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THE SYMMETRY OF DENDRITIC SNOW CRYSTALS

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Snow crystals are of interest in two major respects: (a) meteorologically and (b) artistically. The meteorological interest in snow crystals was greatly enhanced by the work of Langmuir^{1, 2} and Schaefer,³⁻⁶ who have done such extensive pioneering work on the seeding of clouds with material having a structure similar to that of ice, with the object of gaining some control over rainfall throughout the country. Their most effective seeding materials are frozen carbon dioxide and silver iodide. From the artistic standpoint the interest in the beauty of snow crystals goes back to the most primitive times, but we know that as early as 1555 Olaus Magnus, Archbishop of Upsala, published a woodcut of a snow crystal in a book on the general subject of "Natural Phenomena." The most authentic early drawings of snow crystals were made by Scoresby⁷ in 1820. One of the first to use photography for the study of shapes of snow crystals was Hellmann⁸ in 1893. The most extensive work on the photography of snow crystals was carried out by W. A. Bentley, of Jericho, Vermont, who apparently spent a good portion of his life at this task, judging from his publications between 1901 and 1927.9 In 1931 W. J. Humphreys assisted Bentley in compiling about 2,400 of Bentley's most interesting photographs into a beautifully arranged book.¹⁰ All recent work on the study of snow crystals is contained in a well-illustrated book by Nakaya.¹¹ This book lists eighty-seven references and is outstanding for its complete accounts of the experiments of Nakaya and Hanajima in their artificial production of snow crystals to duplicate almost every form produced naturally.

The present discussion deals with the artistic aspects of snow crystals, but it has a scientific interest because it tries to explain the causes of the interesting shapes of snow crystals and, furthermore, because these explanations may be carried over into other fields wherein dendritic growth and branching are evident.

Three outstanding characteristics of dendritic snow crystals are immediately apparent: (a) they exhibit a hexagonal pattern; (b) the crystals are all different in shape, as though no simple law (such as governs "normal" growth) operated to cause a relationship between the crystals; and (c) the branches of the six trees on the dendritic crystals form six almost identical sets. The hexagonal character of snow-flakes is in perfect accord with the crystal structure or atomic arrangement of the water atoms in the ice crystal. Bernal and Fowler have worked out the structure of ordinary ice, or ice I,¹² while the structures of ice formed at high pressures have been worked out by Megaw,¹³ Burton and Oliver,¹⁴ and McFarlan.¹⁵ The fact that no two snowflakes are alike seems to surprise no one, since experience teaches that the probability of a difference existing between two objects increases with the complexity of detail in the objects. However, the fact that the six trees (see Fig. 6) branching from a common center in a snow crystal are almost identical in spite of their intricacy is a thing that excites the wonder of everyone.

It is the great similarity between the six parts of a dendritic branching snow crystal that this paper is written to explain. The problem has often been expressed by the question, "How does one branch of the crystal know what the other branches are doing during growth?" Such regularity and symmetry are not so uncommon among the plants, especially in the flowers and blossoms, and among the animals, particularly in animals of the sea, where hormones and nerves provide a means of coordinating the development and activities of living organisms (Thompson¹⁶); but for an inanimate organism to duplicate its development in growth in such minute detail is not easily explained. The explanation of the co-ordination in growth among the six branches of a snow crystal is based (in this discussion) upon the theory that it is caused by standing waves of the thermal and acoustical type within the crystal. We will first discuss the nature of the standing waves¹⁷ within bodies of various shapes and then discuss the kinetics of the deposition of molecules of H_2O on the crystal.

The Nature of Standing Waves.—When an elastic substance is disturbed by applying some force momentarily to some portion of it so as to displace that portion from its equilibrium position, that portion of the substance will (as soon as the force is removed) return to its initial position. But, owing to the momentum of that portion, upon its arrival at the initial position, it will "coast" beyond equilibrium. Again in a position of nonequilibrium due to "overshooting," the body again finds itself elastically deformed and returns through the equilibrium position with momentum which carries it to the position of original displacement. This process may be repeated many times, depending upon how rapidly the energy is dissipated by friction, either internal or external. The number of times which this cycle is repeated per second is called the frequency ν and depends upon the restoring force F and the mass M of the displaced material; for simple systems this may be expressed as

$$\nu = \frac{1}{2\pi} \sqrt{\frac{F}{M}},\tag{1}$$

where ν is the frequency. At the same time vibrations may be carried to other portions of the body. The number of centimeters per second with which the disturbance is transmitted from one portion of the body to another is called the "velocity" of the wave.

