

Entropy, Order and Disorder

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Abstract: Entropy is one of the few physical properties of a system that cannot be measured directly, but must be deduced or calculated from other properties. It is also a property that has been defined in a rather abstract sense and has not been connected to another observable property or physical variable. Since its formulation as a thermodynamic property, entropy has been linked to the concepts of order, disorder and chaos in ways that are often confusing and scientifically misleading. From the point of view of engineering systems and the subject of Classical Thermodynamics, there is no obvious or even tentative connection between entropy and the "order" or "disorder" of the thermodynamic systems. This short paper gives several examples that demonstrate the disconnection between entropy and disorder in thermodynamic systems.

INTRODUCTION

In the last thirty years, entropy has been popularized in a number of best sellers and has become a concept vaguely familiar to all that consider themselves educated. Needless to say the concept of entropy means something different to all, but they like to relate it to their own experiences of "order" or "disorder." This vagueness surrounding the concept is perilous to all who try to rigorously train the students of thermodynamics on how to use the property entropy in engineering applications.

It has become increasingly popular for scientists and laymen to speak about the apparent anarchy in the world affairs and to refer to the second law of thermodynamics as the "scientific principle" that underlines changes in societies or world politics. Entropy is becoming a concept that has been loosely applied to everything: from power cycles, to the economy, from impoverished third world nations, to a "second Christian reformation" [1]. I believe, that this ambiguity associated with this thermodynamic property stems from the fact that entropy has been associated for more than 100 years with order (or disorder) in thermodynamic systems.

Thermodynamics is a very important part of the Physics and Engineering curricula and the concept of entropy is an integral part of thermodynamics. While most of the other concepts of the subject (such as temperature, density or energy) are intuitively understood, easily defined or well-known to students and professors from their experience in the laboratory, entropy is a rather intricately defined concept. The fact that it cannot be measured directly (there are no "entropy meters") adds to the perplexity for many. Often educators attempt to make this concept, which is usually defined mathematically as an integrating factor or an extensive property of systems through Clausius inequality, more comprehensible by correlating it with empirical concepts such as probability, order or disorder. While consulting on the subject several English-language Thermodynamics textbooks, widely used in the United States I encountered the following statements associated with entropy:

1. "Entropy is a quantitative measure of disorder."
2. "The property that describes randomness or uncertainty is called entropy." This would also imply that randomness is synonymous to uncertainty.
3. "Entropy is a measure of 'mixed-upness' or of the probability of a given state." This would also imply that "mixed-upness" is synonymous to the probability of a given state.
4. "Entropy is a property of matter that measures the degree of randomization or disorder."
5. "Whenever molecular chaos is produced, the ability to do useful work is reduced."

It must be emphasized, however, that in their vast majority, graduate-level textbooks stay clear from the entropy-disorder association [2,3].

It is evident that when the experts (that is the authors of specialized books) on the subject make such ambiguous statements about entropy, the non-experts (that is the students, scientists, practicing engineers or even other professors) may fall into fallacies that lead into the gross misuse of the concept. Because of this, it appears that entropy has been attempted to be used in several of the social sciences and religious studies to explain current phenomena or to predict future trends [3-6]. Of course the second law of thermodynamics, which is an inviolable law of nature, is used (and often abused) to prove the thesis of the author (whatever this may be) or to refute someone else's thesis. Invariably, these abuses stem from a very loose and ambiguous definition of entropy (and very often no definition at all) that is unrelated to the concept of the thermodynamic property entropy, which has rigorously evolved from a physical principle that is known as The Second Law of Thermodynamics.

A BRIEF HISTORICAL BACKGROUND

The origin of the second law of thermodynamics is attributed to Sadi Carnot [7] who first recognized the work-producing limitations of thermal engines and stipulated that these limitations are independent of the working fluid. It must be noted that Carnot's work, the foundation of the Second Law of Thermodynamics, was published eighteen years before the scientific formulation of the first law, as we now

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know it, by Joule. Clapeyron [8] applied Carnot's theory to the properties of substances and produced the first thermodynamic diagrams. Thomson (later Lord Kelvin) [9] expanded the theory of the limitations of heat engines and recognized that Clapeyron's geometric methods may be extended to define a temperature scale, which is independent of the properties of substances, the Thermodynamic Temperature Scale. However, it was Clausius [10,11] who concluded that the theory of the work-producing limitations of heat engines resulted in the fact that the integral:

$$\oint \frac{dQ}{T} \quad (1)$$

when taken around a cycle is always greater than zero in all practical processes. This cyclic integral may be equal to zero only in the idealized type of processes that are called "reversible processes." Clausius [11] recognized that the first statement implies the existence of a potential function or property, which he named entropy and defined *via* the following relation:

$$ds = \frac{dQ^0}{T} \quad \text{or} \quad S_2 - S_1 = \int_1^2 \frac{dQ^0}{T} \quad (2)$$

where Q^0 represents the reversible exchange of heat, that is the exchange of heat during a process composed in its entirety of equilibrium states.

