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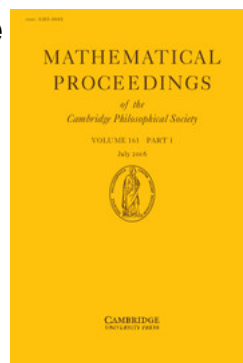
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H. N. V. Temperley

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# STATISTICAL MECHANICS AND THE PARTITION OF NUMBERS

## II. THE FORM OF CRYSTAL SURFACES

By H. N. V. TEMPERLEY

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**ABSTRACT.** The classical theory of partition of numbers is applied to the problem of determining the equilibrium profile of a simple cubic crystal. It is concluded that it may be thermodynamically profitable for the surface to be 'saw-toothed' rather than flat, the extra entropy associated with such an arrangement compensating for the additional surface energy. For both a two- and a three-dimensional 'saw-tooth' the extra entropy varies, to a first approximation, in the same way as the surface energy, i.e. is proportional to  $N^{\frac{1}{2}}$  or  $N^{\frac{2}{3}}$  respectively, where  $N$  is the number of molecules in a 'tooth'. For the simple cubic lattice, the entropy associated with the formation of a tooth containing  $N$  atoms is estimated to be  $3.3kN^{\frac{1}{2}}$ . It is also possible to estimate the variation of the 'equilibrium roughness' of a crystal with temperature, if its surface energy is known.

1. *Introduction.* In a previous paper (9), a study was made of the phenomenon of 'Bose-Einstein condensation', and it was concluded that considerable care has to be taken in using the Fowler-Darwin saddle-point method of integration by steepest descents for the evaluation of the low-temperature thermodynamic properties of any assembly of particles obeying Bose statistics. However, the only model for which really firm conclusions could be drawn was one in which the energy-levels are equally spaced, and it has recently become clear (C. B. Haselgrove and H. N. V. Temperley—unpublished) that the conclusions are, in some respects, special to that model, which does not really represent any actual physical situation. (It can be made to correspond very roughly to a two-dimensional perfect gas, but here orthodox theory does not predict a sharp 'condensation' phenomenon in any case.)

However, the equally spaced model can be handled very much more easily than any other from the point of view of partition theory, both by 'elementary' algebraical methods (see (7)) and also by the analytic (contour-integral) approach. For almost any other spacing of levels the analytic method becomes very much more complicated, requiring extremely heavy analysis (see, for example, Wright (10), Haselgrove and Temperley (unpublished)), while the algebraic method becomes almost unusable. It therefore occurred to the writer to examine whether any further physical applications of the very ingenious 'classical' work on partitions were possible.

One is thus led to a discussion of the form assumed by a growing crystal, the growth being supposed slow enough for each configuration to be one of approximate statistical equilibrium. If we imagine the crystal built up molecule by molecule, it is a fair approximation to assume that the binding energy of each molecule is the same. This assumption is not quite correct, of course, and has eventually to be corrected by introducing a surface energy. Thus we are describing a crystal by an internal energy proportional to its mass, and a surface energy, which is a good approximation for a macroscopic body, or a piece of crystal containing many molecules.

We consider two problems:

(a) The equilibrium shape to be expected if a cubic crystal is grown in the space between two or three walls at right angles.

(b) The explanation of the 'saw-tooth' pattern, with 'teeth' of height equal to several hundred Ångströms, that seems to be characteristic of a real crystal. Such a surface, resembling in profile the surface of the sea with icebergs floating in it, is usually called 'molecularly rough'.

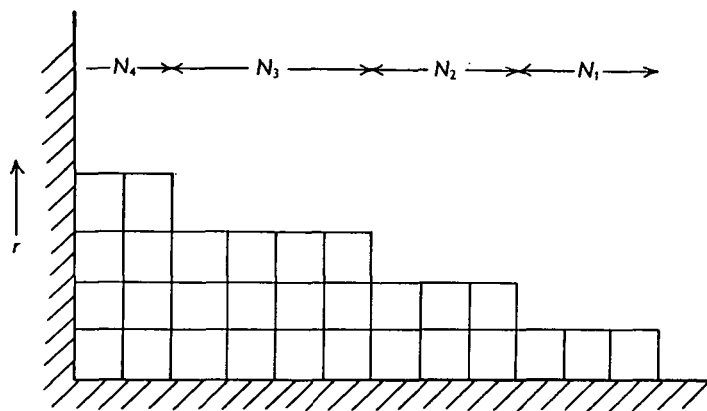


Fig. 1.

We first consider the two-dimensional versions of these problems, the three-dimensional cases being more complicated. We imagine that each atom is represented by a cubical 'brick'. In the three-dimensional version of problem (a), we assume that, as each 'brick' is added, it can only go into a position where it will touch, along faces, three others already there. In the two-dimensional case, we fix our attention on a particular section of the crystal, one molecule thick, and this is built up on the basis that each 'brick', as it is added, touches two others along faces. Contact with a wall is reckoned equivalent to contact with a neighbour, so that, in problem (a), the first cube must go into the angle between the two walls, and the next one in one of the two neighbouring positions and so on (Fig. 1). We assume the interaction energy *proportional to the number of cubes*, which is very nearly correct as long as the above rules for building up the crystal are complied with, because each molecule, as it is added, has exactly three nearest neighbours. A surface built up according to these rules must be molecularly smooth, but can be curved. In the three-dimensional version of problem (b), we consider a crystal that is being built up on a plane substrate. We abandon the assumption that each 'brick' must touch three others when it is added, and this permits the surface to become molecularly rough, gaps in the successive layers enabling isolated 'teeth' to appear (Fig. 2). The loss of interaction energy arising from the fact that the molecules on the surfaces of the iceberg-like portions have not their proper number of neighbours can be allowed for by introducing extra surface energy. On the assumption of statistical equilibrium, this is to be balanced against the gain in entropy arising from allowing the surface to assume a 'saw-tooth' pattern rather than being nearly flat. In the two-dimensional version of this problem this gain

in entropy will be found to be proportional to  $N^{\frac{1}{2}}$ , where  $N$  is the number of molecules in a plane section of a 'tooth', and the extra surface energy required to form a 'tooth' is also proportional to  $N^{\frac{1}{2}}$ . In three dimensions, a result of MacMahon's enables us to prove that the gain in entropy associated with the formation of a 'tooth' containing  $N$  atoms is proportional to  $N^{\frac{3}{2}}$  and to evaluate the numerical factor, while the extra surface energy is also proportional to this. These results appear to mean that a given shape of 'saw-tooth' profile becomes thermodynamically profitable above a temperature at which the entropy gain balances the loss in surface energy. A calculation of the 'most probable' number of atoms to be expected in each 'tooth' has not yet been found possible.

