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LXXXII. *On the Kinetic Theory of Solids (Metals) and the Partition of Thermal Energy.*—Part II. By B. M. SEN, Dacca College, Dacca, Bengal*.

Preface.

IN my previous paper on the "Kinetic Theory of Solids (Metals)," Part I.†, I investigated the theory of the solid state with a rough working model of fourteen molecules placed on a sphere about each individual molecule at the centre. The idea was to make the distance between any two adjacent molecules equal to the radius of the sphere (the body being isotropic) so that the spherical distance between them is 60° . This is geometrically impossible, but the model satisfies this condition approximately together with the condition of symmetry.

In the present paper, I have restated the theory for the cubic and face-centred cubic crystals. These are the two arrangements which are common for the solid state. The arguments have been put briefly. For a more detailed statement the reader is referred to the previous paper.

1. *Potential energy of displacement.*

Let us suppose that six molecules are placed at a distance l from the central molecule, two on each axis. Let the components of the displacement of the central molecule be x, y, z , the others being fixed in their mean positions. Then the potential energy for the displacement x

(1) due to the molecules on the x -axis

$$= f(l+x) + f(l-x) = 2f(l) + x^2 f''(l),$$

(2) due to the pair of molecules on the y -axis

$$2f\left(l + \frac{1}{2} \frac{x^2}{l}\right) = 2f(l) + \frac{x^2}{l} f''(l),$$

(3) due to the pair of molecules on the z -axis

$$2f(l) + \frac{x^2}{l} f''(l).$$

The combined effect of these six molecules for the general displacement

$$= 6f(l) + a^2 \left\{ \frac{2}{l} f'(l) + f''(l) \right\}, \quad \text{where } a^2 = x^2 + y^2 + z^2$$

* Communicated by the Author.

† *Supra*, p. 672.

The equation of energy is, therefore,

$$\frac{1}{2}MV^2 + a^2 \left\{ \frac{2}{l} f'(l) + f''(l) \right\} = \text{const.}$$

If the molecule were at liberty to swing to its natural amplitude, the mean kinetic energy would be equal to its mean potential energy. We make the assumption that this is not the case, the vibrating molecule coming into collision with the adjacent one before reaching the extreme position of the natural vibration*.

2. Amplitude of molecular vibration.

At each collision the forward motion is reversed, so that there is a change of momentum at the point $= 2MV/\sqrt{3}$ at each collision, or $\frac{MV}{\sqrt{3}t_1}$ per sec., where t_1 is the time from one extreme position to the other, and a the maximum displacement. Putting $t_1 = 2\sqrt{3}a/V$, the change of momentum per sec. $= \frac{MV^2}{6a} = \frac{\alpha\theta}{3a}$.

As there are N molecules per sq. cm., the pressure within the mass is found to be $N^{2/3} \frac{\alpha\theta}{3a}$ per sq. cm.

To calculate the pressure at the surface, we suppose that the molecule on the positive side of the yz plane is missing. The potential energy for a displacement x along the x -axis

$$\begin{aligned} &= 4f\left(l + \frac{1}{2}\frac{x^2}{l}\right) + f(l+x) \\ &= 5f(l) + xf'(l) + x^2 \left\{ \frac{2f'(l)}{l} + \frac{f''(l)}{2} \right\}. \end{aligned}$$

The first term is a constant. The second gives a constant force $F = f'(l)$ in the direction of the inward normal. The third term gives a force of restitution proportional to the displacement and changing sign with it. Its mean value is zero.

The permanent force, therefore, is F along the inward normal, where F is the attraction between two molecules. The pressure at the surface is $FN^{2/3}$.

$$\therefore \frac{\alpha\theta}{3a} = F \quad \text{or} \quad a = \frac{\alpha\theta}{3F}.$$

This is the equation which is to replace equation (2) in the former paper.

* A comparison of the relative magnitude of the kinetic and the potential energy terms has been given in the previous paper.

3. Compressibility.

To find the compressibility, we notice that the work done against the molecular forces $= \beta$ per molecule for 1° rise of temperature. Now the pressure at the surface $= FN^{2/3}$. Therefore the work done against it $= 3\alpha_1 FN^{2/3}$ where α_1 is the coefficient of linear expansion.

The work done against the inter-molecular forces per unit volume $= 3F\delta l/N = 3\alpha_1 FN^{2/3}$, there being six molecules arranged about each individual molecule, and

$$\delta a = \delta i = \alpha_1 l.$$

$$\therefore N\beta = 6\alpha_1 FN^{2/3}.$$

$$\therefore F = \frac{\beta}{6\alpha_1 l}, \quad \text{since } Nl^3 = 1.$$

$$\therefore a = \frac{\alpha\theta}{3F} = \frac{2\alpha\theta \cdot \alpha_1 l}{\beta}.$$

$$\text{Now the surface pressure} = NF^{2/3} = \frac{\beta N}{6\alpha_1}.$$

If the pressure be increased by one dyne without change of temperature, it increases by $\frac{6\alpha_1}{N\beta}$ th part of itself.

