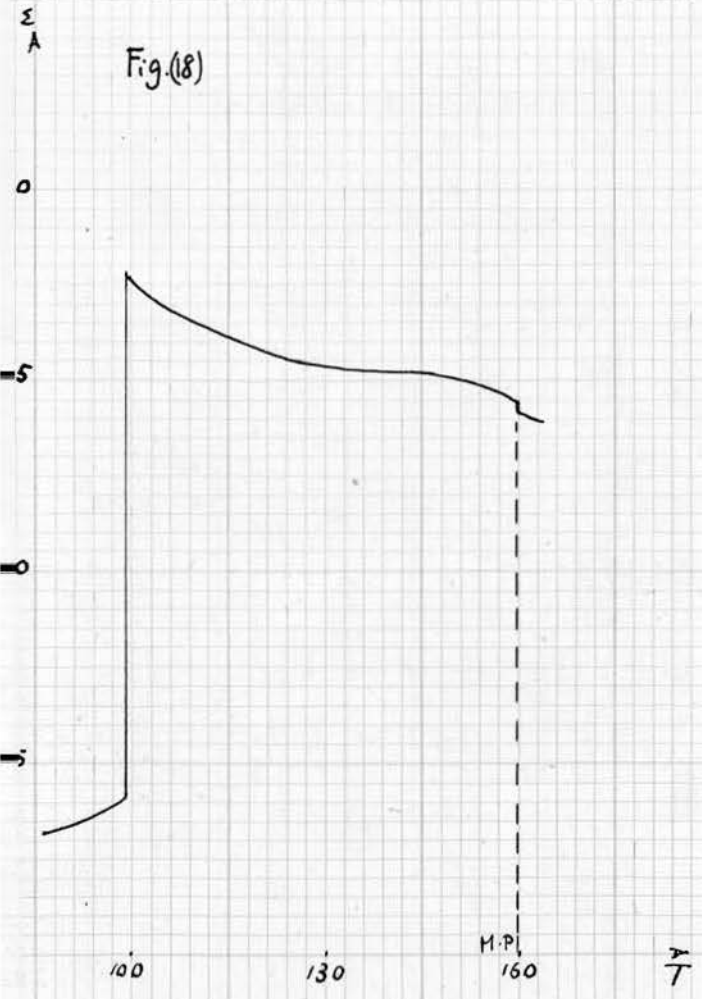
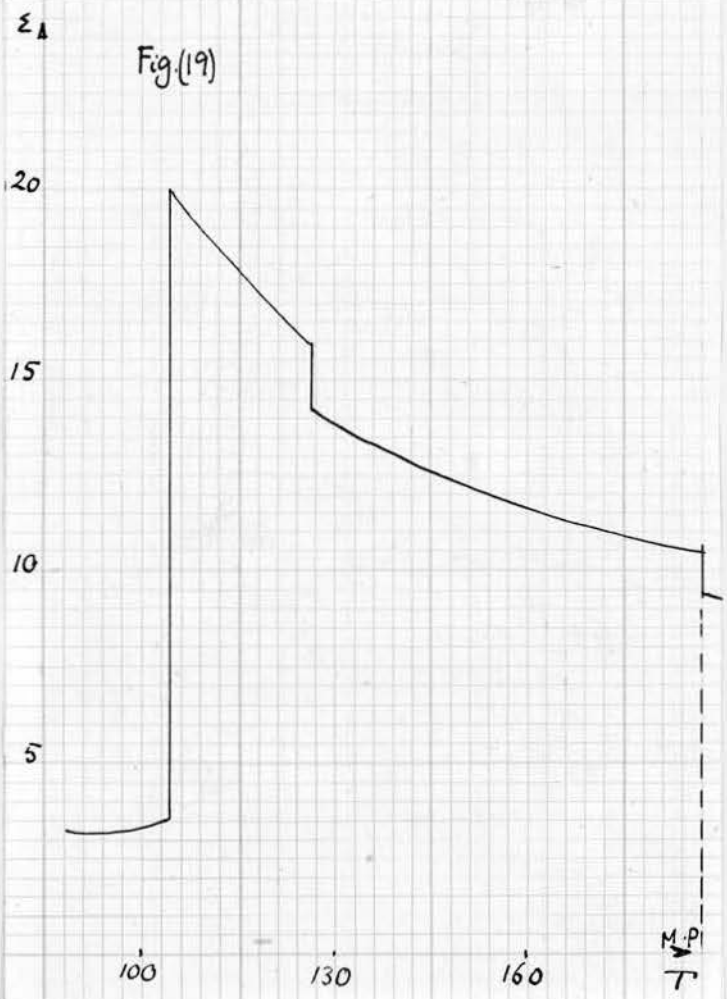


Fig.(19)



there are three transitions in the solid state.