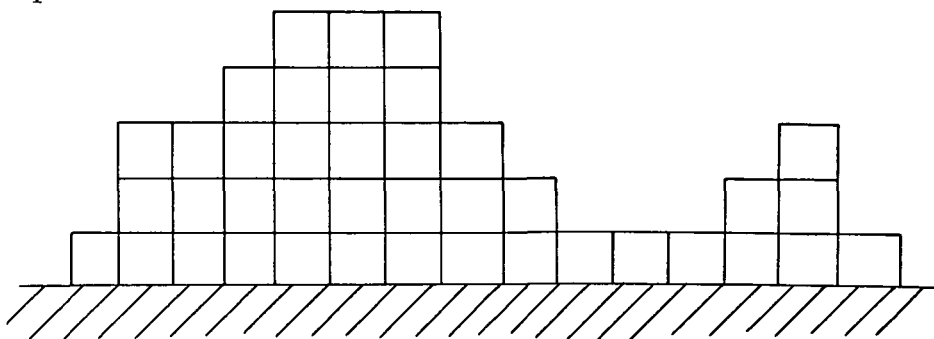


Fig. 2.

2. *Problem (a). The build-up of a crystal between two or three walls at right angles.* In the two-dimensional version of this problem, we consider the two walls to be along the  $X$  and  $Y$  axes, and ask for the number of ways in which  $N$  'bricks' can be packed into the first quadrant, subject to the condition that each must, when it is added, make two contacts along faces. This means that, if we count the number of bricks in each column, starting from the origin, the number must not *increase* as we proceed along the  $X$  axis, though it is permissible for two neighbouring columns to contain *equal* numbers. Thus, what we seek is simply the number of ways in which  $N$  may be represented by a Ferrers graph (Fig. 1), which is shown ((7), chap. 1) to be simply the coefficient of  $z^N$  in the enumerating generating function,  $f(z)$ , defined as follows:

$$f(z) = \frac{1}{(1-z)(1-z^2)(1-z^3)\dots} = \sum_N p(N) z^N. \quad (1)$$

For large  $N$ , it is known (6) that this coefficient  $p(N)$  is given asymptotically by

$$p(N) \approx \frac{1}{4N\sqrt{3}} \exp \sqrt{\frac{2\pi^2 N}{3}}, \quad (2)$$

which leads to an entropy asymptotically equal to  $k\pi(\frac{2}{3})^{\frac{1}{2}} N^{\frac{1}{2}}$  (the exponential factor in  $p(N)$  being the only significant one for large  $N$ ). Further, if the method of steepest descents is applied, which the author has shown in (9) to be legitimate for this generating function, the statistical average number of columns containing  $r$  atoms is, by the general method of statistical mechanics,  $\bar{N}_r = \frac{\theta^r}{1-\theta^r}$ , where  $\theta$  is the critical value of  $z$  determined by  $N = \sum_r \frac{r\theta^r}{1-\theta^r} = \theta \frac{\partial}{\partial \theta} \log f(\theta)$ . The asymptotic form of  $f(\theta)$ , when  $N$  is

large and  $\theta$  consequently nearly equal to unity, can be shown ((5), chap. 8) to be  $f(\theta) \sim \exp\left(\frac{\pi^2}{6(1-\theta)}\right)$ , and we can easily extend the argument to give the following relation between  $N$  and  $\theta$ :

$$N \approx \frac{\pi^2}{6} \frac{\theta}{(1-\theta)^2}. \quad (3)$$

Since  $\bar{N}_r$  is known as a function of  $r$ , we can compute the equilibrium profile of the crystal, for  $r$  represents the height of a column, that is, the  $y$  coordinate (measured in cube-sides) of a point on the surface of the crystal, while  $\bar{N}_r$  represents the number of

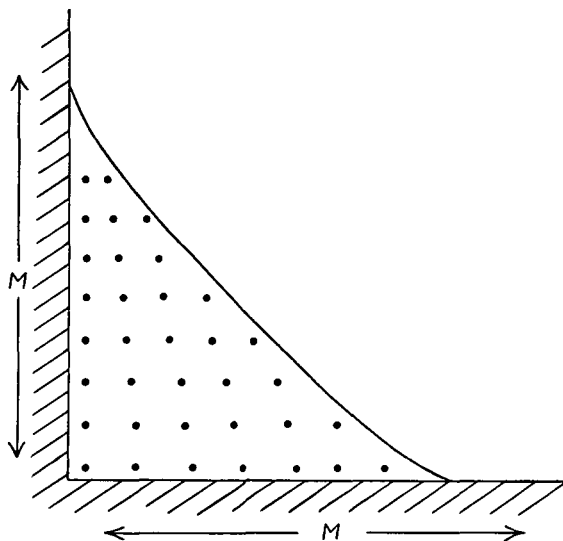


Fig. 3.

