An Overview of the Physical Concept of Entropy

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Abstract

It is often envisaged that science progresses in a linear, sequential fashion that leads to developments in technology. In reality, though, the history of science has numerous examples to the contrary. For example, various technological developments in the 18th century culminated in an efficient steam engine, which utilised heat to perform mechanical work, the driving force of the Industrial Revolution. A side effect of this economically and socially transforming development was that the steam engine stimulated scientific questions about the conduction of heat and the behaviour of materials, especially gases, under changing temperatures and pressures, bringing these queries to the forefront of science in the 19th century.

The crowning achievement of these scientific endeavours was the formulation of the laws of thermodynamics. While these purely phenomenological laws did not depend on any fundamental comprehension of the nature of heat, which was still contentious at the time, they certainly necessitated such an understanding. What was the origin of these laws, and how were they related to other fundamental laws of nature? The second law of thermodynamics was particularly puzzling because it proposed a mysterious new quantity called entropy, and, for the first time, introduced an arrow of time into physics. In order to understand thermal energy, then, it was clearly necessary to comprehend exactly what is entropy and what it entails.

Arriving at a universally accepted definition and explanation of entropy was not quite so straightforward, however. Indeed, it – and the second law itself - has been accorded various interpretations by different eminent scientists since its formulation. The aim of this paper is to shed light on these historical interpretations and their corollaries.

Key words: Boltzmann; Clausius; disorder; dispersion; entropy; information; Kelvin; thermodynamics

“[Classical thermodynamics] is the only physical theory of universal content which I am convinced will never be overthrown.” Albert Einstein, 1949

1. Introduction

On 7 May 1959, the scientist and novelist C.P. Snow gave a public lecture at the Senate House, University of Cambridge, entitled The Two Cultures and the Scientific Revolution (Snow 1959). Snow’s argument was simple, but challenging: “I believe the intellectual life of the whole of western society is increasingly being split into two polar groups. ... Literary intellectuals at one pole - at the other scientists, and as the most representative, the physical scientists. Between the two a gulf of mutual incomprehension - sometimes (particularly among the young) hostility and dislike, but most of all lack of understanding. They have a curious distorted image of each other.”

The lecture achieved more fame (or infamy) than it perhaps merited, in large part because of the vehement ad hominem insults hurled on Snow by the literary critic F. R. Leavis (see Collini 2007, 2013; Leavis 1962;
Ortolano 2009; Tallis 1995; Trilling 1962). Leaving aside the legitimacy or otherwise of Snow’s principal argument, that culture had split into two camps and that the education system was perpetuating this situation, he pronounced in the lecture:

A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative. Yet I was asking something which is about the scientific equivalent of: Have you read a work of Shakespeare’s?

Snow later remarked in the lecture:

I now believe that if I had asked an even simpler question - such as, What do you mean by mass, or acceleration, which is the scientific equivalent of saying, Can you read? - not more than one in ten of the highly educated would have felt that I was speaking the same language. So the great edifice of modern physics goes up, and the majority of the cleverest people in the western world have about as much insight into it as their neolithic ancestors would have had.

The roots of this rift between the natural sciences and the humanities go back much further, however - to the 19th century, and an earlier disagreement between a scientist and a literary critic.¹ This was the celebrated debate between Matthew Arnold and Thomas Huxley in the early 1880s (see Roos 1977) on whether science was as valid an intellectual training as the classical education of literae humaniores and deserved a more prominent place in the university curriculum. Similarly, there was the even earlier protracted exchange between the Victorian polymaths John Stuart Mill and William Whewell on the nature and philosophy of science, moral philosophy, economics, politics and social reform (see Snyder 2006, 2012).

If we take Snow’s assertion about the second law of thermodynamics at face value, perhaps one of the reasons why it seems perplexing is because it introduces the concept of entropy.² Unlike pressure, temperature or energy, entropy is not intuitive.³ Nor is entropy defined unambiguously. The reason for this may be historical, and the fact that it – and the second law itself - has been accorded various interpretations by scientists since its formulation in the 19th century.

