A Hundred Years of Entropy

From primitive machines and the discovery of fire came problems of mechanics and heat. The steam engine brought them forcibly together. Out of the study of heat-to-work transformations that resulted, came our entropy concept, and extension of the reasoning has brought useful applications in far-removed subjects like probability, number theory, information theory and language.

by Mahadev Dutta

PERHAPS THE PARADOX of entropy is that it has so long a history and yet so many remaining puzzles. We might say that the roots of its history go back even to primitive man. In his struggle for existence he used crude appliances and discovered fire. From closer intimacy with more and more developed machines sprang mechanics, and from fire came the theory of heat; the two were quite separate sciences.

Only the invention and impact of the steam engine led to final identification of heat and mechanical energy and thus to the first law of thermodynamics. Experiences with limitations in the heat-to-work conversion were formulated as the second law of thermodynamics; its convenient mathematical form is the entropy law. Successful applications in various sciences and in technology quickly proved its utility as a basic law of nature.

But the inequality in the formulation of the law remains a scientific curiosity. Many attempts have been made and are still being made to analyze the law from many viewpoints: axiomatic, mechanical, statistical-mechanical and purely statistical. Among the results of such studies are Bose-Einstein and Fermi-Dirac statistics, which are of fundamental significance throughout physics.

In communication theory C. E. Shannon, in 1948, used entropy in a completely new context. He defined it for any random process. Out of this definition grew information theory. Shannon's general definition also opened new applications in other fields of human knowledge. In probability theory, it yields a method of statistical estimation. In logic it is used in the discussion of probabilistic inferences. In linguistics even the entropy of a language is defined. In mathematics the entropy concept has been introduced in abstract analysis, approximation theory and number theory.

Successful applications of the notion of entropy in different fields have established the usefulness and generality of the concept, which was originally introduced as the basic concept of thermodynamics and had its applications mostly in some branches of physics, physical chemistry and mechanical engineering.

Background

Many great scientists have contributed to this history. Through the work of Galileo Galilei (1564–1642) and Isaac Newton (1642–1727) mechanics took shape. In this form mechanics was widely accepted after the elegant formulation by Joseph Louis Lagrange (1716–1813) and the extensive calculations of its various applications in celestial mechanics by Pierre-Simon Laplace (1749–1827). Gottfried Wilhelm Leibnitz (1646–1716) considered different forms of mechanical energy and its conservation.

Meanwhile experiences with fire and heat grew in bulk and were known as the "theory of heat," but until the middle of the last century the theory was mainly speculative.

When James Watt made his steam engine in 1765, people began to think of the relations between thermal energy and mechanical energy. Just a little earlier, in 1747, some physiologists, of whom Albert Haller was a pioneer, advocated the friction of blood flow as the source of body temperature. Then, after Watt, experiments of Benjamin Thompson (1798), who became Count Rumford, James Prescott Joule (1840) and their contemporaries led to recognition that heat is a form of energy and to the principle of conservation of energy (Robert Julius Mayer's principle or the first law of thermodynamics).

Mechanics joins heat

With the unification of these two separate streams of human experience, the theory of heat had the proper scientific form, and a new branch of science had its origin; it is mainly concerned with transformations of heat into mechanical work and the reverse and is known as "thermodynamics." Soon transformations of heat and work into and out of other forms of energy—chemical, electric, magnetic, electromagnetic—were also studied.

Before Mayer's clear formulation of the first law of thermodynamics (about

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1842) and its acceptance, men had experienced the limitations in transformations of heat into work. Nicolas Leonard Sadi Carnot (1828) noticed these clearly in his investigations on cycles representing the working of heat engines.[1] These limitations necessitated the formulation of the second law of the thermodynamics. As Max Planck tells us in a book of his,[2] it was formulated by Rudolf Clausius (1850), William Thomson, Lord Kelvin (1851), and Wilhelm Ostwald independently in different languages. It is easily seen that these different formulations represent essentially the same fact. According to Clausius,[3] "A transformation of which the final result is to transform into work heat extracted from a source which is at the same temperature throughout is impossible." Ostwald's principle is, "Perpetual motion of the second kind (which can transform heat into work without any limitation) is impossible." Another version of the law, very convenient for mathematical development, is expressed in terms of entropy, which was first introduced by Clausius[4] in 1865 (in 1855, according to Guggenheim[5]) in his discussions of heat cycles.

