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ENTROPY. PART I: STATISTICS AND ITS MISLEADING DISORDER

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ABSTRACT

The overwhelming majority of scientists, engineers, and other professionals believe that: (*a*) statistical mechanics explains thermodynamics, and provides explicit expressions of entropy (for example, $S = k \ln \Omega$); and (*b*) in general, each entropy represents disorder in a system and, in particular for given values of energy, volume, and amounts of constituents, the largest value of the entropy represents the ultimate disorder (thermodynamic equilibrium state). The purposes of this paper are to present both theoretical and experimental evidence that refutes these beliefs and to show that the spontaneous increase in thermodynamic entropy represents a nonstatistical, natural tendency to perfect order rather than disorder. The arguments are presented in two parts. Brief discussions of the premises and conclusions of the statistical interpretation of thermodynamics, the association of the statistical entropy with disorder, and inconsistencies that arise from such an association are presented in Part I. A nonstatistical exposition of thermodynamics, the interpretation of entropy as a measure of the quantum-theoretic shape of molecules, and the association of the entropy of classical thermodynamics with perfect order are presented in Part II.

1 INTRODUCTION

With very few exceptions, over the past thirteen decades scientists and engineers have been sharing and promulgating the almost religious belief that entropy is not a fundamental scientific concept. Instead, they view it as a measure of ignorance or lack of detailed information about a macroscopic system and a monotonic indicator of disorder.

Despite many correct and practical numerical results, review of the theoretical premises and the experimental evidence casts serious doubt about the validity of the prevalent belief, and brings to the forefront the need for both a more rigorous examination of the premises of statistical thermodynamics, and the consideration of contemporary quantum-theoretic ideas.

The purposes of this two-part paper are to review the statistical ideas and disorder, and to summarize a unified quantum theory of mechanics and thermodynamics and a nonquantal exposition of thermodynamics which lead to the demonstrable conclusions that thermodynamics is a general, nonstatistical theory of physics that admits mechanics (both classical and conventional quantum) as one limiting case (zero entropy physics), and classical thermodynamics as another limiting case (largest entropy physics). In the quantum theory, entropy is a well-defined and mathematically precise monotonic indicator of order. The monotonic indicator is a measure of the quantum-theoretic spatial shape of the molecules of a system, in the same sense that $mv^2/2$ and not some other expression is a measure of the kinetic energy of a particle.

The beliefs of many eminent scientists about both the statistical explanation of thermodynamics and entropy and disorder, and two experiments that prove that the statistical interpretation of thermodynamic phenomena cannot be correct are summarized in Part I. A road map through an interconnected series of theoretical developments that are not only complete, noncircular, and unambiguous, but also consistent with all the empirical evidence, and that prove that thermodynamics is a nonstatistical theory, and entropy a monotonic indicator of order are discussed in Part II.

Part I is organized as follows. A summary of the beliefs of many scientists about the statistical explanation of ther-

modynamics, and the relation between entropy and disorder is presented in the second section, experiments that contradict both the statistical interpretation of entropy, and the connection between entropy and disorder in the third and fourth sections, and concluding remarks in the fifth section.

2 STATISTICAL MECHANICS, ENTROPY, AND DISORDER

Newton's enunciation of the three laws of classical mechanics (1666) is one of the greatest achievements of the human mind (Tolman, 1962). Their advent met with unprecedented success in a broad spectrum of applications from stars and planets to molecules and radiation. This success was so impressive and overwhelming that scientists were convinced that every natural phenomenon could and should be regularized by use only of the laws and theorems of classical mechanics. So, two centuries after Newton's time, when the laws of classical thermodynamics were enunciated by Clausius (1867), it was only natural that scientists felt compelled to explain these laws and their theorems by using classical mechanics.

2.1 Maxwell's demon and the statistical method.

Maxwell (1871) is one of the great scientists who believed that all physical phenomena are mechanical, but numerical difficulties with macroscopic systems force us to abondon the mechanical explanation and resort to the statistical method. He said: "One of the best established facts in thermodynamics is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or of pressure without the expenditure of work. ...But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being, whose attributes are still as essentially finite as our own, would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any great number of them, arbitrarily selected, is almost exactly uniform. Now let us suppose that such a vessel is divided into two portions A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole, so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics." An then, he continued: "In dealing with masses of matter, while we do not perceive the individual molecules, we are compelled to adopt what I have described as the statistical method of calculation and to abandon the strict dynamical method, in which we follow every motion by the calculus." It is noteworthy that the statistical method of calculation implies irreversibility, whereas the strict dynamical model does not.