$\therefore a$ diminishes by $\frac{6\alpha_1}{N\beta}$ th part of itself.

$$\therefore \frac{\delta a}{a} = -\frac{6\alpha_1}{N\beta} = \frac{\delta l}{a}.$$

$$\therefore \frac{\delta l}{l} = -\frac{a}{l} \cdot \frac{6\alpha_1}{N\beta}.$$

$$\therefore C = -3 \frac{\delta l}{l} = \frac{18\alpha_1}{N\beta} \cdot \frac{a}{l},$$

$$= 36\alpha_1^2 \cdot \frac{\alpha\theta}{N\beta^2}.$$

$$\therefore \beta^2 = 36\alpha_1^2 \frac{\alpha\theta}{CN}$$

$$\text{or } \beta = 6\alpha_1 \sqrt{\frac{\alpha\theta}{CN}}.$$

This is the equation which has to be substituted for (4) in the former paper. It will be noticed that this value of β increases the value of F and diminishes the value of a in the ratio of 24 : 19.

4. *Face-centred Cubic Crystals.*

This arrangement consists in having a molecule placed at the eight corners of a cube and one at the centre of each of the six faces. To find the arrangement of the molecules about any individual one, we note that there are two types, viz. those at the corners and those at the centres of the faces. For both the types it will be found that the following arrangement gives the requisite number of molecules situated nearest to each individual molecule O.

With O as centre describe a sphere of radius l and draw a system of three great circles intersecting one another at right angles. Each great circle is divided into four quadrants by the other two. At the middle point of each of these twelve quadrants place a molecule. With a series of such models we can build up a body of the face-centred cubic crystal type, the edge of the cube being $\sqrt{2}l$. It may be noted that there are twelve molecules surrounding each individual molecule instead of the fourteen in the isotropic arrangement, and that the spherical distance between any two adjacent molecules not on the same co-ordinate plane is 60° . In the isotropic model the distance between any two on the same great circle is 60° .

Let us calculate the potential energy of the displacement of the central molecule. Take the planes of the great circles for the co-ordinate planes. Take two straight lines in the xy -plane, the x_1 and the y_1 axes, bisecting the angles between the x and the y axes. Place four molecules at the extremities of the x_1 and the y_1 axes. Put similarly four at the extremities of the y_2 and z_2 axes which bisect the angles between the y , z axes in the yz -plane, and also four at the extremities of the z_3 and x_3 axes which bisect the angles between the z , x axes in the zx -plane. Let (x, y, z) be the most general displacement of the central molecule. It can also be written in the form (x_1, y_1, z) , (x, y_2, z_2) , (x_3, y, z_3) , so that

$$x^2 + y^2 + z^2 = x_1^2 + y_1^2 + z^2 = x^2 + y_2^2 + z_2^2 = x_3^2 + y^2 + z_3^2 = a^2 \quad (\text{say}).$$

For the four molecules on the x_1 , y_1 axes, the potential energy due to the displacement x_1 .

$$\begin{aligned} &= f(l + x_1) + f(l - x_1) + 2f\left(l + \frac{1}{2} \frac{x_1^2}{l}\right), \\ &= 4f(l) + x_1^2 \left\{ \frac{f'(l)}{l} + f''(l) \right\}. \end{aligned}$$

That due to the displacement y_1

$$= 4f(l) + y_1^2 \left\{ \frac{f'(l)}{l} + f''(l) \right\}.$$

That due to displacement z

$$\begin{aligned} &= 4f\left(l + \frac{1}{2} \frac{z^2}{l}\right), \\ &= 4f(l) + 2z^2 \cdot \frac{f'(l)}{l}, \\ &= 4f(l) + z^2 \left\{ \frac{f'(l)}{l} + f''(l) \right\} + z^2 \left\{ \frac{f'(l)}{l} - f''(l) \right\}. \end{aligned}$$

The total energy due to the four molecules

$$= 4f(l) + a^2 \left\{ \frac{f'(l)}{l} + f''(l) \right\} + z^2 \left\{ \frac{f'(l)}{l} - f''(l) \right\}.$$

The total energy due to the twelve molecules

$$\begin{aligned} &= 12f(l) + 3a^2 \left\{ \frac{f'(l)}{l} + f''(l) \right\} + a^2 \left\{ \frac{f'(l)}{l} - f''(l) \right\}, \\ &= 12f(l) + 2a^2 \left\{ \frac{2f'(l)}{l} + f''(l) \right\}. \end{aligned}$$

It may be noted that the variable part of the potential energy is just double of the corresponding portion of the potential energy for the cubical system. It vanishes if the force is proportional to the inverse square of the distance. This fact seems to give a special significance to the inverse-square law.

Following the same line of argument we get the following equations :—

$$a = \frac{\alpha\theta}{6\sqrt{2}F},$$

$$\beta = 3\left(1 + \frac{1}{\sqrt{2}}\right)\alpha_1 \sqrt{\frac{\alpha\theta}{CN}} = 5.1\alpha_1 \sqrt{\frac{\alpha\theta}{CN}}.$$

This value of β is greater than the corresponding value obtained in the case of the isotropic arrangement by about 5 per cent. The value of F is increased and that of a diminished by the same amount.

June 30, 1921.