cube sides that one has to travel along the  $x$  axis for  $y$  to increase or decrease by unity (see Fig. 1). This gives us, for  $r$  and  $\bar{N}_r$  large,  $r = y$  and  $\frac{dy}{dx} \approx -\frac{1}{\bar{N}_r} \approx \frac{\theta^v - 1}{\theta^v}$ , which can be integrated to give  $x \log \theta - \log(1 - \theta^v) = \text{constant}$ , which has to be taken equal to zero in order to get an equation symmetrical in  $x$  and  $y$ , which equation is

$$\theta^x + \theta^y = 1. \quad (4)$$

Theoretically, this curve is asymptotic to the coordinate axes; in practice values of  $x$  and  $y$  less than unity are not of physical interest. From (3) and (4) we have:

$$\left. \begin{aligned} \text{For } y = 1; x &\approx \sqrt{\left(\frac{3}{2\pi^2}\right) N^{\frac{1}{2}} \log N} \text{ (the length of each wall covered by the crystal),} \\ \text{For } y = x; (x^2 + y^2)^{\frac{1}{2}} &\approx \frac{2^{\frac{1}{2}} \log 2}{\pi} (6N)^{\frac{1}{2}} \text{ (shortest distance from the origin to the} \\ &\text{crystal surface).} \end{aligned} \right\} \quad (5)$$

These are rather artificial conditions, for we suppose that the binding energy between a molecule and a wall is precisely the same as that between two molecules. This model represents what might be expected if a crystal with a re-entrant angle is allowed to grow. The first stage (Fig. 3) represents the turning of the sharp re-entrant angle into

a concave depression. Equations (1)–(5) continue to describe the situation until the new growth extends to the limits of the re-entrant angle (Fig. 4). After this, the process can be followed further if we replace the generating function (1), which enumerates partitions unrestricted both in number and size of parts, by one enumerating partitions for which: (a) no part is larger than  $M$ , (b) no partition may contain more than  $M$  separate parts,  $M$  being the length of the arms of the re-entrant angle (measured in lattice distances). This function is known to be

$$g_M(z) = \frac{(1 - z^{M+1})(1 - z^{M+2}) \dots (1 - z^{2M})}{(1 - z)(1 - z^2) \dots (1 - z^M)}. \quad (6)$$

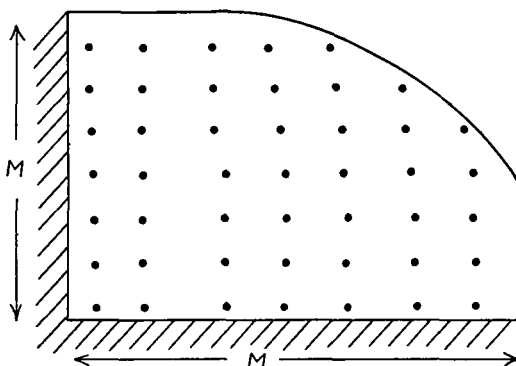


Fig. 4.

This well-known result can best be proved in the following way. The number of partitions of  $N$  satisfying requirement (a) is the coefficient of  $z^N$  in

$$(1 + z + z^2 + z^3 + \dots)(1 + z^2 + z^4 + z^6 + \dots) \dots (1 + z^M + z^{2M} + z^{3M} + \dots)$$

or  $\frac{1}{(1 - z)(1 - z^2) \dots (1 - z^M)}$ , which is the same generating function as  $f(z)$  except that factors beyond  $1 - z^M$  are omitted. If, further, we require that there are to be exactly  $M$  parts, we require the coefficient of  $x^M z^N$  in  $\frac{1}{(1 - xz)(1 - xz^2) \dots (1 - xz^M)}$ , and if there are to be  $M$  or less parts, we require the coefficient of  $x^M z^N$  in

$$\frac{1}{(1 - x)(1 - xz)(1 - xz^2) \dots (1 - xz^M)}.$$

This generating function in two variables can be dealt with by the familiar technique used in (9) (expanding it in ascending powers of  $x$ , and deriving a recurrence relation between the coefficients by replacing  $x$  by  $xz$ ), which leads to expression (6). This generating function is a polynomial, its highest term being  $z^{M^2}$ , and can therefore safely be dealt with by the method of steepest descents, provided of course that  $N$  is significantly less than  $M^2$ , and, by processes similar to those used by Auluck and Kothari (2), we conclude that the number of partitions in which both part magnitude and number of parts must be less than  $M$

$$p'_M(N) \approx \frac{1}{4N\sqrt{3}} \exp \left[ \frac{\pi\sqrt{(2N)}}{3} - \frac{2\sqrt{(6N)}}{\pi} \exp \left( \frac{-\pi M}{\sqrt{(6N)}} \right) \right] \quad (M^2 \gg N), \quad (7)$$

while for the other extreme case of  $N$  only slightly less than  $M^2$  we must replace  $N$  in (7) by  $M^2 - N$ . Comparing formula (7) with Auluck and Kothari's (2) formula (22) for  $p_M(N)$  ( $p_N(\nu)$  in their notation), the number of partitions in which *either* restriction (a) or restriction (b) is applied, whereas  $p'_M(N)$  enumerates the partitions in which *both* apply; we see that

$$\frac{p'_M(N)}{p(N)} \sim \left( \frac{p_M(N)}{p(N)} \right)^2 \quad (M^2 \gg N),$$

a result that we should intuitively expect, the effect on the entropy of both restrictions acting together being double that of either of them separately. In spite of the fact that the generating function for  $p'_M(N)$  has been much studied (see, for example, (7)), the writer believes that asymptotic formulae such as (7) have not been deduced before.