From its inception, the meaning and the value of the second law of thermodynamics were matters of controversy (see Kragh and Weininger 1996). Thus, for example, the Czech chemist František Wald (1861-1930), said that, while the first law, or the principle of conservation of energy, was “perfectly natural and self-evident”, effectively a “postulate of reason”, the second law was an anomaly (Wald 1889). There was

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¹ The word ‘scientist’ was coined by William Whewell in 1833; before this time, the general terms in use were ‘natural philosopher’ and ‘man of science’.

² Entropy is the thermodynamic property of a system introduced by the second law. There are four laws of thermodynamics: the zeroth, first, second and third laws (the zeroth law was an afterthought, introduced in the early 20th century, when the first and second laws had become so firmly established that there was no hope of going back and renumbering them). The first three laws introduce a thermodynamic function of a system: the temperature, T, springs from the zeroth law; the internal energy, U, appears in the first law; and entropy, S, emerges from the second law. We can think of U as a measure of the quantity of energy that a system possesses, and S as a measure of the quality of that energy: low entropy means high quality; high entropy means low quality.

³ As Mansfield and O’Sullivan (2011: 258) point out, rather circuitously: “Entropy [is] a somewhat abstract concept ... It is not possible to provide a concrete physical meaning for entropy as a macroscopic concept but a feeling for the role of the concept in thermodynamic processes can be developed ... from studying situations which involve entropy”.
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no clear, intuitive interpretation for entropy, its central conceptual parameter, and no satisfying physical explanation for the necessary increase of entropy in natural processes. For most chemists, Wald (1889) wrote, entropy was a “mathematical ghost”, and the second law itself was a “blank mathematical formula”, which was difficult for even sophisticated students of nature to understand.

Wald was by no means alone in this opinion. Many physical scientists found the meaning of the second law to be obscure and the concept of entropy to be opaque. Arguably, one of the reasons for this is that, although the second law is ‘phenomenologically valid’ (Shankar 2014), it is not a ‘fundamental law’ (Barrow 2014) in the sense that the universal law of gravitation is, for example. According to one interpretation, it tells us that, without external intervention, things will tend to become more disordered – that is, entropy increases – in a closed system (Darrow 1944): This is a reflection of probability. There are so many more ways for things to become disordered as time passes than for them to become ordered that we tend to observe disorder increasing, unless something intervenes to reduce it. Thus, the second law does not lay down an ironclad rule that the entropy of a closed system could never decrease; it merely states that the probability for it to do so is extremely low (Newton 2009).

The aim of this paper is to overview the different interpretations of entropy, which persist to the present day, and the second law, generally, about which “uneasy feelings ... have been around for a long time”, and on which “controversies about deeper meanings remain” (Kimball 2015: 85-86).

2. The Second Law of Thermodynamics

Thermodynamics - a word coined in 1854 by William Thomson (later Lord Kelvin, 1824-1907), from the Greek therme (heat) and dynamis (power) - “was born from the collision of two existing nineteenth-century physical theories” (Kuhn 1962: 67). It emerged in the earliest days of the Industrial Revolution, when the steam engine and other technologies were drawing attention to phenomena related to heat, about which little was known at the time. Although heat appeared to be a force – it can be put to work – its operations could not be explained by Newtonian mechanics. A theory of heat was clearly needed, and one duly appeared in the second half of the eighteenth century, formulated by the French chemist Antoine Lavoisier (1743-1794). This ‘caloric theory’ conceived heat to be an invisible and weightless fluid (caloric) and understood it to be a force. Two insights into the nature of heat eventually emerged, however, from experiments and observations – but they appeared to contradict each other.