If the body is not infinite in extent but is limited to some defined shape, the waves will be reflected at the boundaries, and the reflected waves will mix with other oncoming waves. There are certain frequencies of vibration whose values v are such that there is a sort of coherence between all reflected waves and the oncoming waves. For these frequencies, which are called "characteristic frequencies," socalled "standing waves" result. The standing waves appear not to be moving. Their apparent stationary condition results from the fact that the oncoming and reflected waves have equal amplitude and equal frequencies and their velocities are equal but in opposite directions. The frequencies of standing waves depend upon the initial conditions of displacement and upon the shape and dimensions of the body. These conditions are called "boundary conditions." From the boundary conditions the characteristic frequencies may be solved for, provided that the boundary conditions are sufficiently simple.^{18, 19} The shapes for which solutions may be obtained are (a) linear systems, parallelograms, and parallelepipeds, to which one-dimensional, two-dimensional, and three-dimensional Fourier series apply, respectively; (b) circular systems and cylindrical systems, to which Bessel functions apply; and (c) spherical systems, to which Legendre polynomials apply.

It may be assumed that a long, unbranched spine of a dendritic crystal of snow complies very nearly to a one-dimensional system. When in transverse vibration, the displacement $\phi(x, t)$ of a point at distance x along its length at any instant of time t can be expressed by the Fourier series

$$\phi(x, t) = \sum_{m} A_{m} \cos \frac{2\pi m x}{a} \cos 2\pi \nu_{m} t, \qquad (2)$$

where a is the length of the spine, m is an integer, and A_m is the amplitude of the mth wave. In this respect the spine is analogous to a vibrating string free at both ends. As is known to all musicians, the relative values of the amplitudes A_m for each m value (or harmonic) is influenced (1) by the position x_p at which the string is plucked, struck, or bowed and (2) by the position x_d at which the string is arrested by the finger. The point of greatest interest to us is that, in a string of length a which is arrested at the center, for example, all wave lengths a/m' are reduced in amplitude, where m' is an odd integer; or, in general, if the string is damped at some distance from the end expressed by a/g where g is any chosen integer, then the string cannot vibrate at any wave lengths except those which are expressed by $\lambda_p = 2a/gm''$, where m' is any integer.

If it is assumed that the arresting of a vibrating string by placing a finger on that point is equivalent to loading the string at that point with a mass which is infinite in comparison to the density of the string, then it becomes of interest to know what may happen if the added mass is finite. We shall not go into this matter, but fortunately this problem has been worked out,¹⁷ and we shall merely state the results: (1) a mass of weight m attached to a string reduces the frequency of vibration of all standing waves except those for which the point of attachment is a node, and (2) the mass reduces the amplitude of vibration at the point of attachment. As the mass is increased, the amplitudes and frequencies decrease, until at infinite mass fully developed nodes are induced.

The two-dimensional standing waves, as observed on a rectangular drumhead,¹⁸ are very convenient to study, because when such a drumhead is set into vibration by striking, sawdust scattered upon the membrane is observed to accumulate upon the nodal points or nodal lines. When such a drumhead is struck and then arrested at some point, other points are observed to be induced nodes, as evidenced by the accumulation of sawdust in small piles at these positions. Or, if the drumhead is arrested by placing a straight edge one-third of the way along the *a* dimension, then an induced nodal line is formed at 2a/3.

Examples of Branching in Snow Crystals.—The theory which we wish to present is that snow crystals grow from the deposition of water molecules upon small nuclei of ice which are under thermal vibration corresponding to a temperature of 250° -273° K.; the molecules strike and bounce off the nuclei, with relatively few sticking; the number of those which strike and stay to contribute to the size of the growing crystal is greatly influenced by the frequency and amplitude of vibration at any point on the crystal; if a portion of a spine or branch of a dendrite becomes more heavily loaded than the surrounding portions, the vibrations are somewhat restricted, as is a string with a mass attached; these loaded portions become more loaded with further growth; therefore, the growth from the loaded point becomes a runaway process, and thus branching occurs; finally, the loaded portion simulates a node, and the induced nodes sponsor growth at other portions according to a defined pattern.

To clarify the process described in the above paragraph, let us discuss a number of the pictures from the book by Bentley and Humphreys.¹⁰ First let us imagine that Figure 1 is an enlarged photograph of a very small nucleus which in the later stages of its growth has experienced "normal" growth for a sufficiently long time to have established a "normal" hexagonal shape. If conditions were to change so as to be conducive to dendritic growth,²⁰ then the six corners would find themselves receiving more molecules and losing more heat of crystallization than the flat portions. If this situation prevailed, the corners would "sprout" dendrites, as shown in Figure 2.