Maxwell's sharp-witted being was subsequently nicknamed "Maxwell's intelligent demon" by Thomson (1874), and created what Thomson called the reversibility paradox (Brush, 1986a), that is, raised the question: "How can irreversibility result from molecular motions and collisions which are themselves (according to Newton's laws of motion) reversible in time?"

2.2 Boltzmann, entropy, and disorder.

Boltzmann began his lifelong, pioneering, and creative study of the atomic theory of matter as a doctorate candidate (Brush, 1986b). He tried to explain the second law of thermodynamics, misconstrued as $dS > 0$, by using classical mechanical principles but concluded that such an explanation could not be completed without the statistical approach introduced by Maxwell. Upon adopting the statistical approach, Boltzmann made trailblazing contributions that are preeminent to date, and that include the Boltzmann equation and the H-theorem.

In 1876, Boltzmann's professor Loschmidt (Brush, 1986b) brought the reversibility paradox to the attention of Boltzmann, and he quickly converted the apparent difficulty into a new conceptual advance. He asserted that "systems tend to pass from ordered to disordered states, rather than the reverse, because the number of disordered states is so much greater than the number of ordered states ...."

This explanation suggested to Boltzmann that entropy — previously a rather mysterious quantity — should be interpreted as a measure of disorder, and the tendency toward larger values of entropy as a tendency toward greater disorder. Moreover, he defined entropy S by the relation

$$S = \mathrm{k} \log \Omega \tag{1}$$

where Ω is the number of microscopic configurations corresponding to a given macroscopic state, and k Boltzmann's constant.

2.3 Brillouin and information.

In addressing the question of entropy, Brillouin (1962) states: "Entropy is usually described as measuring the amount of disorder in a physical system. A more precise

statement is that *entropy measures the lack of information* about the actual structure of the system. This lack of information introduces the possibility of a great variety of microscopically distinct structures, which we are, in practice, unable to distinguish from one another. Since any one of these different microstructures can actually be realized at any given time, the lack of information corresponds to actual disorder in the hidden degrees of freedom."

"This picture is clearly illustrated in the case of the ideal gas. When we specify the total number n of atoms, their mass m, their degeneracy factor g, and the total energy E, we do not state the positions and velocities of each individual atom. This is the lack of information leading to the entropy. Since we do not specify the positions and velocities of the atoms, we are unable to distinguish between two different samples of the gas, when the difference consists only in different positions and velocities for the atoms. Hence we can describe the situation as one of disordered atomic motion."

Nuances in terminology notwithstanding, it is noteworthy that the information-theoretic approach is the underlying key idea of all statistical explanations of thermodynamics, in general, and the interpretations of various entropies, in particular. In view of the enormous and impressive empirical evidence about the objective reality, accurate reproducibility, and permanent impact of thermodynamic phenomena on our resources and our environment, it is amazing that so many people continue to try to understand the subject through statistical measures of ignorance. With some hindsight, such an attitude is like saying that no child will ever look like his parents because we do not know the details of the genome.

2.4 Feynmann, the laws of physics, and disorder.

In trying to understand entropy and irreversibility, Feynmann (1963) considers the mixing of white and black molecules, and comments: "Gradually the whites worm their way, by accident, across into the space of blacks, and the blacks worm their way, by accident, into the space of whites. If we wait long enough we get a mixture. Clearly, this is an irreversible process in the real world, and ought to involve an increase in the entropy."

"Here we have a simple example of an irreversible process which is completely composed of reversible events. ...So we have an irreversibility which is based on reversible situations. But we also see the *reason* now. We started with an arrangement which is, in some sense, *ordered*. Due to the chaos of the collisions, it becomes disordered."