It is rather unfortunate however that Clausius did not resist the temptation to apply the entropy concept to cosmology by concluding his work with the now famous statement "Die Entropie der Welt strebt einem Maximum zu," (the entropy of the world which most probably means the universe—tends to a maximum). This statement of Clausius would be correct if:

- The universe were an isolated system (this Clausius believed, because in the same paper he stated that the energy of the universe is constant) and
- It were possible to extrapolate physics based on terrestrial phenomena to the length and time macroscales of the universe.

The probabilistic connection of entropy started with the work of Boltzman [12] who in his exposition of the theory of gases remarked that the quantity:

$$H = k \ln(w), \quad (3)$$

has all the observable characteristics of entropy. In the last equation, w is the number of microscopic ways in which a given macroscopic state can be realized, subject to the constraint of a specified total energy or, in the light of quantum theory, the quantum levels in the range of energy of the system. It must be emphasized that in his original work, Boltzman never mentioned "randomness," "disorder," "chaos" or even "uncertainty" in connection to entropy. However, he is often credited (blamed might be a better word) for "proving that entropy is a measure of disorder."

In his seminal work on the equilibrium of heterogeneous substances Gibbs [13] used the Clausius definition of entropy according to equation (2). He also developed Boltzman's ideas further by introducing the concept of statistical

ensembles [14] and named the quantity w in Boltzman's equation, "the thermodynamic probability." Although Gibbs was well aware that w is different from common probabilities as used in statistics, the power of the word "probability" in this term contributed to the misunderstanding that entropy is associated with probabilities and, by extend with random events. Also in his efforts to verbally describe the concept of entropy, Gibbs on several occasions said that it is correlated to the "mixed-upness" of a system. This might have been an unfortunate choice of words, which was interpreted by some to mean "disorder." For this reason, the references to entropy as a synonym to disorder or as a quantitative measure of disorder have proliferated in the 20th century.

ENTROPY, PROBABILITIES AND DISORDER - SOME EXAMPLES

It is clear that entropy has been quantitatively defined independently of the probability theory. Even if the concept of probabilities and the associated ideas of randomness and probability distributions were never formulated, entropy would still have had a well-defined meaning as a thermodynamic property. In Boltzman's expression, w represents the number of microstates compatible with a given total energy level, a quantity that can be calculated independently of the probabilistic theory. It is rather astonishing, therefore, that entropy has been so closely associated with probabilities and randomness. What is even more surprising is that entropy has been associated so closely with the order or disorder of systems and, sometimes, of social groups and societal systems. This, because order is a subjective concept for most, while entropy is an objective one: As a subjective concept, disorder has different meanings to different persons or groups of persons, while entropy, an objectively defined concept and a quantity that is calculated from measurable properties must have the same meaning and measure to all. It is only in crystallography, where the degree of order or disorder is objectively defined and used in a scientifically appropriate way, but this is not the way the two concepts are used by most individuals and, for this reason there is a great deal of ambiguity in their use. For example, the concept of order or disorder to an anarchist is totally different from the same concept to a pastor or a policeman. On the other hand, the concept of entropy is a mathematical concept that is rigorously defined and may be calculated for any substance. It has the same meaning everywhere and, entropy differences in processes have the same numerical value to everyone who has the ability to perform the mathematical operations dictated by equation (2). Because of this, all scientists have agreed on numerical values of entropy and entropy changes for materials, which are universally acceptable. Therefore, from a purely logical point of view one must not associate the subjective concept of disorder and the objective concept of entropy in statements such as "entropy is the quantitative measure of disorder." Disorder, being a subjective concept, cannot possibly have a measure or a numerical value.

There is another reason for not associating entropy with "mixed-upness", "order" or "disorder," at least with the macroscopic systems that are treated by Classical Thermodynamics. There are physical processes where it is doubtful whether an increase of entropy results in more disorder, while in other cases clearly an entropy increase results in a more orderly thermodynamic system. Here are some exam-

ples, which may serve as food for thought for any proposed relationship between disorder and entropy:

1. Entropy is an extensive property. A simple way to increase the entropy is by including more material by changing the boundaries of the thermodynamic system. Thus, the entropy of the air in the whole classroom is twice the entropy of the air in half of the same classroom. Nobody would argue, however, that the disorder of the doubled system is greater than the disorder of the original since all the internal variables in the two systems are identical. This points out to the fact that it is not entropy *per se* that one should associate with disorder but specific entropy, the entropy per unit mass, per mole or per unit volume.