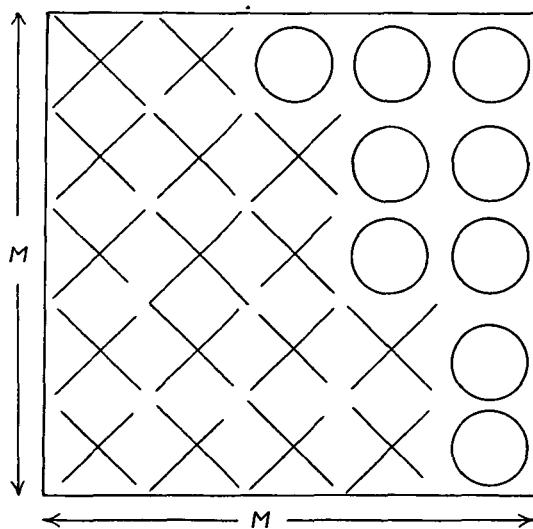


Fig. 5.

We can also deduce results of physical interest by a very simple argument based on symmetry considerations. In Fig. 5 the crosses, arranged in a Ferrers graph neither of whose dimensions may be greater than  $M$ , can be fitted into the bottom left-hand corner of a square  $M \times M$ , the vacant spaces in the square (noughts) forming another Ferrers graph fitted into the top right-hand corner of the square. We thus conclude that  $p'_M(N) = p'_M(M^2 - N)$ , and equation (4), representing the profile of the statistical mean state, can apply either to the distribution of *molecules* when  $M^2 \gg N$  or to the distribution of *vacancies* in the upper corner of the square when  $M^2 \gg M^2 - N$ . The statistical profile may be expected, by symmetry, to be plane when  $N = \frac{1}{2}M^2$ , concave, as has already been shown, when  $N < \frac{1}{2}M^2$ , and therefore convex when  $N > \frac{1}{2}M^2$  (Figs. 3, 4). We can thus trace the successive stages by which a re-entrant angle is filled up, and the tendency of crystals to form plane faces and convex corners is thus, in part at least, accounted for by entropy considerations. It is, however, an observed fact that the surfaces of crystals as grown are not exactly plane, but are molecularly rough and possess 'saw-teeth' many molecular diameters high even when elaborate polishing processes are used. This suggests that such a configuration shows a gain in

free energy over a strictly plane face and may thus be the true equilibrium one to be expected if the rate of growth is slow enough. We shall deduce below some further partition formulae, which the author believes to be new, which seem to throw some light on this question. The two-dimensional problem can actually be treated without partition theory, as is shown in §5.

3. *Problem (b). The growth of a crystal on a plane substrate.* We relax the restrictions made in formulating problem (a) in order to permit configurations such as that shown in Fig. 2. Restricting ourselves for the present to the two-dimensional problem, we suppose each 'tooth' built up of rows in such a way that there is *no overhang*, that is, the bottom face of each cube must touch either the substrate or a cube in the row below. Thus, two rows with the same number of cubes must go above one another, two rows with  $n$  and  $n - 1$  cubes can have a vacancy at either end of the upper row and can thus be disposed in two ways, two rows differing in length by two cubes can have one vacancy at each end of the upper row or both vacancies at one end, and can thus be disposed in three ways, and, generally, two rows differing in length by  $r$  cubes can be disposed in  $r + 1$  ways. Thus we arrive at a new generalization of the linear partition problem, for, to find the entropy associated with the formation of a 'tooth' containing  $N$  atoms, we ask for the number of ways in which  $N$  can be represented by a Ferrers graph, *but allow the rows to be slid over one another as long as this can be done without overhang*. (We do not consider cases where there are gaps in the rows, for a gap in any row necessarily implies one in all the rows above it, and thus implies the formation of another 'tooth', whereas we are considering the entropy associated with a single 'tooth'.)

The above definition enables us to determine the generating function if we specify the length of the 'base' of a 'tooth', the base being the row of cubes nearest the substrate. Let  $h_r(z)$  be the generating function for a tooth whose base is definitely known to be of length  $r$ . The row above the base may have any length from zero to  $r$ . If it is also of length  $r$ , it can be fitted on to the base in only one way, and the molecules above it themselves constitute a 'tooth' of base  $r$ , which is enumerated by the same generating function  $h_r(z)$ . If the row above the base is of length  $(r - 1)$ , it, and the molecules above it, constitute a 'tooth' of base  $(r - 1)$ , which can be fitted on to the bottom row in two ways, and such 'teeth' are enumerated by the generating function  $h_{r-1}(z)$ . We thus obtain the following expression for  $h_r(z)$ :

$$h_r(z) = z^r[h_r(z) + 2h_{r-1}(z) + 3h_{r-2}(z) + \dots + 1], \quad (8)$$

the outside factor  $z^r$  occurring because there are necessarily  $r$  molecules in the base, and the successive terms in the bracket enumerate the cases where there are  $r, r - 1, r - 2, \dots, 0$  molecules in the row above the base. The corresponding relationship for ordinary partitions, in which we only recognize one way of placing the successive rows on top of one another to form a Ferrers graph, is

$$f_r(z) = z^r[f_r(z) + f_{r-1}(z) + f_{r-2}(z) + \dots + 1],$$

which is easily seen to be satisfied by the well-known expression enumerating partitions into parts the largest of which is  $r$ ,

$$f_r(z) = \frac{z^r}{(1-z)(1-z^2)(1-z^3)\dots(1-z^r)}.$$



I have not succeeded in finding the *general* form of  $h_r(z)$ , though it can be calculated from (8) for any specified value of  $r$ , the first four functions being

$$\begin{aligned} h_1(z) &= \frac{z}{1-z}, & h_2(z) &= \frac{z^2(1+z)}{(1-z)(1-z^2)}, & h_3(z) &= \frac{z^3(1+z)^2}{(1-z)(1-z^2)(1-z^3)}, \\ h_4(z) &= \frac{z^4 + 3z^5 + 2z^6 + z^7 + z^8}{(1-z)(1-z^2)(1-z^3)(1-z^4)}. \end{aligned} \quad (9)$$