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4 For example, all fundamental processes are reversible because one can imagine reversing their direction of change without violating a law of physics. On the other hand, all actual thermodynamic processes are irreversible. Thermodynamic processes, in practice, always proceed in one direction.
5 Entropy is often identified as a measure of disorder: if matter and energy are distributed in a disordered way, as in a gas, then the entropy is high; if the energy and matter are stored in an ordered manner, as in a crystal, then the entropy is low.
6 As Carroll (2008: 50) explains this rarity: “[T]here are more ways to arrange a given number of atoms into a high-entropy configuration than a low-entropy one”.
8 William Thomson (Lord Kelvin) asserted that, “the steam engine has done much more for science than science has done for the steam engine”, meaning that it was the work done on the development of the steam engine that led to the formulation of the laws of thermodynamics. On the development of the steam engine, see Derry and Williams (1961), chapter 11; or Rosen (2010).
9 We now know that heat is not a fluid or some such entity. In everyday language, heat is both a noun and a verb. Heat flows; we heat. The noun ’heat’ refers to the energy absorbed or dissipated by heating or cooling. Heat is a mode of transfer of energy. Heat is the transfer of energy by virtue of a temperature difference between a system and its surroundings. Heat is the name of a process, not the name of an entity. Energy is transferred as heat (that is, as the result of a temperature difference).
The first insight was that of Sadi Carnot (1796-1832), a military engineer in Paris, who was investigating how to improve the efficiency of the steam engine (see Bynum 2012). In 1824, Carnot derived a series of plausible conclusions on steam engines from the assumption that heat is a *caloric*, which does work as it passes from a higher to a lower temperature reservoir.10 Carnot found that the limiting efficiency of a heat engine depends only on the temperatures between which the engine operates, and not on the substance that is used in the engine. The most efficient engine is modelled by an ideal cycle (the Carnot cycle) of expansion and contraction in which the engine works reversibly, the *caloric* being conserved in going back and forth between the two temperature endpoints with no heat diverted to friction or dissipation.

The second insight appeared to James Joule (1818-1889), who, while working in his family’s brewery in Manchester, performed a series of ingenious experiments and managed to obtain highly accurate measurements of various conversions of heat and electrical, mechanical and chemical energy into one another. Joule was the first person to determine the mechanical equivalent of heat: the amount of mechanical work required to produce a unit of heat. His work promoted the idea of the conversion of energy, and set off a battle between proponents of conversion and conservation.

The conflict between *conservation* (Carnot’s approach) and *conversion* (Joule’s approach) came to a head in the 1840s. Physicists were in a quandary during this “period of pronounced professional insecurity” (Kuhn 1962: 68); did the use of the heat-force involve conservation or conversion of heat: does the total amount of heat remain the same, or does heat get converted into something else? A way through the impasse was offered by two seminal figures, each of whom considered the notion of change, and in particular the transformation of heat into work, from a new perspective.

The German physicist Rudolf Clausius (1822-1888) reflected on the flow of heat between bodies of different temperatures, and was the first, in 1850, to identify a version of the second law of thermodynamics. He argued that the conflict between Carnot and Joule was only apparent, and that, in reality, two principles are involved (Clausius 1850). One involves the *conservation of something* (not heat, and later called energy) in exchanges of heat and mechanical work; the other involves the *conversion* of heat into energy, and the property that heat cannot flow spontaneously from a colder body to a hotter one, with the rest of the universe remaining unchanged.11 Thus, Clausius elevated normal observations about heating and cooling to the status of a general physical law: a cooler object never heats a hotter object.

The other influential figure was the British physicist William Thomson (Lord Kelvin), who ruminated on the essential structure of the steam engine, and, in 1851, formulated a distinct version of the second law. Kelvin’s approach concerns the operation of a heat engine, a device that uses a temperature difference to produce work. In abstract form, a heat engine comprises three elements: a hot source of energy; a device – a piston or turbine – for converting heat into work; and a cold sink, a reservoir for discarding any unused energy as heat. The last of these, the cold sink, is not always readily discernable, for it might just be the immediate environment of the engine, not something specifically designed. While others considered the heat source as the crucial component, or perhaps the piston, Kelvin identified the invisible as indispensable, and saw the cold sink as essential. He realised that to remove the surroundings would stop the heat engine. Kelvin’s statement of the second law of thermodynamics is that some heat in every engine “is irrevocably lost to man, and therefore ‘wasted’ although not annihilated” (Thompson 1910: 288).

10 In 1824 Carnot published Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance (Reflections on the Motive Power of Heat) – the first theoretical explanation of the thermodynamics of steam power. In this treatise, Carnot stated that steam engines “seem destined to produce a great revolution in the civilized world”, but that “their theory is very little understood”. The book includes the notion of conservation, reversibility and the ‘Carnot cycle’. It was largely ignored, however, and Carnot published nothing further.