"So far as we know all the fundamental laws of physics, like Newton's equations, are reversible. Then where does irreversibility come from? It comes from order going to

disorder, but we do not understand this until we know the origin of the order."

Though indeed all the *known* fundamental laws of physics are reversible, it is noteworthy that neither Feynmann nor almost all other scientists ever pose the legitimate question: "are the known fundamental laws of physics correct but incomplete?" In Part II, we will see that an affirmative answer to this question opens new scientific vistas that resolve the inconsistencies about general thermodynamics and broaden the realm of quantum theory.

2.5 Penrose, disorder, and lack of specificity of the definition of entropy.

Among many others, the issue of entropy and disorder is addressed by Penrose (1989). He writes: "Why is it that in the world in which we happen to live, it is the causes which actually *do* precede the effects; or to put things in another way, why do precisely coordinated particle motions occur only *after* some large-scale change in the physical state and not *before* it. In order to get a better physical description of such things, I shall need to introduce the concept of *entropy*. In rough terms, the entropy of a system is a measure of its manifest *disorder*. ...But what precisely *is* the entropy of a physical system? We have seen that it is some sort of measure of manifest disorder, but it would appear, by my use of such imprecise terms as 'manifest' and 'disorder', that the entropy concept could not really be a very clear-cut scientific quantity."

"Thus, irreversibility seems to be merely a 'practical' matter. We cannot *in practice* unscramble an egg, though it is a perfectly allowable procedure according to the laws of mechanics. Does our concept of entropy depend upon what is practical and what is not?"

"Recall ...that the physical concept of *energy*, as well as momentum and angular momentum, *can* be given precise mathematical definitions in terms of particle positions, velocities, masses, and forces. But how can we be expected to do as well for the concept of 'manifest disorder' that is needed for making the concept of entropy mathematically precise? Surely, what is 'manifest' to one observer may not be so to another."

Professor Penrose's remarks are very puzzling in view of the universal, overwhelming, and extremely important empirical evidence that cries for a rational, complete, noncircular, and unambiguous explanation. Such an explanation is discussed in Part II.

The preceding (Sections 2.1 to 2.5) are a few of the comments made by a number of eminent scientists about the statistical explanation of thermodynamics. Admittedly, the list is very short, and the comments selected. Neverthe-
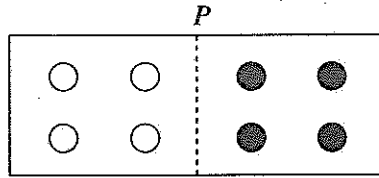
Figure 1. Configuration of four white (A) and four black (B) flashlight batteries on each side of the line P.

Figure 2. One of the configurations with three white (A) and one black (B) battery on the left of line P, and three black and one white batteries on the right side of line P.

less, these comments provide a representative sample about statistical mechanics, entropy, and disorder, and reflect the views of almost all scientists and engineers. In the next two sections, we describe two typical numerical examples which purport to quantify the meanings of entropy and disorder at the macroscopic and microscopic levels.

3 MIXING OF COLORED BATTERIES

In both scientific and popular discussions of statistical mechanics, the concept of entropy is illustrated by considering mixtures of colored balls (Denbigh, 1968). To facilitate the experimental verification of our conclusions, instead of balls we consider four flashlight batteries painted white, and four flashlight batteries painted black, and configure them in a flat container. Each white battery is denoted by A and each black by B. In one configuration, all white batteries A are to the left of the dotted line P (Fig. 1), and all black batteries B are to the right. It is clear that there is only one configuration of the type shown in Fig. 1, and therefore,

$$\Omega_{4:0} = 1 \qquad (2)$$

where $\Omega_{i:j}$ stands for the number of configurations in which there are i A batteries to the left and j to the right of P.