2. All associations of entropy with randomness or disorder stem from the molecular description of matter, which is essentially related to the subject of statistical mechanics or thermodynamics. A higher level of disorder is usually attributed to higher molecular velocities (e.g. in the case of an increase of temperature) or larger volume occupied by the molecules (e.g. in an isothermal expansion of a gas). When one looks at the system from the macroscopic point of view of Classical Thermodynamics it is very difficult to associate entropy changes with increased disorder. There is no apparent reason to associate increased disorder to the isothermal expansion of a macroscopic system or to the isobaric heating of it. In many other cases, an entropy increase of a macroscopic system may be even associated to a decrease of entropy. For example, consider a system that is composed of several subsystems, separated by adiabatic walls. Some of these subsystems are cold, (C) and some hot, (H) as shown in the first part of Fig. (1). When the adiabatic wall constraint is removed, heat is exchanged between the subsystems, which eventually reach an intermediate temperature and are classified as warm (W). According to thermodynamic theory, an irreversible process has occurred and the entropy of the second state is higher than that of the first. However, a glance at Fig. (1), which gives a schematic representation of the system in its two states proves that the second state is certainly more uniform and its schematic appears to be more "orderly." Similar diagrammatic representations of macroscopic systems undergoing processes, looked upon from the classical thermodynamics point of view, fail to reveal an increase in the disorder of the system when the entropy increases. For this reason, it is difficult in the context of classical thermodynamics to even make a correlation between the concepts of entropy and disorder.

3. One may consider a rather classical experiment, which is similar to Joule's experiment: A mass of gas is enclosed in part A, one of the two identical halves of an adiabatic container. The second half B is empty. When a hole in the partition opens, gas from A enters B until the pressures in the two parts are equal. For an ideal gas undergoing this irreversible process the specific entropy increases by an amount,

$$s_2 - s_1 = R \ln(2), \quad (4)$$

| | | | |
|---|---|---|---|
| H | C | H | H |
| C | H | H | C |
| C | C | H | C |
| C | H | C | H |

State 1: Adiabatic partitions between hot and cold subsystems of a thermodynamic system.

| | | | |
|---|---|---|---|
| W | W | W | W |
| W | W | W | W |
| W | W | W | W |
| W | W | W | W |

State 2: Adiabatic partitions are removed and subsystems reach thermal equilibrium. The entropy of the system has increased, that is, $S_2 > S_1$.

Fig. (1). Which system has higher "disorder?"

where R is the gas constant. One may also argue on qualitative grounds that the "order" of the gas molecules has decreased in the system, or that the "disorder" has increased because the gas molecules have more space to move. In this case, the concept of disorder is closely associated to the amount of space the gas molecules have in their disposal. The association of entropy and disorder was developed from qualitative analogies as in the above example. One can see, however, that the analogy is very superficial and is based on a loose definition of disorder as analogous to the space occupied by the molecules. If one then keeps the total volume constant and, by a heat transfer process, decreases the temperature of the gas, would the disorder increase, decrease or remain the same. Clearly, the entropy would decrease.

4. In a similar way with example 3 it is often contended that, when the molecules of a given gas move faster in a closed system, e.g. because of heat addition, then the disorder in the gas increases. In this case, disorder is analogous to the velocities of the gas molecules, while in the previous example disorder is analogous to space occupied. In the same case, thermodynamics predicts also an increase in the entropy of the gas. However, how can one explain in terms of disorder the fact that the entropy of 1 mole of Argon at 25 °C is 154 J/K, while the entropy of 1 mole of Helium at the same temperature is 127 J/K? The massive molecules of Argon move more slowly than the smaller and much faster molecules of Helium. It is obvious here that a logical relationship between entropy and disorder is difficult to establish on the quantitative grounds of the average velocity of the molecules.