11 In thermodynamics, the word ‘spontaneous’ means not needing to be driven by doing work of some kind. Broadly speaking, ‘spontaneous’ is a synonym of ‘natural’. Unlike in everyday language, spontaneous in thermodynamics has no connotation of speed: it does not mean fast. Instead, it refers to the *tendency* for a change to occur.
The statements by Clausius (that heat does not flow spontaneously from a cooler to a hotter body) and Kelvin (that a cold sink is essential to the operation of a heat engine) are both laws of nature based on exhaustive observations. They refer to different phenomenon, but they are logically equivalent, and one can treat either as a phenomenological statement of the second law of thermodynamics. The version one prefers is a matter of taste and convenience. If one wants a second law in the language of natural phenomena, one adopts Clausius’s statement. If one wants a second law in the language of technology, one adopts Kelvin’s.

It was not until several years later that Clausius (1865) introduced a more concise and analytical formulation of the second law. In doing so, he coined the word ‘entropy’ for what he had been calling “the transformational content of the body” to describe the tendency of the energy transfer process to occur spontaneously. Entropy is a state function denoted by the letter $S$. Etymologically, the name is from the Greek *entropia* (a turning toward), and the letter $S$ appears to be arbitrary. In choosing the word entropy, Clausius wrote:

I prefer going to the ancient languages for the names of important scientific quantities, so that they mean the same thing in all living tongues. I propose, accordingly, to call $S$ the entropy of a body, after the Greek word “transformation.” I have designedly coined the word entropy to be similar to energy, for these two quantities are so analogous in their physical significance, that an analogy of denominations seems to me helpful.

But, as Cooper (1968) remarked on this appellation:

By doing that, rather than extracting a name from the body of the current language (say: lost heat), he succeeded in coining a word that meant the same thing to everybody: *nothing*.

In effect, two fundamental quantities, internal energy and entropy, are defined by the first two laws of thermodynamics. The internal energy $U$ is a function of the state of the system whose differential is given by the equation expressing the first law:

$$dU = dQ + dW$$

where $dQ$ and $dW$ are, respectively, the heat added to the system and the external work on the system in an infinitesimal process. For a simple fluid, the work is given by:

$$dW = -p\,dV$$

where $p$ is the pressure on the system and $V$ is the volume. The entropy $S$ is that state function whose differential is given by:

$$dS \geq \frac{dQ}{T}$$

A state function means that when the thermodynamic state is defined – for example, by giving the temperature and pressure – the entropy of the state is also defined.

The letter $S$ was not used at the time for other thermodynamic properties; it was an unused neighbour of $P$, $Q$, $R$, $T$, $U$ and $W$, all of which had already been ascribed to other physical quantities.

Quoted in Cooper (1968).
where $T$ is the absolute temperature. The equality holds for reversible processes, and the inequality of irreversible ones.

The significance of the concept of entropy was not evident to Clausius’s contemporaries when he introduced it in 1865. Indeed, even Clausius did not view entropy as the basic concept for understanding the second law. He preferred to express the physical meaning of that law in terms of the concept of ‘disgregation’, another word that he coined, which he interpreted in molecular and mechanical terms (Clausius 1862; see Klein 1969). Clausius restricted his use of entropy to the role of a summarising concept. In the memoir in which it was introduced, he kept the traditional thermodynamic concepts, heat and work, at the centre of his thinking and derived the experimentally useful consequences of the two laws without using the entropy function.

Clausius (1867) summarised the first and second laws of thermodynamics with the brief but portentous statement: “The energy of the universe is constant; the entropy of the universe tends toward a maximum”. The latter clause is expressed as $S \geq 0$ and it marked the first time that an inequality appeared in physics (later examples included Heisenberg’s Uncertainty Principle, and the limiting speed of light). This introduced an overall direction to time: the so-called ‘arrow of time’. It is difficult to overstate the impact of this on physics. Up until this work, the legacy of Newton’s clockwork mechanics was that the universe was cyclical and might continue forever in the same form. The arrow of time implied that a process that increased the entropy of an isolated system could not be reversed, since decreasing the entropy was forbidden.