Next, we consider a configuration in which there is one A to the right and one B to the left of P (Fig. 2). The A battery can be placed in any one of the four right-hand sites, and the B battery in any one of the four left-hand sites. So the number of configurations

$$\Omega_{3:1} = 16 \qquad (3)$$

Continuing this kind of configuring, and calculating the number of configurations of different types we find the results listed in Table I. We see that the total number of configurations is 70, and that the most likely (36 out of 70) is the one corresponding to two A and two B on each site adjacent to P. According to Boltzmann's definition of entropy, the configuration with the most possibilities prevails,
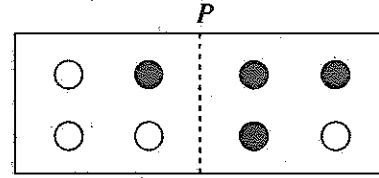
Table I

Batteries to the left of P	Batteries to the right of P	Number of configurations
$4A$	$4B$	1
$3A + B$	$A + 3B$	16
$2A + 2B$	$2A + 2B$	36
$A + 3B$	$3A + B$	16
$4B$	$4A$	1

and its entropy is

$$S_{2:2} = k \ln 36 \qquad (4)$$

Next, we examine whether the preceding results conform to empirical evidence. For given values of the energy, the volume, and the amounts of constituents of a system, a very well established and universally recognized thermodynamic experience is that the higher the value of the entropy the less the ability of the system to do work. So the question must be raised: Does $S_{2:2}$ reflect this universal empirical fact? The answer to the question is an unqualified *no*! The reason is that each battery is a system, that is, both its spatial coordinates and its probabilistic features are separable from and uncorrelated with the spatial coordinates and probabilistic features of any other battery, respectively (Gyftopoulos and Beretta, 1991a). Moreover, none of the instantaneous values of the properties of any of the batteries is affected by the volume of either the flat container or any of its sites. So no matter which configuration we consider at any instant in time, the amount of work that can be done either by each battery or by all the batteries collectively is the same for each of the 70 configurations. Because both the shape and the state of each battery are unaffected by its spatial location within the flat container, it follows that neither the value of any $S_{i:j}$ nor of $S_{2:2}$ is relevant to any

thermodynamic considerations. More precisely, none of the values of $S_{i \cdot j}$ affects the adiabatic availability (Gyftopoulos and Beretta, 1991b) of any of the batteries, individually or collectively.

This indisputable conclusion can be readily verified experimentally. All we need is 280 type A identically prepared batteries painted white, and 280 type B identically prepared batteries painted black. At any instant in time, we can create the 70 configurations listed in Table I, and check the work that each configuration can do. Upon performing the experiments, we find that the work is the same for all configurations.

If the budget permits it, we can also check the effect of entropy generated by irreversibility as a result of the spontaneous internal discharge of each battery. To this end, we arrange many groups of 70 configurations, and check the work that can be done by one or more members of each group at a different instant in time. Upon performing this experiment, we find that the work decreases and, therefore, the entropy increases spontaneously regardless of configuration because the entropy increase is due to the internal discharge of each battery and not to the configuration.

In closing, it is noteworthy that all the conclusions just cited are true for any number of colored batteries, and would continue to be valid even if the colored batteries were moving randomly within the stationary flat container, provided we consider only the electricity from each and all batteries. Said differently, here the disorder defined by Boltzmann has no effect whatsoever on the entropy of the system.

4 MIXING OF IDEAL GASES

Next, we consider the isothermal mixing of two distinguishable gases, say A consisting of n_A molecules of argon, and B consisting of n_B molecules of butane. This mixing has many similarities to the mixing of colored batteries, but also some fundamental differences.

Prior to mixing, A is in a container of volume V_A at temperature T and pressure p, and B in a container of volume V_B and at T and p. Temperature T is sufficiently high, and pressure p sufficiently low so that each gas behaves as ideal. Upon mixing, each gas occupies the same volume $V = V_A + V_B$, and the mixture is at temperature T, and has an experimentally verifiable thermodynamic entropy $S_A + S_B + S_{irr}$, where S_{irr} is the entropy of mixing generated spontaneously and given by the relation

$$S_{irr} = n_A \, k \, \ln \frac{V}{V_A} + n_B \, k \, \ln \frac{V}{V_B} \, , \qquad (5)$$

and S_i and n_i are the entropy prior to mixing and the number of molecules of gas i, respectively.