5. There is another classical example of a system consisting of two identical solid masses, one at thermodynamic temperature T_1 and the other at T_2 . The two solids are allowed to interact until thermal equilib-

rium is reached and they both are at the average temperature $(T_1 + T_2)/2$. There is a specific entropy increase associated with the process:

$$s_2 - s_1 = c \ln\{(T_1 + T_2)^2/4T_1T_2\}, \quad (5)$$

where c is the specific heat of the solid material. However, in this case one cannot associate an increase of disorder for the system with the process of equalization of temperatures. If anything, the macroscopic system at the second state seems more orderly than at the first state, because the temperature of the two parts is more uniform. One of course may argue that the molecules of the originally colder solid are moving faster in the second state than in the first state and the molecules of the originally hotter solid are moving slower. The net result of the redistribution of velocities may be an increase of disorder. This argument, however, is subject to debate because there is not a generally accepted relationship between distributions of molecular velocities (or amplitudes of vibration) and disorder. Both contentions that the disorder of the system has increased during the process and that the disorder has decreased seem to be equally plausible, depending on what a person calls "disorder." Those who use similar arguments to justify the relationship between disorder and entropy seem to define disorder in terms of entropy.

6. Consideration of systems originally in a metastable state (supercooled steam, supersaturated solutions, chemical reactions etc.) provides a multitude of examples where the final state appears more orderly, although there is an irreversible process and, hence, an increase of entropy. Let us consider a supersaturated solution of a solid with negative heat of solution ($\Delta H < 0$ and $\Delta S < 0$) such as sodium trisulfate in water. Initially, all the mass of the solid is dissolved in water. The solution is placed in an adiabatic container, precipitation of the solid is caused (e. g. by dropping a small crystal of the solid substance) and separation of the two phases. The process is irreversible and therefore $\delta S > 0$. Also since the process took place in an adiabatic container, there is no change of the total energy. Thus, we have for every small step this process:

$$\delta \tilde{H} C_p \delta T - \Delta H \delta n = 0, \quad (6)$$

and

$$\delta \tilde{S} C_p \delta T/T - \Delta S \delta n > 0, \quad (7)$$

where C_p is the specific heat of the solution and δn the amount of solids that precipitated. Equation (6) yields that $\delta T < 0$, because $\Delta H < 0$. Thus, we have the interesting result that the temperature of the solution dropped, while some of the solute precipitated to form a more "orderly" phase, while the entropy of the system increased.

In the above thought experiment we see that in the final state, the molecules of the solution move slower as a result of the decrease in temperature and, in addition, crystals of the solid (which is the most "orderly" of the phases) appeared, having precipitated from the solution. Although there is an entropy increase, the system achieved a more "orderly" state, an observation which defies the notion that changes in entropy are accompanied by disorder changes of the same sign. Of course, one could argue here that in the initial state of the system, the solute particles are very much ordered so as to be more ordered than in the solid itself. An argument

like this, however, contrary to all intuitive concepts of "order" aims at explaining more "order" in terms of entropy rather than entropy in terms of "order".

7. The second law of Thermodynamics may be looked upon as the tendency of natural processes that occur in isolated systems to "flatten gradients" or, eventually to "destroy gradients," or, by extend to "remove all existing recognizable structure" on the way to reaching equilibrium with a resultant increase in entropy. Thus, when cold, white milk is added to a hot, black cup of coffee, it is natural for the temperature and concentration gradients in the cup to level off and disappear in time. This "gradient destroying" or "structure removing" tendency of natural systems leads to lost opportunities to produce work and this is what real, irreversible processes do. Therefore, "loss of gradients" or "removal of structure" may be associated with the increase in entropy and lost opportunities to produce work. While, the "destruction of gradients" or the "removal of structure" from an isolated system may be somehow linked to the intuitive concept of "disorder" in the system, there is no strict mathematical correlation or correspondence between the first two concepts and the last (disorder).
8. One should mention the study of Prigogine and Stengers [13] who calculated the quantity H , which Boltzman [10] identified with entropy. They did their calculations with a Gibbsian ensemble using the phase space instead of the energy levels. The result was that the quantity H remains constant with time. After a discussion on the ambiguity of the ideas of order and disorder they concluded that their results prove that "there is no change of order whatsoever in the frame of dynamic theory." Prigogine and Stengers [13] continue that from the theory of mechanics and dynamics (on which statistical thermodynamics is based) one can never make conclusions about changes in order, regardless of how the concept of order is conceived or defined.
9. Finally, one may address the notion of certain "scientific historians" or anthropologists who will claim that the human society (and the same applies to politics and religions) is continuously becoming more disorderly because it obeys an inviolable scientific principle, namely the Second Law of Thermodynamics. Despite all the calamities of the modern humans, our society is more orderly and civilized than that of two centuries ago and certainly by far more orderly than the society of the Middle Ages. The world may not be ideal but thermodynamics and entropy should not be blamed for it.

ACKNOWLEDGEMENTS

The author is indebted to a reviewer who pointed out the concept of the removal of recognizable structures and resulted in the comment (7), above.

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Received: January 23, 2008

Revised: March 03, 2008

Accepted: March 03, 2008