The accepted laws of physics show no such asymmetry, each direction in time, forward and backward, is treated by the laws without distinction, and that’s the origin of a huge puzzle.15

3. Macroscopic Formulation of the Second Law

The most general formulation and interpretation of the second law was that enunciated by Clausius. He observed that there are many processes that occur spontaneously in nature and always in one direction, e.g., the expansion of a gas in a vessel; the mixing of two different gases; and the heat transfer from a hot to a colder body. These are quite different processes but they have one thing in common: they always proceed in one direction, never proceeding spontaneously in the reverse direction. But it is far from clear that all of these processes are governed by the same law of nature.

Clausius realised the common principle, however, and postulated that there is only one law that governs these disparate processes. Even before formulating the second law, Clausius’s postulate was an outstanding achievement considering the fact that none of these processes was understood at the time on a molecular level.

Clausius started from one particular process: the spontaneous flow of heat from a hot to a cold body. Based on this specific process, Clausius conceived of the new quantity that he called entropy, the change in which was defined as:

$$dS \geq \frac{dQ}{T}$$

Clausius’s extraordinary accomplishment was the generalisation from one spontaneous process to any spontaneous process; and the realisation that there is some quantity that determines the direction of the unfolding events - a quantity that always changes in one direction in a spontaneous process.

With this new concept of entropy, one could proclaim the general formulation of the second law: in 15 Greene (2004).
any spontaneous process occurring in an isolated system, the entropy never decreases. This formulation embraces many processes and sowed the seeds of the mystery associated with entropy, a quantity that does not subscribe to a conservation law. How can a quantity (entropy) increase indefinitely and why? Johann Loschmidt (1821-1895) asked this question in 1876. We still have no fully satisfactory answer. That many reversible fundamental processes do not necessarily compose a reversible thermodynamic process is known as Loschmidt’s paradox or the reversibility paradox.16 Our failure to resolve this paradox suggests that the laws governing the interactions of fundamental particles do not form a complete picture of nature and need to be supplemented with additional physics equivalent to the second law. It is not surprising, then, that the second law and entropy have been shrouded in mystery.17

4. Microscopic Formulation of the Second Law

Towards the end of the 19th century, the atomistic theory of matter became firmly established. The kinetic theory of heat, developed by James Clerk Maxwell (1831-1879), Ludwig Boltzmann (1844-1906) and others, was based on the assumption of the existence of atoms and molecules, and had successfully explained the concepts of pressure, temperature and heat. Heat was interpreted in terms of the energies of an ensemble of individual molecules. Under this interpretation, the first law of thermodynamics was simply an extension of the principle of conservation of energy, which now embraced thermal energy. The kinetic theory of heat could not, however, explain entropy and the second law of thermodynamics.

A huge stride towards understanding entropy and the second law was made possible following Boltzmann’s statistical interpretation of entropy in terms of the total number of microstates of a system, consisting of a huge number of particles (see Cercignani 1998).

The traditional thermodynamic quantities, such as temperature and pressure, refer to large-scale average properties of a gas. The fine structure, however, consists of huge numbers of molecules moving around and colliding with one another. The same large-scale state can arise from innumerable different small-scale states, because minor differences on the small scale average out. Boltzmann, therefore, distinguished macrostates and microstates of the system: large-scale averages and the actual state of the molecules. Using this, he showed that entropy, a macrostate, could be interpreted as a statistical feature of microstates, as expressed in the equation:

\[ S = k \log W \]

Here, S is the entropy of the system; W is the number of distinct microstates that can give rise to the overall macrostate; and k is a constant, known as the Boltzmann constant, whose value is 1.38 x 10⁻²³ joules per kelvin.18

It is this formula that motivates the interpretation of entropy as disorder (Boltzmann 1896). The idea is that fewer microstates correspond to an ordered macrostate than to a disordered one. We can understand why this is by considering a pack of playing cards. For simplicity, assume we have just six cards, marked 2, 3, 4, J, Q and K. If we put them in two separate piles, with the low-value cards in one pile and the court cards in

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16 Loschmidt’s paradox: All thermodynamic systems are composed of fundamental particles, all thermodynamic processes are composed of the interactions of fundamental particles, and all interactions of fundamental particles are reversible; but all non-idealised thermodynamic processes are irreversible.