This abrupt decrease of the dielectric constant, either at the melting point or in the solid state, was explained [9][10][19] as due to a transition from free rotations of the molecules to fixed orientations; small rotational oscillations round these fixed orientations occur similar to the thermal vibrations of the molecules. A thorough treatment of the subject with regard to the experiments and explanations was given by Smythe [21].

Frenkel, [10] considered $\sqrt{\overline{\theta^2}}$ where θ is the angle of vibration of a dipole, as a measure of the degree of disorder; when this attains a certain value ($\frac{\pi}{2}$ say) it passes to a state of complete disorder (free rotations). For a system of dipoles he uses the mutual energy between the dipoles instead of the average field adopted by others. A system of linear dipoles vibrating in one plane was treated in his book.

We shall adopt the same idea as his, treating each dipole as vibrating in two dimensions instead of one.

<u>The Dielectric Constant Below the Transition Point</u>.

We shall consider the dipoles below the transition point as vibrating round certain orientations, regularly

arranged throughout the crystal. As pointed out by Frenkel, there may be more than one of such arrangements and they may pass from one arrangement to another. We shall only calculate the electric moment for one regular arrangement. The electric moment for several arrangements can then be found easily if we know the probability of each arrangement.

Let $x_\sigma^{(i)}$ $(\sigma = 1, 2, 3)$ be the co-ordinates of a unit vector along the dipole referred to orthogonal axes, one $(\sigma = 3)$ along the stationary orientation of the dipole, then

$$x_1^{(i)2} + x_2^{(i)2} + x_3^{(i)2} = 1 \qquad (5.1)$$

If we regard $x_1^{(i)}$, $x_2^{(i)}$ as small then $x_3^{(i)}$ can be written

$$x_3^{(i)} = 1 - \tfrac{1}{2} x_1^{(i)2} - \tfrac{1}{2} x_2^{(i)2} \qquad (5.2)$$

up to the second power in $x_1^{(i)}$, $x_2^{(i)}$.

Let $l_s^\sigma(i)$ $(s = 1, 2, 3)$ be the components of a unit vector along the axis σ of the orthogonal set of a molecule i, referred to the crystal axes.

The components of a unit vector, along the dipole, referred to the crystal axes, will then be

$$\begin{aligned} x_s'(i) &= \sum_{\sigma=1}^{3} l_s^\sigma(i)\, x_\sigma^{(i)} \\ &= l_s^{(3)}(i) + \sum_{\sigma=1}^{2} l_s^\sigma(i)\, x_\sigma^{(i)} - \tfrac{1}{2} l_s^{(3)}(i) \sum_{\sigma=1}^{2} x_\sigma^{(i)2} \end{aligned} \qquad (5.3)$$

also

$$\begin{aligned} x_s'(i) x_{s'}'(j) = {} & l_s^{(3)}(i)\, l_{s'}^{(3)}(j) + \sum_{\sigma=1}^{2} \left\{ l_s^{(3)}(i)\, l_{s'}^{\sigma}(j)\, x_\sigma^{(j)} + l_{s'}^{(3)}(j)\, l_s^{\sigma}(i)\, x_\sigma^{(i)} \right\} \\ & + \sum_{\sigma\sigma'}^{2} l_s^{\sigma}(i)\, l_{s'}^{\sigma'}(j)\, x_\sigma^{(i)} x_{\sigma'}^{(j)} - \tfrac{1}{2} l_s^{(3)}(i)\, l_{s'}^{(3)}(j) \sum_{\sigma=1}^{2} \left(x_\sigma^{(i)2} + x_\sigma^{(j)2} \right) \end{aligned} \qquad (5.4)$$