The entropy change from state A to state B is generally defined[6] as

$$S_B - S_A = \int_A^B \frac{d'Q}{T}$$

where $d'Q$ is the heat absorbed by the system at the temperature T and the path of integration is taken as reversible, that is, through successive states of equilibrium as ideally visualized in infinitely slow processes of transformation. On account of the first law, in order that the definition be independent of path, the following must be an exact differential

$$\frac{d'Q}{T} = \frac{dU + p dV}{T}, \textit{ or}$$

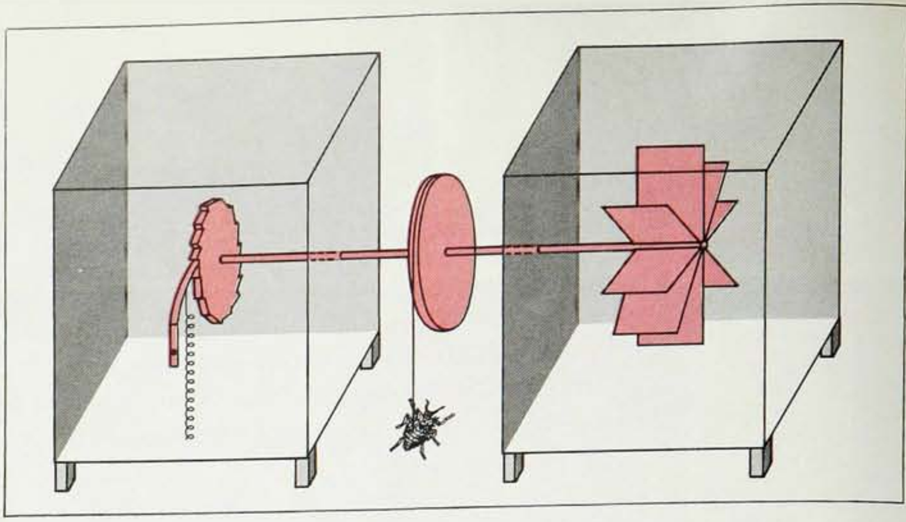
$$\frac{d'Q}{T} = \frac{dU + \Sigma X_i dx_i}{T}$$

(p and V are pressure and volume; X_i's and x_i's are other quantities similar to p and V). Generally, in textbooks, the absolute temperature is introduced as the integrating factor of the Pfaffian for $d'Q$ representing the conservation of energy and the entropy as the integral. Definition also suggests that in cases of irreversible transformations, the change of entropy is to be calculated along a suitable reversible path from A to B. At this point, there are some conceptual difficulties which, even at the present day, require some careful considerations. The entropy principle (the second law) is expressed, "The entropy of the universe (or an isolated system) can not decrease":

$$\Delta S \nless 0$$

Thus the second law shows the direction of thermodynamic changes, and in doing so it takes on a unique importance in natural philosophy. The notion of unidirectional flow of time is the basis of human experience of the physical world and of science. It is compatible with biological cycles: birth and germination, growth and death and decay. But most of the fundamental laws of physics remain unchanged when time t is changed to $-t$; for these laws the notion of unidirectional time flow is not essential. Only the unidirectional change of entropy of the universal system or a completely isolated one provides a plausible ground for the concept of unidirectional flow of time.

According to Henri Poincaré[7] (1854–1912), the entropy principle, as far as its form is concerned, has a unique distinction from all other laws of physics. Usually laws of nature are expressed in terms of equality or covariance. But in the entropy principle (and also in other versions of the second law) it is done by inequality. This peculiarity has been stirring the curiosity of a large number of scientists, and investigations have been made to put forward some sort of explanation along different lines and from different standpoints.



FEYNMAN'S PERPETUAL-MOTION MACHINE. Thermal motion of air molecules would make the windmill turn in both directions, were it not for the ratchet-and-pawl. The windmill should thus turn slowly in one direction, perhaps lifting a bug. Air molecules responsible for the rotation would slow down and the air surrounding the windmill would cool. Feynman points out, though, that the pawl is also subject to random temperature motion, which may lift it sufficiently to permit the ratchet to turn backward every so often. Furthermore, the pawl acts not just as a stopping device but also as a mechanism able to drive the axle in the "forbidden" direction. Feynman shows that work is performed only if the temperature of the air surrounding the windmill differs from that of the pawl and its environment, and that the second law of thermodynamics is quantitatively obeyed. (From J. Waser, *Basic Chemical Thermodynamics*, W.A. Benjamin, 1966, and R.P. Feynman, R.B. Leighton, M. Sands, *The Feynman Lectures*, Addison-Wesley, 1964.)