If viewed superficially, Eq. (5) may appear paradoxical compared to the results discussed in the previous section. The reason is as follows. Because the behavior of each of the gases is ideal, each gas molecule is a system, that is, both its spatial coordinates and probabilistic features are separable from and uncorrelated with the spatial coordinates and probabilistic features of any other molecule, respectively. Moreover, if we adopt the apparently innocuous classical mechanics view that each molecule can be visualized as a rigid sphere, then there would be no difference between mixing argon and butane molecules and mixing of colored batteries discussed in Section 3. And yet, in contrast to the batteries which experience no entropy of mixing, here the mixing of molecules does result in the spontaneous generation of entropy by each molecule — $k \ln(V/V_A)$ by an A molecule, and $k \ln(V/V_B)$ by a B molecule. Moreover, the entropy increase per molecule is independent of whether the number of molecules is large or small, including unity.

Some authors try to justify the entropy increase (Eq. (5)) by arguing that the larger the volume the larger the number of microstates. In view of the behavior of the mixed batteries, this argument is unconvincing because, in the case of the batteries, the results show that the entropy is independent of the volume of the flat container. Moreover, if viewed classically, the number of microstates of each molecule of the mixture is infinite both for the initial volume and for the final volume. So, which infinity is larger? It is clear that a much more rational and rigorous explanation is required. We discuss a quantum-theoretic explanation in Part II.

5 CONCLUDING REMARKS

In the preceding sections, comments by eminent scientists are cited to illustrate the widely held belief that entropy is a statistical, monotonic measure of disorder, and disorder is defined as the number of microstates that are most likely to occur in a macroscopic system. In addition, two experiments are discussed which have practically identical classical mechanical features and yet yield results contrary to the premises and predictions of statistical classical mechanics and the empirical evidence about thermodynamics.

In view of this background which is as old as the subject itself, it behooves us to ask whether the beliefs are consistent both with the correct laws and theorems of thermodynamics and the rich totality of the empirical evidence. If we take the view that thermodynamic phenomena represent a physical reality independent of the evolution of homo sapiens, then we must conclude that the empirical evidence is beyond the realm of mechanics, either classical or conventional quantum, because entropy is beyond the realm

of these two sciences. This conclusion is analogous to the approach taken regarding the geocentricity versus heliocentricity of the solar system. After many millennia, the issue was decided not solely on the basis of appearances and accuracy of numerical results but also on the basis of logical consistency and breadth of experiences.

The questions raised by the statistical interpretation of thermodynamics are discussed in Part II of this paper. They lead to the irrefutable conclusion that the beliefs are not consistent with either the correct laws and theorems of thermodynamics or the empirical evidence, and provide the motivation for a new, quantum-theoretic approach to the issue of the relation between mechanics and thermodynamics. Instead of disorder, one of the results of both the correct laws and the quantum-theoretic approach is that each thermodynamic equilibrium state represents perfect order.

REFERENCES

Brillouin, L. 1962, *Science and Information Theory*, Academic Press Inc., New York, pp. 160–161.

Brush, S.G., 1986a, *The Kind of Motion We Call Heat*, North-Holland, New York, p. 83.

Brush, S.G., 1986b, ibid., pp. 231–243.

Clausius, R., 1867, "On Different Forms of the Fundamental Equations of the Mechanical Theory of Heat and Their Convenience for Application," in the *Second Law of Thermodynamics*, ed. J. Kestin, Dowden, Hutchinson, and Ross, Inc., pp. 162–193.

Denbigh, K., 1966, *The Principles of Chemical Equilibrium*, Cambridge University Press, pp. 55–56.

Feynmann, R.P., Leighton, R.B., and Sands, M., 1963, *The Feynmann Lectures on Physics*, Addison Wesley Publishing Co., Reading, Massachusetts, pp. 46-1–46-9.

Gyftopoulos, E.P., and Beretta, G.P., 1991a, *Thermodynamics: Foundations and Applications*, Macmillan, New York, pp. 10–17, and p. 20.

Gyftopoulos, E.P., and Beretta, G.P., 1991b, ibid., Ch. 5.

Maxwell, J.C., 1871, *Theory of Heat*, Longmans, Green and Co., London, Chapter 12.

Penrose, R., 1989, *The Emperor's New Mind*, Oxford University Press, pp. 308–310.

Tolman, R.C., 1962, *The Principles of Statistical Mechanics*, Oxford University Press, pp. 16–42.