It is, however, possible to obtain relatively simple expressions for the complete generating function  $h(z) = \sum_{r=0}^{\infty} h_r(z)$  which enumerates arrangements of cubes to form a 'tooth', without the length of the base being specified. We write (8) in the following way:

$$h_0(z) = 1, \quad (8a)$$

$$h_1(z) = z + zh_1(z), \quad (8b)$$

$$h_2(z) = z^2 + 2z^2h_1(z) + z^2h_2(z), \quad (8c)$$

$$h_3(z) = z^3 + 3z^3h_1(z) + 2z^3h_2(z) + z^3h_3(z), \quad (8d)$$

$$h_4(z) = z^4 + 4z^4h_1(z) + 3z^4h_2(z) + 2z^4h_3(z) + z^4h_4(z). \quad (8e)$$

Summing the right-hand sides in columns, we get

$$h(z) = \frac{1}{1-z} + \frac{1}{(1-z)^2} (zh_1(z) + z^2h_2(z) + z^3h_3(z) + \dots).$$

Multiplying equations (8b), (8c), (8d), ... respectively by  $z, z^2, z^3, \dots$ , and again summing the right-hand side in columns, we get

$$zh_1(z) + z^2h_2(z) + z^3h_3(z) + \dots = \frac{z^2}{1-z^2} + \frac{z^2}{(1-z^2)^2} [z^2h_1(z) + z^4h_2(z) + z^6h_3(z) + \dots],$$

and the series in brackets can be evaluated by multiplying (8b), (8c), (8d), ... respectively by  $z^2, z^4, z^6, \dots$  and summing in columns as before. This process can be continued indefinitely and we conclude that

$$\begin{aligned} h(z) &= 1 + \frac{z}{1-z} + \frac{z^2}{(1-z)^2(1-z^2)} + \frac{z^3}{(1-z)^2(1-z^2)^2(1-z^3)} \\ &\quad + \frac{z^4}{(1-z)^2(1-z^2)^2(1-z^3)^2(1-z^4)} + \dots \end{aligned} \quad (10)$$

An alternative proof of this result can be given by means of Ferrers graphs, and this provides an interesting interpretation of each of the terms in (10). Consider, for example, the term with numerator  $z^4$ , which we can factorize into

$$\frac{z^4}{(1-z)(1-z^2)(1-z^3)(1-z^4)} \frac{1}{(1-z)(1-z^2)(1-z^3)}.$$

The first factor enumerates partitions into exactly four parts, while the second enumerates partitions into three or less parts. Fig. 6 shows a typical arrangement of molecules to form a 'tooth' of height four units, and the dotted line breaks up this arrangement into two Ferrers graphs, the right-hand graph containing exactly four parts, while the left-hand graph in this instance contains three parts, but might equally well contain two or one. The possible graphs on the right-hand side of the dotted line are enumerated by the first factor above, while those on the left-hand side

are enumerated by the second factor. The two factors multiplied together thus enumerate all possible combinations of two Ferrers graphs satisfying these conditions, and thus all 'teeth' of height four units. If we make the convention that the dotted line is always to be drawn as far to the left as possible while the other conditions are satisfied, then each 'tooth' can only be broken up into two graphs in one way, so that each arrangement is counted exactly once. Summing over all possible heights of 'tooth', the result (10) follows,  $h(z)$  enumerating 'teeth' of which neither the height nor the base is specified, while each term in (10) enumerates 'teeth' of a certain height.

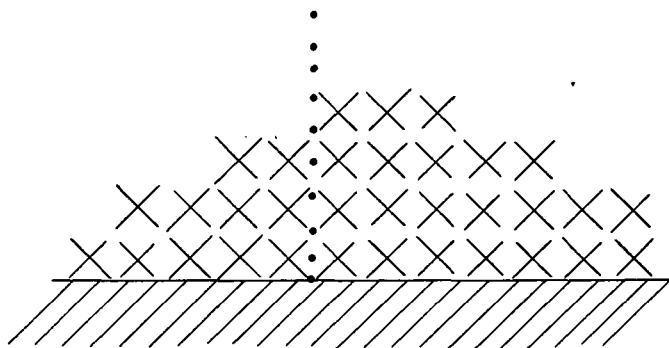


Fig. 6.

For a 'tooth' of fairly large height,  $h$ , the generating function becomes practically equal to  $z^h[f(z)]^2$ , where  $f(z)$  is defined by equation (1). The number of ways in which a tooth containing  $N$  molecules ( $N \gg h$ ) can be formed can be shown, by the method of steepest descents, to be proportional to  $\exp(2\pi\sqrt{\frac{1}{3}N})$ , and the equilibrium profiles of the two halves of the 'tooth' can be discussed by an extension of the argument leading to equation (4), which remains correct if the  $x$  and  $y$  axes are taken to be respectively along the substrate and along the dotted line in Fig. 6.  $\theta$  is, however, now related to  $N$  by the equation  $N \sim \frac{\pi^2\theta}{3(1-\theta)^2}$  instead of by (3), because the generating function is approximately  $[f(z)]^2$  instead of  $f(z)$ .

Expression (10) is not suitable for analytical work if the height of the 'tooth' is not specified, but it is natural to suspect a close connexion between the generating function  $h(z)$  and  $[f(z)]^2$ . We prove in the appendix the relation

$$h(z) - 1 \equiv [f(z)]^2 (z - z^3 + z^6 - z^{10} + \dots), \quad (11)$$

the indices in (11) being the successive triangular numbers. The series in brackets approaches the value  $\frac{1}{2}$  as  $z \rightarrow 1$ , and therefore has a negligible effect on the entropy resulting from a generating function containing  $f(z)$ , which behaves like  $\exp\left(\frac{\pi^2}{6(1-z)}\right)$  as  $z \rightarrow 1$ , so that we can safely replace  $h(z)$  by  $[f(z)]^2$  for the purpose of calculating entropies.