In classical thermodynamics

When the laws of thermodynamics are accepted as hypotheses and the consequences of these laws are studied, the subject is referred to as "classical thermodynamics." From this study one gets the laws of phase transformations, those of chemical reactions, an elegant theory of dilute solutions and also many other results useful in engineering. In a simple and straightforward way the results of thermodynamics are extended to include all forms of energy and problems of surface tension, elastic and fluid media, electric and magnetic phenomena in which heat is evolved or absorbed.

In this connection, it is to be noted that entropy, as usually defined, contains an arbitrary constant. For application in mechanical engineering and similar other subjects, entropy is evaluated with reference to a standard position. But for applications in some subtle problems like evaluation of chemical equilibrium or ionization, knowledge of the entropy constant is important. It is evaluated with the help of the third law,[6] which, in Planck's terms can be expressed, "As the absolute temperature tends to zero, the entropy of a pure substance tends to zero."

In axiomatic thermodynamics

Quite close to the classical development are two elegant axiomatic formulations of entropy and the entropy principle, one due to Constantine Carathéodory[8] and the other due to R. Giles.[9] In the first the concept of heat is introduced as the secondary concept. The principle of conservation of energy is accepted but formulated without using the concept of heat for adiabatic changes. Adiabatic enclosures or adiabatic changes of coördinates are taken as undefined concepts or facts of experience. Then a postulate, considered very plausible and named "Carathéodory's Principle," is expressed: "In every neighborhood of a point P in the space of states, there exists a point inaccessible from P adiabatically." From this principle and from a general discussion of the Pfaffian, entropy and absolute temperature are introduced and the notion of heat is formed. After Carathéodory, discussions along the line have been made by Max Born[10] (1921), Alfred Landé[11] (1926) and Tatiana Ehrenfest-Afanassjawa[12] (1925). After nearly 30 years, the interest in this approach has been revived, and several workers are now trying to explore the different aspects of this theory.

This theory is entirely a "local" one as opposed to a "global" one. When in the investigations of physical or geometrical problems, differential calculus and differential equations are used, considerations of local properties or, as a German would say, "properties at small," play the most important role. Such a theory is referred to as a "local" theory. On the other hand, where techniques of integral calculus, measure theory or set functions are used, considerations of global problems or "properties at large" become prominent. Such theory is "global" theory.

In 1964 Giles[9] started with some primitive, undefined concepts, namely, of an operation + and a relation →, among states of a thermodynamic system, and internal states with some elementary axioms, and built up a formal, mathematical theory. In this theory the entropy function is constructed as a real-valued functional of states satisfying some sort of ordering and the condition that it is zero for a suitably introduced mechanical state. Giles's theory is global.

A mechanical approach

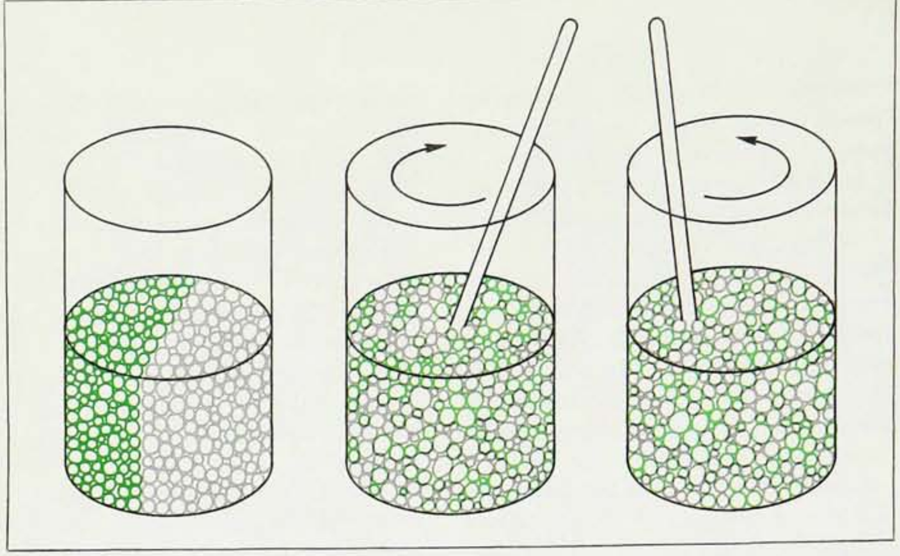
The first attempt to construct a function behaving like entropy from a mainly mechanistic standpoint is due to Ludwig Boltzmann[13] and Clausius.[14] For a single mechanical system executing periodic motion, a function behaving like entropy is constructed by using mechanical concepts and equations. One uses the principle of adiabatic invariance, formulated entirely in the terminology of mechanics but not strictly in the framework of classical mechanics. Later J. J. Thomson[15] (1884) also put forward a mechanical explanation of entropy that is closely similar to that of Boltzmann and Clausius. Writing in 1908, Poincaré[16] told us that Hermann L. F. von Helmholtz (1821–1894) also made similar efforts. Paul Ehrenfest,[17] while proposing its applicability in some quantum problems, reported briefly some aspects of the theory of Boltzmann and Clausius in an appendix. I have also given a brief report of this approach in a book to be published soon.[18] But most scientists, even Boltzmann himself, were not satisfied with this theory.