Since the resultant moment in the absence of an external field is zero, then

$$\sum_{j} \ell_s^{(3)}(j) = 0 \tag{5.5}$$

Substituting for $x_s'(i)$, $x_s'(i)\,x_{s'}'(j)$ from (5.3) (5.4) into the expression for W given by (1.35), then equating the linear terms in W_0 to zero, we obtain

$$\sum_{j\,s'} (g - g\lambda^{-1})^{ij}_{ss'}\, \ell_{s'}^{(3)}(j) = 0 \tag{5.6}$$

By use of equations (5.5) (5.6) we obtain for W (Considering only dipolar interactions) the expression

$$\begin{aligned} -W = &-\frac{p^2}{2\alpha} \sum_{ij} \sum_{ss'} (g - g\lambda^{-1})^{ij}_{ss'}\, \ell_s^{(3)}(i)\, \ell_{s'}^{(3)}(j) \\ &-\frac{p^2}{2\alpha} \sum_{ij} \sum_{ss'} \sum_{\sigma\alpha'}^{2} (g - g\lambda^{-1})^{ij}_{ss'}\, \ell_s^{\sigma}(i)\, \ell_{s'}^{\alpha'}(j)\, x_\sigma^{(i)}\, x_{\alpha'}^{(j)} \\ &+ p \sum_{j\sigma} \sum_{ss'} (g\lambda^{-1})_{ss'}\, E_{s'}' \left[\ell_s^{\sigma}(j)\, x_\sigma^{j} - \tfrac{1}{2}\, \ell_s^{(3)}(j)\, x_\sigma^{(j)2} \right] \end{aligned} \tag{5.7}$$

Putting

$$\begin{aligned} \alpha_{\sigma\alpha'}^{ij} &= \frac{p^2}{\alpha kT} \sum_{ss'} (g - g\lambda^{-1})^{ij}_{ss'}\, \ell_s^{\sigma}(i)\, \ell_{s'}^{\alpha'}(j) \\ &+ \frac{p}{kT}\, \delta_{ij}\, \delta_{\sigma\alpha'} \sum_{ss'} (g\lambda^{-1})_{ss'}\, E_{s'}'\, \ell_s^{(3)}(i) \end{aligned} \tag{5.8}$$

$$\lambda_\sigma^{i} = -\frac{p}{kT} \sum_{ss'} (g\lambda^{-1})_{ss'}\, E_{s'}'\, \ell_s^{(\sigma)}(i) \tag{5.9}$$

then

$$\frac{W}{kT} = \frac{W_0}{kT} + \frac{1}{2} \sum_{ij} \sum_{\sigma\alpha'}^{2} \alpha_{\sigma\alpha'}^{ij}\, x_\sigma^{i}\, x_{\alpha'}^{j} + \sum_{i\sigma} \lambda_\sigma^{i}\, x_\sigma^{i} \tag{5.10}$$

The probability for a given configuration is given by

$$\rho Z = \exp.\left\{-\frac{1}{2}\sum_{ij}^{N}\sum_{\sigma\sigma'}^{2} \alpha_{\sigma\sigma'}^{ij} x_{\sigma}^{(i)} x_{\sigma'}^{i'} - \sum_{i\sigma} \lambda_{\sigma}^{i} x_{\sigma}^{i}\right\} \qquad (5.11)$$

where

$$Z = \int\cdots\int \exp.\left\{-\frac{1}{2}\sum_{ij}\sum_{\sigma\sigma'} \alpha_{\sigma\sigma'}^{ij} x_{\sigma}^{i} x_{\sigma'}^{j} - \sum_{i\sigma} \lambda_{\sigma}^{i} x_{\sigma}^{i}\right\} dx^{(1)}\cdots dx^{(N)} \qquad (5.12)a$$

i.e

$$Z = \left\{\frac{(2\pi)^{2N}}{|\alpha|}\right\}^{\frac{1}{2}} \exp.\left\{\frac{1}{2}\sum_{ij}^{N}\sum_{\sigma\sigma'}^{2} (\alpha^{-1})_{\sigma\sigma'}^{ij} \lambda_{\sigma}^{i} \lambda_{\sigma'}^{j}\right\} \qquad (5.12)b$$