After a very much longer time the dendritic "sprouts" will have grown to quite extended lengths, as shown in Figure 3. Up to this point, the growth of the dendrites can be explained on the basis of the known theories.²⁰ To account for the branching, however, one must consider the standing-wave phenomena.

FIGS. 1-6.—Some typical snow crystals photographed by W. A. Bentley. (Reproduced by permission from *Snow Crystals*, by Bentley and Humphreys. Copyright 1931, McGraw-Hill Book Co.)





FIG. 2







FIG. 5



FIG. 6

Let us consider that each of the six spines in Figure 3 is an array of molecules²¹ arranged in the order required by the structure of ice and that all the molecules are in thermal agitation in a manner demanded by the theories of black-body radiation and Planck's distribution law, but that the distribution of energies between the modes of vibration is influenced by the boundary conditions. If one of the spines becomes loaded at some point, say one-fourth the distance from their point of attachment, then nodes are induced at equal intervals along the spine. As shown in Figure 4, these nodes will "sprout" dendritic branches that are equally spaced. Figure 5 shows the equal spacing of the branches on a dendrite where the interval is one-eleventh of the spine length, and the nuclear size is extremely minute.

The question may arise as to how the waves which stand in one of the six branches are coupled with those in the other five branches. Experimentally one may build a model of six such spines from thin drill-rod material and weld them together, then place them on a thin dental rubber dam sheet. Sawdust may be used to study the wave forms produced by vibrating them. The torque through the point of intersection transmits the same frequencies and induces the same nodes in all branches in an identical manner.

Figure 6 is an interesting example of a crystal which changed its vibrational modes. This crystal grew dendritically from the center O to the point S according to some system of loading, then grew a slender spine from S to T, and then rebranched systematically again. Also, one may notice secondary branches such as the one marked B. Many of the secondary and tertiary branches have been inhibited by interference or shielding by their neighbors.

Returning to Figure 1, which was chosen for its simplicity, we see markings which indicate that it has formed complete hexagons at several stages in its development. Each time after (or during) the filling-in process, changing conditions produced further dendritic growth. Similar "filling-in" scars can be seen in Figure 2 at G'.

These markings on the interior of the crystals are almost as interesting as the branching characteristics of snow crystals. The complicated markings such as are shown in Figure 4 are a sort of a written record of the atmospheric conditions through which the crystal has gone in its relatively long experience of having been carried up and down repeatedly by upcurrents and gravity between elevations at which the temperature, humidity, and pressure differ extremely with altitude. A study of these markings should eventually become valuable to meteorologists. Nakaya¹¹ and his co-workers have established, in their experiments on the synthetic production of snow crystals, the conditions of ambient temperature, humidity, and supercooling under which each of the various types of snow crystals is formed. If it can be assumed that natural snow crystals of a given type can be used as evidence of the conditions in the air, then meteorology has a new tool.

In this discussion there is one point that has not been clarified. This point has to do with the question, "What is the mechanism by which some point on a dendritic spine becomes more heavily loaded with molecules than other points?" We shall consider this point statistically.

Some Statistics of Snow Formation.—Let us consider some facts which might enable us to imagine what goes on in the atmosphere during the growth of a snow crystal.

At 0° C., saturated air contains 4.835 gm. of water per cubic meter, according to the Smithsonian tables. At 20° C. the air is saturated when there is only 0.892 gm.

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This means that if saturated air at 0° C. is chilled to -20° C., per cubic meter. about four-fifths of the suspended water molecules will precipitate as ice as fast as these molecules can establish (or find) nuclei upon which to deposit. Expressed in partial pressures, the 4.835 gm. of H_2O per cubic meter is about 0.006 atmosphere, or 4.56 mm. of mercury. This does not appear to be a very high pressure, but it represents 1.6×10^{17} molecules of H₂O per cubic centimeter mixed with about 200 times this many molecules of air. At this congestion, the water molecules are only 0.2×10^{-3} millimeter apart. They do not have far to go to associate with one another, and they should not require very long to accomplish much, since the H₂O molecules are traveling at a mean velocity of 62,700 cm/sec. For example, if an ice crystal is suspended in the saturated atmosphere at 0° C., it is bombarded with water molecules at the rate of 2.5×10^{21} molecules per square centimeter per second, that is, about 1/250 mole/sec. This means that every 28 seconds there will be about 79 calories of heat deposited per square centimeter if every molecule sticks (this is assuming a heat of sublimation of 675 cal/mole). This accumulation of heat would raise the temperature and melt the crystal (79 cal/mole is the heat of fusion of ice).