It is of interest to compare numerically the gain in entropy due to the formation of a 'tooth' with the probable value of surface energy loss. Suppose that a two-dimen-

sional section of a 'tooth' consists of a rough triangle, containing  $N$  atoms, spaced at a lattice distance  $2 \text{ \AA}$ ., so that its height and semi-base are both of the order of  $2N^{\frac{1}{2}} \text{ \AA}$ . The entropy associated with the formation of such a section of a 'tooth' is  $\frac{2\pi}{\sqrt{3}} kN^{\frac{1}{2}}$ , where  $k$  is Boltzmann's constant. The increase of surface energy associated with the formation of the section is approximately  $8(\sqrt{2}-1)\sqrt{2} N^{\frac{1}{2}} \times 10^{-16} \times S$ , where  $S$  is the surface energy in ergs/cm.<sup>2</sup>. If the crystal is formed at room temperature it is thermodynamically profitable for such 'teeth' to form on a flat surface provided that  $kT > 1.26 \times 10^{-16} S$ , which means that  $S$  must not exceed 300 ergs/cm.<sup>2</sup>. Physically, the condition is that  $kT$  is comparable with the energy to remove one molecule. Little is known of the surface energies of solids, but values of this order of magnitude have been calculated, and experimentally verified, by M. M. Nicolson (unpublished). However, he worked with the alkali halides and the oxides of the alkaline earths, which have melting-points of the order of thousands of degrees. Nothing seems to be known about the surface energy of a crystal in contact with a saturated solution, or with its liquid at its melting-point.

4. *The three-dimensional case.* A result of MacMahon ((7), p. 241) enables one to calculate the entropy associated with a crystal growing in a three-dimensional right-angled corner, the molecules being placed according to the rules laid down for problem (a) above (p. 685). By an extremely ingenious but very complicated argument he shows that the generating function enumerating such arrangements (three-dimensional Ferrers graphs) is

$$m(z) = \frac{1}{(1-z)(1-z^2)^2(1-z^3)^3 \dots} \quad (12)$$

The entropy associated with the number of possible arrangements of  $N$  molecules can be obtained (V. Nanda, unpublished) by the method of steepest descents, the asymptotic form of the generating function as  $z \rightarrow 1$  being  $\frac{2\zeta(3)}{(1-z)^2}$ , where  $\zeta$  is the Riemann zeta function and the relation between  $N$  and  $\theta$ , the position of the saddle-point, being  $N \sim \frac{2\zeta(3)}{(1-z)^3}$ , and the corresponding entropy term is  $3.2^{-\frac{1}{3}}[\zeta(3)]^{\frac{1}{3}} kN^{\frac{1}{3}}$ .

A more precise result has already been obtained by Nanda (unpublished), who has considered the same generating function in a different physical context. The apparently simple form of expression (12) suggests that a very simple derivation should be possible, but this is an illusion, though Chaundy (3) has given a shorter derivation. The problems of deriving an equation analogous to (4), and of determining the rigorous generating function, appropriate to the three-dimensional version of problem (b), seem likely to prove very difficult.

It does, however, seem possible to arrive at a reasonably accurate estimate of the extra entropy associated with a three-dimensional 'tooth', containing  $N$  atoms, by two independent arguments which give results that agree fairly closely. In the first place consider a 'tooth' in the form of a triangular prism of length  $4p \text{ \AA}$ ., the base and height of the triangle being  $4p$  and  $2p \text{ \AA}$ ., respectively. With a lattice spacing of  $2 \text{ \AA}$ ., each triangular layer contains  $p^2$  molecules, and so is associated with an extra entropy

$\frac{2k\pi p}{\sqrt{3}}$  by the two-dimensional theory given above. There are  $2p$  layers, so that the total number of atoms will be  $2p^3$ , and the total entropy  $\frac{4k\pi p^2}{\sqrt{3}}$ . This suggests an entropy of  $kN^{\frac{1}{3}}4.3^{-\frac{1}{3}}\pi$  or  $4.5kN^{\frac{1}{3}}$  in the three-dimensional case, on the assumption that the typical three-dimensional 'tooth' is not too far removed in shape from a wedge. An error also arises from the fact that we have neglected the correlation between the sizes of neighbouring triangular layers required by our assumptions, so this value is probably an over-estimate.

A more reliable estimate can be obtained by modifying the figure  $3.2^{-\frac{1}{3}}[\zeta(3)]^{\frac{1}{3}}kN^{\frac{1}{3}}$  that follows from MacMahon's generating function (12), and gives us a lower limit as it enumerates just those three-dimensional 'teeth' which are bounded by two vertical planes at right angles. We have already found that the generating function (10) can be replaced effectively by the square of the generating function (4), because of the possibility of representing the general two-dimensional arrangement by means of two Ferrers graphs put 'back to back' in the manner shown in Fig. 6. Similarly, we can infer with some confidence that the generating function enumerating three-dimensional 'teeth' is effectively the fourth power of MacMahon's generating function, four of his arrangements fitting together along their plane faces to make a three-dimensional 'tooth'. However, not every 'tooth' can be 'sliced up' in this fashion, while others can be 'sliced up' in a variety of different ways to make four MacMahon arrangements, so that the (1-1) correspondence which exists in the two-dimensional case does not hold here. On the other hand, neither of these uncertainties is likely to introduce an error as great as a factor of  $N$ , in either direction, in the number of possible arrangements for a given  $N$ , so that the error in the entropy is unlikely to be as large as  $k \log N$ , which is negligible compared with  $kN^{\frac{1}{3}}$ . (For example, the number of different ways in which a given 'tooth' can be so 'sliced up' cannot possibly exceed, and is probably very much less than, the number of cubes in the bottom layer, which is less than or equal to  $N$ .) The entropy that follows from a generating function  $[m(z)]^4$ , where  $m(z)$  is MacMahon's generating function (12), is

$$\Phi_3(N) \sim 3[\zeta(3)]^{\frac{1}{3}}kN^{\frac{1}{3}} \sim 3.3kN^{\frac{1}{3}}. \quad (13)$$

This agrees reasonably well with the first value, which we considered to be an over-estimate, while the value  $2.2kN^{\frac{1}{3}}$  that follows from MacMahon's generating function (12) is an under-estimate.