$|\alpha|$ is the $(2N \times 2N)$ determinant of $\alpha_{\sigma\sigma'}^{ij}$ and (α^{-1}) is the reciprocal of the matrix α. From (5.12)a, the averages of x_{σ}^{i} and $x_{\sigma}^{i} x_{\sigma'}^{j}$ are given by

$$Z\,\overline{x_{\sigma}^{i}} = -\frac{\partial Z}{\partial \lambda_{\sigma}^{i}}$$

$$Z\,\overline{x_{\sigma}^{i} x_{\sigma'}^{j}} = -2\frac{\partial Z}{\partial \alpha_{\sigma\sigma'}^{ij}} \qquad (5.13)$$

also, by use of (5.3),

$$\overline{p_s^{(i)}} = p\,\ell_s^{(3)}(i) + p\sum_{\sigma=1}^{2} \ell_s^{\sigma}(i)\,\overline{x_{\sigma}^{(i)}} - \frac{p}{2}\ell_s^{(3)}(i)\sum_{\sigma=1}^{2}\overline{x_{\sigma}^{(i)2}} \qquad (5.14)$$

By use of (5.12)b and (5.13), and retaining only terms linear in E' we obtain

$$\overline{p_s^{(i)}} = -p\sum_{\sigma=1}^{2} \ell_s^{\sigma}(i)\sum_{j\sigma'}(\alpha^{-1})_{\sigma\sigma'}^{ij}\lambda_{\sigma'}^{j} \qquad (5.15)$$

where

$\alpha_{\sigma\sigma'}^{ij}$ is given instead of (5.8), by

$$\alpha_{\sigma\sigma'}^{ij} = \frac{p^2}{\alpha kT}\sum_{ss'}(g - g\lambda^{-1})_{ss'}^{ij}\,\ell_s^{\sigma}(i)\,\ell_{s'}^{\sigma'}(j) \qquad (5.16)$$

$$= \frac{p^2}{a^3 kT} A_{\sigma\sigma'}^{ij} \quad (\text{say})$$

Let

$$C_{ss'} = \frac{1}{N^{(1)}} \sum_{ij} \sum_{\alpha\alpha'}^{2} (A^{-1})^{ij}_{\alpha\alpha'} \ell_s^{\alpha}(i) \ell_{s'}^{\alpha'}(j) \qquad (5.17)$$

then

$$\sum_i \overline{p}_s^{(i)} = N^{(0)} a^3 \sum_{s'} (Cg\Lambda^1)_{ss'} E'_{s'} \qquad (5.18)$$

By use of equations (1.46) and (5.18) one obtains

$$\frac{1}{a^3 N^{(1)}} \sum_i \overline{\mu}_s^{i} = \frac{4\pi}{3} P_s = \sum_{s'} \left[\frac{\Lambda^{-1}}{1-\beta f \Lambda^{-1}} (\beta + Cg\Lambda^1) \right]_{ss'} E'_{s'} \qquad (5.19)$$

Using the definition (1.52) for P_s we obtain the tensor equation

$$\frac{\varepsilon-1}{3} = \frac{3\varepsilon_0}{2\varepsilon_0+1} \left[\frac{\Lambda^{-1}}{1-\beta f \Lambda^{-1}} \beta + \frac{\Lambda^{-2} g C}{1-\beta f \Lambda^{-1}} \right] \qquad (5.20)$$

This equation is the same as (1.53) with the tensor C replacing the tensor $\frac{p^2}{a^3 kT} Q$. From (5.17) C is independent of p or T .

For isotropic solids

$$\frac{\varepsilon_0-1}{3} = \frac{\varepsilon_0+2}{3} \beta + \frac{3\varepsilon_0}{2\varepsilon_0+1} C_0 \qquad (5.21)$$

Using the fact that the stationary orientations of the dipoles are regularly distributed we may refer to a molecule i by means of two letters h, k ; the first defining the unit cell and the second a particular molecule inside the unit cell. Then $\ell_s^{(1)}(k)$ is the same for all h and this will be written $\ell_s^{(1)}(k)$, also we may express

$$\gamma_{ss'}^{kk'} = \sum_h \lambda_{ss'}^{hkk'} \qquad (5.22)$$

The conditions (5.5) and (5.6) can then be written

$$\sum_{k} \ell_s^{(3)}(k) = 0$$

$$\sum_{k's'} \left(g - g\gamma^{-1}\right)^{kk'}_{ss'} \ell_{s'}^{(3)}(k') = 0 \qquad (5.23)$$