To be more precise, let us consider an actual snow crystal of over-all dimensions of $100 \ \mu$ or about $1/10 \ mm$. Assume that it is similar to the one pictured in Figure 3 having six spines, each 20 times as long as wide and about one-tenth as thick as wide. Such a crystal has an area of 10^{-6} square centimeter. Such an area is bombarded with 2.5×10^{15} water molecules per second. Using the figure 1.4×10^{15} and the volume occupied by water molecules in ice, one concludes that the crystal should grow at a rate of about one centimeter per second in all directions. This velocity of growth is much more rapid than observed rates,⁶ since observed rates are approximately $100 \ \mu$ in 30 seconds or $10^{-4} \ cm/sec$. We are forced to conclude that even at fast rates of growth only about four out of every thousand molecules which strike the crystal surface stick; the other 996 bounce off.

As pointed out by private communication from Sterling B. Hendricks, the present argument applies not only to the sublimation processes but also to the surface migration of water molecules on ice. Murphy²² has shown that in the bipedal random walk of water at 0° C. there are 10⁵ skips along the surface for each jump off the surface, and at -100° C. the ratio is 10⁸.

Now let us consider the vibrations within the ice crystal. The longest thermal vibration in the crystal has a wave-length twice the length of the spine or about $1/_{i0}$ mm, that is, in the far infrared, not far from the black-body maximum at 0° C.; and the shortest possible wave is twice the interatomic distance, or about 3 A, that is, in the X-ray region and negligibly weak in intensity. Assuming that the velocity of sound in ice is about 1,500 m/sec, we may calculate the lowest frequency of vibration of a dendritic spine to be 1.5×10^7 and for the highest frequency 6.6×10^{12} cycles/sec. This means that even for the lowest possible frequency of oscillation of the spine of an ice crystal only about 10^{-7} second is required to complete a wave cycle. Using the structure of ice, we may calculate the area of a unit cell of the crystal to be about 33×10^{-16} square centimeter. Following, in our imagination, the oscillation of a unit cell back and forth once every 10^{-7} second, and an exposed area of only 33×10^{-16} square centimeter, in an atmosphere where it is being bombarded at a rate of 2.5×10^{22} times per second per square centimeter with water molecules, we can calculate the number of bombardments per cycle per

unit cell to be approximately 8. Since only one of these out of each thousand sticks, we may conclude that, on the average, we must consider an expanse of about 300 unit cells to see one captured molecule per cycle at the slowest possible vibration rate. For higher frequencies the times are shorter and the expanse (over which one may expect an average of one capture per cycle) is greater.

This means that, while we may calculate the average number of molecules captured by a given area per second, we have no means of saying for certain that this really happens. Watching a single area in which we expect one molecule to be captured and confining our observations to the short time of one cycle, we have a good probability of seeing no molecules captured, or we have a fair probability of seeing two captured. According to our earlier study of vibrating strings, if two are captured, the system is loaded more heavily in this region than the average, and further captures are more likely on the next cycle. The runaway process has begun!

Fortunately, the probability of capturing any portion of the expected number of molecules is a problem in a field of statistics which has been worked out.²³ In calculating the deviations from expectation, Poisson developed an equation which has proved reliable in many problems such as production control, plant breeding, and other fields where data can be collected:

$$P(n) = \frac{\epsilon^n e^{-\epsilon}}{n!},\tag{3}$$

where P(n) represents the probability of n molecules falling on an area where ϵ molecules were expected to fall. This equation can be used to calculate the probability that any chosen area of a crystal may become abnormally overloaded with molecules during one vibration cycle. From a table of Poisson probability values²³ (p. 458), we see that, for $\epsilon = 1$, the probability of getting what we expect is about the same as the probability of getting none. The probability of getting 2 is about one-half that of getting 1, and the probability of getting 3 is about one-sixth. The maximum probability is always on the expected number; for example, when $\epsilon = 5$ the maximum probability is .175 for n = 5, and when $\epsilon = 10$ the maximum probability is .125 in the neighborhood of n = 10. The tables teach us that if we expect 1 molecule per unit area for a given cycle, we have a probability of about 1 out of 3 of getting it; if we expect 5 molecules, we have a probability of 1 out of 5 of getting it, and if we expected 10, our probability is 1 out of 8. The total probability is unity in any set, but the bulk of the probability is scattered over the many unexpected groupings of events.

This all means that, according to statistics, an uneven loading is very likely in a single vibration of a dendritic spine, and branching is easily initiated.

An interesting experiment would be to grow a piezoelectric crystal while vibrating, to see whether fins could be included at the nodes of the vibrations.

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EXCITATIONS AND POLYMERIZATION

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As described previously,¹ fluorescent substances, if frozen in water, show peculiar forms of long-lived electronic excitations. It has been suggested that the long lifetime of these excitations is due to their triplet state. It has also been shown