5. *An alternative treatment of the two-dimensional problem.* I am grateful to Prof. L. Onsager for pointing out that the generating function for the two-dimensional problem can, subject to the assumptions already mentioned, be evaluated exactly. The result obtained is not quite equivalent to (10), which is the generating function for a single 'tooth', whereas the generating function for an entire boundary can be written down as follows:

We may imagine the boundary to be built up from left to right, vertical columns of 'bricks' being added one at a time. Then, when we add the  $(m+1)$ th column, three situations are possible: (a) the top of the  $(m+1)$ th column may be level with that of the  $m$ th, (b) the top of the  $(m+1)$ th column may be above that of the  $m$ th, (c) the top

of the  $(m+1)$ th column may be below that of the  $m$ th. In case (a) the addition of the  $m$ th column has added one horizontal cube face, but no vertical cube face, to the boundary. In cases (b) or (c) one horizontal face and  $k_m$  vertical faces have been added,  $k_m$  being the difference in height of the  $(m+1)$ th and  $m$ th columns. The factor in the generating function associated with the extension of the boundary by one horizontal step is thus

$$\begin{array}{ccc} x + x(y + y^2 + y^3 + \dots) & + & x(y + y^2 + y^3 + \dots), \\ \text{Case (a)} & & \text{Case (b)} \quad \text{Case (c)} \end{array}$$

where the index of  $x$  counts the horizontal boundary faces while that of  $y$  counts the vertical ones. In cases (b) and (c) we have to sum over all possible values of  $k_m$ , the height of the  $m$ th 'step', so that the complete factor in the generating function is

$$x + \frac{xy}{1-y} + \frac{xy}{1-y} = \frac{x(1+y)}{1-y}, \quad (14)$$

and the generating function for a boundary containing  $l$  horizontal faces is the  $l$ th power of this expression. Since only forward steps are allowed in the horizontal direction, this expression describes possible configurations of a boundary that is free from 'overhang' as defined above (p. 689). To obtain the statistical mechanical partition function for a boundary containing  $l$  horizontal faces, we simply have to replace  $x$  and  $y$  by  $z$ , where  $z = e^{-E/kT}$  and  $E$  is the energy per exposed cube face. The partition function for a boundary of  $l$  steps is thus  $z^l \left( \frac{1+z}{1-z} \right)^l$ , and the corresponding free energy of such a boundary is therefore

$$F = lE - kTl \log \left( \frac{1+z}{1-z} \right), \quad (15)$$

whereas that of a boundary consisting simply of  $l$  horizontal faces is just  $lE$ .

There is thus always a gain in free energy if the boundary is allowed to become rough, and there is no prediction of a sudden transition temperature. We arrived at an apparent transition temperature above (p. 692) by assuming a definite shape for the average 'tooth', a triangle of height equal to half its base, whereas the average shape is itself a function of temperature. We can calculate the average vertical height of a 'step' quite simply from expressions (14) or (15)—it is simply the average index of  $z$  in the expression  $\frac{1+z}{1-z}$ , so that we have

$$\overline{k_m} = z \frac{\partial}{\partial z} \log \left( \frac{1+z}{1-z} \right) = \frac{2z}{1-z^2}, \quad (16)$$

which increases steadily from zero to infinity as the temperature rises. The temperature at which  $\overline{k_m}$  is unity, so that the average boundary is inclined at  $45^\circ$  to the horizontal, and the 'teeth' would have the approximate profile assumed above (p. 692), is given by  $z = \sqrt{2} - 1$  or  $E = 0.88kT$ . This is not the same as the temperature calculated above, which is that at which a flat surface and one with '45° teeth' would have equal free energies. The temperature at which the '45° tooth' is the *most likely profile* is  $\frac{4S \times 10^{-16}}{0.88k}$ , since  $E = 4S \times 10^{-16}$  for a lattice spacing of  $2 \text{ \AA}$ . This temperature is appreciably higher than the former value, as one might expect.

A direct comparison of the two calculations is possible if we calculate the entropy associated with  $l$  horizontal lattice distances. At the temperature at which  $z = \sqrt{2} - 1$ , the most probable profile is a 'tooth' of base  $l$  and height  $\frac{1}{2}l$ , containing  $\frac{1}{4}l^2$  atoms. The estimated entropy associated with this was  $2\pi \cdot 3^{-\frac{1}{2}} k(\frac{1}{4}l^2)^{\frac{1}{2}} = 1.81kl$ , while, from equation (15) we have

$$\Phi = -\frac{\partial F}{\partial T} = lk \log \left( \frac{1+z}{1-z} \right) + lkT \frac{\partial z}{\partial T} \frac{2}{1-z^2} = lk \log \left( \frac{\sqrt{2}}{2-\sqrt{2}} \right) + \frac{lkT}{z} \frac{\partial z}{\partial T} = 1.78kl,$$

the agreement between these two quite distinct methods of estimating the entropy being very satisfactory.

It should be mentioned that expression (14) has an alternative interpretation in terms of the Ising model of a ferromagnet. It can be interpreted as the generating function associated with a boundary drawn between a 'plus' and a 'minus' domain in the two-dimensional square lattice,  $x$  representing the Boltzmann factor associated with replacing a like vertical pair of nearest neighbours by an unlike one,  $y$  being the equivalent factor for horizontal pairs. The boundary described by (14) has the property of never cutting itself, but it is not quite the most general boundary with this property, because we have completely forbidden *backward* steps in the  $x$  direction. If expression (14) becomes equal to unity, it means that a boundary can be drawn right across the lattice at no cost in free energy, which must mean that long-range order has broken down. The condition that (14) becomes unity is, in fact, precisely equivalent to the condition for the critical temperature in a plane square Ising lattice

$$\sinh(2J/kT) \sinh(2J'/kT) = 1$$

(Onsager(8)). This method can also be applied to the plane hexagonal and honeycomb lattices, for which it again locates the known critical temperature precisely, provided that two of the three interactions are equal. A further application has been made to the plane-square lattice with second nearest neighbour interaction (considered by Domb and Potts(4), using an expansion method), and gives values for the critical temperature in close agreement with those estimated by them; no closed expressions for the partition function being known for this case.