If n is the number of dipoles in a unit cell then, from (5.17)

$$C'_{ss'} = \frac{1}{n} \sum_{kk'} \sum_{\alpha\alpha'}^{2} \left(A^{-1}\right)^{kk'}_{\alpha\alpha'} \ell_s^{\alpha}(k)\, \ell_{s'}^{\alpha'}(k') \qquad (5.24)$$

where, according to (5.16) and (5.22)

$$A^{kk'}_{\alpha\alpha'} = \sum_{ss'} \left(\frac{g - g\gamma^{-1}}{\beta}\right)^{kk'}_{ss'} \ell_s^{\alpha}(k)\, \ell_{s'}^{\alpha'}(k') \qquad (5.25)$$

Stability Below the Transition Point.

In the absence of an external field, the configurational probability, instead of (5.11) and (5.12), is given by

$$\rho Z = \exp.\left\{-\frac{1}{2} \sum_{ij} \sum_{\alpha\alpha'}^{2} \alpha^{ij}_{\alpha\alpha'} x_\alpha^i x_{\alpha'}^j\right\} \qquad (5.26)$$

$$Z = \left\{\frac{(2\pi)^2 N^{\alpha}}{|\alpha|}\right\}^{\frac{1}{2}} \qquad (5.27)$$

Integrating equations (5.26) over all x except $x^{(i)}$ one obtains

$$\rho^{(i)}(x^{(i)})\, Z^{(i)} = \exp.\left\{-\frac{1}{2} \sum_{\alpha\alpha'}^{2} \beta^{(i)}_{\alpha\alpha'} x_\alpha^{(i)} x_{\alpha'}^{(i)}\right\} \qquad (5.28)$$

$$Z^{(i)} = \left\{\frac{(2\pi)^2}{|\beta^{(i)}|}\right\}^{\frac{1}{2}} \qquad (5.29)$$

where $|\beta^{(i)}|$ is 2×2 determinant of $\beta^{(i)}_{\alpha\alpha'}$

By use of (5.13) and (5.27) one obtains

$$\overline{x_a^{(i)} x_{a'}^{(i)}} = (\alpha^{-1})^{ii}_{aa'} \quad , \tag{5.30}$$

and from (5.29)

$$\overline{x_a^{(i)} x_{a'}^{(i)}} = (\beta^{-1})_{aa'} \tag{5.31}$$

One sees from (5.30),(5.31) that the tensor $\beta^{(i)}$ appearing in (5.28) is the reciprocal of the 2×2 tensor $(\alpha^{-1})^{ii}$. According to equation (5.28) the projection of a unit vector along the dipole on a plane normal to its stationary orientation has the same probability everywhere on the curve

$$\sum_{aa'}^{2} \beta_{aa'}^{(i)} x_a^{(i)} x_{a'}^{(i)} = \text{const} \tag{5.32}$$

This is an ellipse or hyperbola according as

$$|\beta^{(i)}| \gtrless 0 \tag{5.33}$$

or, since $|\beta^{(i)}| = \frac{1}{|(\alpha^{-1})^{ii}|}$, the condition (5.33) is equivalent to

$$|(\alpha^{-1})^{ii}| \gtrless 0 \tag{5.34}$$

Therefore a first condition for harmonic oscillations round stationary orientations is

$$|(\alpha^{-1})^{ii}| > 0 \tag{5.35}$$

for all i

If $a_1^{(i)}$, $a_2^{(i)}$ are the semi-major and -minor axes respectively of the ellipse (5.32) $[|\beta^{(i)}| > 0]$.

then

$$\overline{R_i^2(\mathcal{U}^{(i)})} = a_1^{(i)} a_2^{(i)} = \frac{\mathcal{U}^{(i)}}{|\beta^{(i)}|^{1/2}} \qquad (5.36)$$

where $R_i(\mathcal{U}^{(i)})$ is a radius vector from the centre of the ellipse (5.32) to a point on it.