In statistical mechanics

Boltzmann[19] in 1877 or a bit earlier was the first to put forward an interpretation of entropy using some statistical arguments along with mechanical reasoning for a mechanical model. Boltzmann's H theorem demonstrates the existence of a function, $-\Sigma f_n \log f_n$, behaving like an entropy. He also proposed a simple relation between entropy and probability referred to as the "Boltzmann principle." The present-day form of the principle connecting entropy with probability (strictly, thermodynamic probability) and its plausibility are mainly due to Planck,[20] Ehrenfest,[21] and others. J. Willard Gibbs advocated the probabilistic interpretation as early as 1876.[6] Gibbs's famous book proposing an elegant formulation of statistical mechanics was published in 1902.[22] In this he established the great similarity between the average value of the index of a probability distribution and the entropy. In these theories, entropy is conceived mainly as an ensemble property, a statistical concept. These statistical lines of investigation had the widest support amongst physicists including the pioneers like Albert Einstein, Paul A. M. Dirac, and others.

The statistical arguments used in the above theories lead to the idea of fluctuations of physical quantities. Results about fluctuations that one gets from the arguments, have been verified by experiments designed in other branches of physics—even quantitatively. Satyendra Nath Bose's famous work,[23] in which the notion of weight of a state rather than that of the distribution of particles was introduced into the usual method based on thermodynamic probability, not only yielded Bose statistics for photons but also stimulated contributions of very significant results like Bose-Einstein statistics[24] and Fermi-Dirac statistics.[25] It also revived an earnest search for the real significance of basic concepts like entropy. Einstein,[26] Planck,[27] Erwin Schrödinger[28] and others made critical scrutiny of the entire standpoint of the subject. At present Bose and Fermi statistics are considered to reveal very fundamental properties of elementary particles. These results have been accepted as more significant and fundamental than the statistical mechanics itself.

During the years from 1924 to 1926, Charles G. Darwin and R. H. Fowler[29] proposed a slightly different approach to thermodynamic problems. According to their proposal, all thermodynamic quantities are to be taken as average quantities. Full discussion of the method and its applications can be seen in the well known treatise of Fowler.[30] The elegant book of A. I. Khinchin[31] shows that Fowler's method is related to the central-limit theorem of the theory of probability,



ORDERLY ARRANGEMENT of two groups of balls is destroyed by stirring in a clockwise direction. The entropy of the system is increased. Stirring in counterclockwise direction does not increase the order; in fact, the entropy of the system increases more, in accordance with the entropy principle of the second law of thermodynamics.

and A. H. Koppe[32] deduced the results of Darwin and Fowler by application of the Fourier transform and its approximate evaluations.

In communication theory

In the mathematical theory of communication Shannon[33] proposed a measure of information, choice and uncertainty associated with a random event as

$$H = -\Sigma P_i \log P_i$$

where P_i is the probability of the ith outcome of the random event. Using the terminology of statistical mechanics, he called his H an "entropy." It is also simply related to the capacity of the channel. Entropy plays a very important role in information theory. It provides a measure of information and thus has access to different branches of human thought.[34]

Probability, statistics, etc.