These results are of interest in that they show that, for these simple models in which computation is possible, the 'boundary tension', or free energy of a domain boundary, remains finite until the critical temperature is actually reached, instead of vanishing at some slightly lower temperature.

6. *Conclusion.* It thus seems quite possible that the formation of 'teeth' on a crystal may be explicable purely on entropy considerations, the greater number of ways of realizing a rough surface compensating for the extra surface energy, so that a rough surface is the true equilibrium one at all temperatures. It may well be that, by the time the crystal has cooled to a temperature at which the equilibrium roughness is small, the mobility of the molecules has fallen to a low value. One may conclude further that the 'teeth' on the same surface should be nearly equal in size, because  $N_1^{\frac{1}{2}} + N_2^{\frac{1}{2}}$  assumes a maximum value for  $N_1 = N_2$  if  $N_1 + N_2$  is fixed. A more speculative possibility is that one may ultimately be able to calculate the equilibrium number of molecules in a 'tooth', left undetermined by the theory in its present state.

I should like to thank Miss V. E. Marting for suggesting this problem, and for helpful discussions. I should also like to thank Dr F. C. Auluck for his very helpful discussions on the theory of partitions, and Prof. L. Onsager for suggesting the alternative treatment of the two-dimensional case.

*Note added in proof.* During the working out of the ideas reported in this paper, various papers, by F. C. Frank and others, have brought forward theoretical and experimental evidence that crystal growth occurs preferentially in the neighbourhood of "screw" dislocations, and that a single such dislocation may initiate growth over an entire face. The present paper only attempts to predict the equilibrium form of a face after growth has ceased for a long time.

It is perhaps worth pointing out that equation (8) is equivalent to the simpler recurrence relation

$$(1 - z^r) h_r(z) = 2zh_{r-1}(z) - h_{r-2}(z), \quad r \geq 2,$$

and that an expansion of the generalized generating function  $h(y, z) = \sum_r y^r h_r(z)$  is possible by the same method that was used to derive (10).

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#### APPENDIX

*Proof of equation (11).* We have, by adding terms up from the left, the following result:

$$1 + \frac{2z - z^2}{(1 - z)^2} + \frac{2z^2 - z^4}{(1 - z)^2(1 - z^2)^2} + \frac{2z^3 - z^6}{(1 - z)^2(1 - z^2)^2(1 - z^3)^2} + \dots \equiv [f(z)]^2,$$

which may also be written

$$\left. \begin{aligned} 2 + \frac{2z}{1 - z} + \frac{2z^2}{(1 - z)^2(1 - z^2)} + \frac{2z^3}{(1 - z)^2(1 - z^2)^2(1 - z^3)} + \dots \equiv [f(z)]^2 + 2, \\ + 1 + \frac{z^2}{(1 - z)^2} + \frac{z^4}{(1 - z)^2(1 - z^2)^2} + \frac{z^6}{(1 - z)^2(1 - z^2)^2(1 - z^3)^2} \end{aligned} \right\} \quad (\text{A } 1)$$

The following identity is also well known

$$f(e^{i\theta}, z) = \frac{1}{(1 - ze^{i\theta})(1 - z^2e^{i\theta})(1 - z^3e^{i\theta}) \dots} \equiv 1 + \frac{ze^{i\theta}}{1 - z} + \frac{z^2e^{2i\theta}}{(1 - z)(1 - z^2)} + \dots,$$

and a similar result holds for  $f(e^{-i\theta}, z)$ .

$$\begin{aligned}
 \text{Then} \quad 1 + \frac{z^2}{(1-z)^2} + \frac{z^4}{(1-z)^2(1-z^2)^2} &\equiv \frac{1}{2\pi} \int_0^{2\pi} f(e^{i\theta}, z) f(e^{-i\theta}, z) d\theta \\
 &= \frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{\prod_{r=1}^{\infty} (1 - 2z^r \cos \theta + z^{2r})}. \quad (\text{A } 2)
 \end{aligned}$$

Putting the integrand into partial fractions, treating  $\cos \theta$  as the variable, and using the result

$$\frac{1}{2\pi} \int_0^{2\pi} \frac{d\theta}{1 - 2z^r \cos \theta + z^{2r}} = \frac{1}{1 - z^{2r}} \quad (|z| < 1),$$

$$\begin{aligned}
 \text{we find} \quad 1 + \frac{z^2}{(1-z)^2} + \frac{z^4}{(1-z)^2(1-z^2)^2} + \dots \\
 \equiv [f(z)]^2 [(1-z) - z(1-z^2) + z^{1+2}(1-z^3) - z^{1+2+3}(1-z^4) + \dots]. \quad (\text{A } 3)
 \end{aligned}$$

Subtracting equation (A 3) from (A 1) we obtain equation (11) of the text.

At my suggestion, Auluck (1) has studied the type of two-dimensional packing in which each molecule is midway between its neighbours of the rows below and above it, this leading to a plane hexagonal lattice in which each atom has six nearest neighbours. He finds that the generating function given in equation (10) of the text is replaced by

$$1 + \frac{z}{1-z} + \frac{z^3}{(1-z)^2(1-z^2)} + \frac{z^6}{(1-z)^2(1-z^2)^2(1-z^3)} + \dots \quad (\text{A } 4)$$

(the powers in the numerators being now the triangular numbers) which also leads to an entropy of the order of  $kN^{\frac{1}{2}}$  associated with the formation of a 'tooth' containing  $N$  molecules.

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