Since the elementary volume between the ellipses $\mathcal{U}^{(i)}$ and $\mathcal{U}^{(i)} + d\mathcal{U}^{(i)}$ is $\frac{\pi}{|\beta^{(i)}|^{1/2}} d\mathcal{U}^{(i)}$, then

$$Z^{(i)} \overline{R_i^2} = \int_0^\infty \overline{R_i^2(\mathcal{U}^{(i)})}\, e^{-\frac{1}{2}\mathcal{U}^{(i)}} \frac{\pi\, d\mathcal{U}^{(i)}}{|\beta^{(i)}|^{1/2}}$$

$i \cdot e$

$$\overline{R_i^2} = \frac{2}{|\beta^{(i)}|^{1/2}} = 2|(\alpha^{-1})^{ii}|^{1/2} \qquad (5.37)$$

$\overline{R_i^2}$ is the average of the square of the project-ion of a unit vector along the dipole i on a plane normal to its stationary orientation. It is clear that

$$\overline{R_i^2} < 1 \qquad (5.38)$$

for all i, then

$$2|(\alpha^{-1})^{ii}|^{1/2} < 1 \qquad (5.39)$$

for all i. This is a second condition for harmonic oscillations round the stationary orientation.

By use of (5.16) one can rewrite the two conditions for harmonic oscillations

$$\begin{aligned} |(A^{-1})^{ii}| &> 0 \\ 2|(A^{-1})^{ii}|^{1/2} &< \frac{p^2}{a^3 kT} \end{aligned} \qquad (5.40)$$

for all i.

A transition from rotational oscillations to free rotations will happen at the temperature T_0 given by

$$2\left|(A^{-1})^{ii}\right|^{\frac{1}{2}} = \frac{p^2}{a^3 k T_0} \qquad (5.41)$$

for the greatest $\left|(A^{-1})^{ii}\right|$ in the unit cell. It may be noticed from (5.40) that the higher the value of p and the lower the temperature, the more stable is the ordered configuration of the dipoles. The experimental comfirmation of this result has been noticed by Smythe (21).

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REFERENCES.

(1) Bernal, J.D., and Fowler, R.H., J. of Chem'l Physics, Vol. 1, 515 (1933).

(2) Landolt Börnstein Phys. Chem. Tabellen, Zweiter Erganzungsband II, 1005 (1931)

(3) Landolt Börnstein Phys. Chem. Tabellen, Dritter Erganzungsband I, 118, 153 (1935)

(4) Clusius, Z. Elektrochen, 39, 598 (1933).

(5) Debye, P., Phys. Z. 36, 100, 193 (1935).

(6) Dorsey, Properties of Ordinary Water Substances (1940).

(7) Errera, J., J. de. Phys., (6), 304-311, (1924).

(8) Eucken, A., Göttg. Nachr. (1946)

(9) Fowler, Proc. Roy. Soc. London, 149, 1,(1935).

(10) Frenkel, Kinetic Theory of Liquids, (1943)

(11) Fröhlich, H., Trans. Faraday Soc. No. 34, Vol. XLIV, Part 4, April, (1948).

(12) Granier, J., Compte Rendue (179) 1313-1318,(1924).

(13) Handbuch der Physik, Band XXIV, 2 (1933) p. 38.

(14) International Critical Tables, Vol. VI., McGraw Hill Book Co. Inc., New York,(1929).

(15) Kirkwood, J., J. Chem'l Phys., 7, 911 (1939).

(16) Murphy, E.J., Trans. Am. Electroch. Soc., 65, 133 (1934).

(17) Onsager, L., J. Am. Chem. Soc. 58, 1486-1493, (1936).

(18) Owston, P.G., and Kathleen Lonsdale, J. of Glaciology, Vol. 1, No. 3, 1948 (p.118-123).

(19) Pauling, J.,Phys. Rev. 36, 430 (1930).

(20) Pauling, J., Am. Chem'l Soc. 57, 2681 (1935).

(21) Smythe, C.P., Chem'l Rev. 19, 329-361 (1936).

(22) Smythe, C.P. and Hitchcock, J., Am. Chem. Soc. 54, 4631 (1932).

REFERENCES (Contd.)

(23) Smythe, C.P. and Hitchcock, D., J. Am. Chem. Soc. 55, 1830 (1933).

(24) Smythe, C.P., and Hitchcock, D., J. Am. Chem. Soc. 56, 1084 (1934).

(25) Smythe, C.P. and McNeight, H., J. Am. Chem. Soc., 58, 1597 (1936).

(26) Smythe and Walls, J. Chem'l Physics, 3, 557, (1935).

(27) Weyman, J., J. Am. Chem. Soc. 53, 3292, (1931).

(28) Wintch, H., Helv. Phys. Acta 5, 126-144, (1932).