For the introduction of entropy into communication theory, Shannon represented a discrete information source as a random process and used the terminology of this process freely.[35] So Shannon's definition of entropy has a direct and close relation with probability theory. Entropy is used[36] as an important concept in the logical discussions of probable inferences. It is also seen that different problems of the theory of statistics can be solved by introducing the notion of entropy or the information, which is defined as the negative of entropy.[37]

Shannon even calculated the entropy of the English language.[34] Entropies of some other languages have also been calculated. A. N. Kolmogroff has associated the concept of entropy with abstract sets in abstract analysis. A comprehensive discussion of entropy in different branches of abstract analysis is in a recent lecture of G. G. Lorentz.[38]

Essentially statistical approach

Since 1951, I have been developing an essentially statistical approach to thermodynamics.[39] In this development discussions of thermodynamics have been based on the theory of estimation of statistics instead of the usual mechanical notions. I look upon measured values of some fundamental entities as sample values. The exponential distribution is taken as the distribution of thermodynamic states from arguments similar to the usual Baysian arguments[39] or as consequences of the additivity of fundamental entities.[40]

Then, I estimate the parameters by a principle practically the same as Ronald A. Fisher's principle of maximum likelihood. With this distribution, I calculate mean values and write the equation for conservation of the fundamental entities. The integral of this equation yields the usual thermodynamic entropy and different integrating factors related to important thermodynamic quantities. Here the entropy is obtained as a constant k times the logarithm of the Fisher likelihood function with the parameters replaced by the maximum-likelihood estimates. For detailed discussion of this method you can consult my book.[18]

Since 1957, E. T. Jaynes[42] has been developing a purely probabilistic approach based on the method of maximal entropy estimation of information theory. He has taken entropy, as defined by Shannon, to be the basic concept to start with. All other thermodynamic quantities, in Schrödinger's way, he has identified by analogy with parameters and expressions that appear in his discussion.

B. Mandelbrot,[43] since 1959, has been studying the parallel development of physical statistics and mathematical statistics. According to him almost all concepts and propositions of physical statistics are essentially similar to the corresponding concepts of the others. They only differ in notation and terminology.

I have shown[44] that the method of maximum entropy estimation, that of exponential distribution in which parameters are estimated by the principle of maximum likelihood and that based on Gauss's principle of the arithmetic mean[45] are equivalent. This result clearly shows how my method and Jaynes's are related and also throws light on the interrelation between the method of Darwin and Fowler and other methods of statistical mechanics. Further I have also shown that for an ergodic population, that is, for a population in which Bernoulli's theorem is valid, $1/N$ times the logarithm of the likelihood function converges in probability to the entropy function of information theory. If this definition of entropy is accepted, the notion of entropy can be introduced for every statistical population. Recently[46] from this discussion I have established the equivalence of the principal methods of statistical mechanics.

In number theory

I have already mentioned many applications of entropy in different branches of human knowledge. But these do not appear to be complete. Moreover, the possibilities of the application of entropy to newer fields are not yet completely exhausted. Let me mention a simple application of a new type of problem. In the theory of numbers, in the problem of decimal representation of numbers, the frequency of occurrence of a particular digit has been studied with great interest.[47] (We might better say the "probability" in the sense used by Venn, Richard von Mises, and Harold Crammers.) A number is said to be "simply normal" if the frequency of every digit is equal to $1/r$, r being the scale of notation. A number is said to be "normal," if it is simply normal when the scale of notation is any power of r. From our above discussion, it appears that the notion of entropy can be introduced easily and by this introduction not only all definitions can be directly introduced in terms of entropy, but also many propositions can be deduced easily. In a recent work,[48] I have done this, and some results have been proved very easily. Also one can introduce some new notions (degree of normalcy, etc.). With computers this method may provide another means of verifying the principle of entropy maximization.

And in general

Shannon's definition of entropy has its origin in Boltzmann's H theorem.[19] Now one can see easily that this theorem can be demonstrated for a class of H function where in the definition of H, P_i is replaced by p_i^a, α being real and positive. It appears to be interesting to study the consequences of taking $H\alpha$ for H in the discussions of thermodynamics, information theory and other branches of knowledge where entropy has been used. This type of function has already been considered in the study of the axiomatic basis of information theory.

The general notion of entropy, as introduced by Shannon, has proved its significance in a vast field of human knowledge. But, it appears that the full significance of this concept is not yet fully explored.

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