17 Hawking (1988) distinguished between a “psychological direction of time” and the “thermodynamic arrow of time; the direction of time in which disorder or entropy increases.”

18 Energy is expressed in joules (J). 1J = 1kgm²s⁻². We could think of 1J as the energy of a 2kg ball travelling at 1ms⁻¹. Each pulse of the human heart expends about 1J of energy.
the other, we have an ordered arrangement. In fact, it retains traces of order if we shuffle each pile, but keep the piles separate, because however we do this, the low-value cards are all in one pile and the court cards are in the other. If, however, we shuffle both piles together, the two types of cards can become mixed, with arrangements like 4QK2J3. Intuitively, these mixed-up arrangements are more disordered.

How does this relate to Boltzmann’s formula? There are 36 ways to arrange the cards in their two piles: six for each pile. But there are 720 ways (6!) to arrange all six cards in order. The type of ordering of the cards that we allow – two piles or one – is analogous to the macrostate of a thermodynamic system. The exact order is the microstate. The more ordered macrostate has 36 microstates; the less ordered one has 720. So the more microstates there are, the less ordered the corresponding macrostate becomes. Since logarithms get bigger when the numbers do, the greater the logarithm of the number of microstates, the more disordered the macrostate becomes. Here,

\[ \log 36 = 3.58 \quad \log 720 = 6.58 \]

These are effectively the entropies of the two macrostates. Boltzmann’s constant just scales the values to fit the thermodynamic formulism when dealing with gases.

The two piles of cards are like two non-interacting thermodynamic states, such as a container with a partition separating two gases. Their individual entropies are each \( \log 6 \), so the total entropy is \( 2 \log 6 \), which equals \( \log 36 \). So the logarithm makes entropy additive for non-interacting systems: to obtain the entropy of the combined (but not yet interacting) system, add the separate entropies. If we now let the systems interact (remove the partition), the entropy increases to \( \log 720 \).

The more cards there are, the more pronounced this effect becomes. Assume that we split a standard pack of 52 playing cards into two piles, with all the red cards in one pile and all the black cards in the other. This arrangement can occur in \((26!)^2\) ways, which is about \(1.62 \times 10^{53}\). Shuffling both piles together we get \(52!\) microstates, or approximately \(8.07 \times 10^{67}\). The logarithms are 122.52 and 156.36, respectively, and, again, the second is larger.

Boltzmann’s formulation of the second law drew criticism from many of his contemporaries, who objected to the seeming conflict between the so-called time reversal or time symmetry of the Newtonian equations of motion and the time asymmetry of the behaviour of Boltzmann’s entropy. This conflict between the reversibility of the molecular motion and the irreversibility implied in the second law was a profound one, and could not be resolved. How can one derive a quantity that distinguishes between the past and future (i.e., always increasing with time), from equations of motion that are indifferent to the past and the future?

Boltzmann’s response to the reversibility objection was that the second law holds most of the time, but in very rare cases it can go the other way, i.e., entropy might decrease with time. This was untenable. The (macroscopic) second law of thermodynamics, like any other law of physics, was conceived and proclaimed as being absolute. No one had ever observed a violation of the second law. Boltzmann, however, insisted that the second law is statistical; entropy does increase most of the time, but not all the time.

5. Interpretations of Entropy

We have referred to entropy as a measure, in some sense, of the disorder of a system. For example, if we consider the case of the isothermal expansion of a gas, its molecules and their constant energy are distributed over a greater volume; the system is correspondingly less ordered in the sense that we have less chance of predicting successfully where a particular molecule and its energy will be found; and the entropy increases correspondingly.

Disorder, however, is only one of several quite different interpretations of entropy that has been proposed in the history of thermodynamics. Ever since Clausius introduced the concept, people have endeavoured to find
a qualitative meaning for entropy. Many explanations of entropy begin with a description of what happens in a spontaneous process (e.g., expansion) and then observe that a particular descriptive term – disorder, say – correlates with the change in entropy. From these correlations, one can assume, incorrectly, that the descriptor also describes entropy. This practice is prevalent, and together with the variety of interpretations, might account for some of the mystery and confusion surrounding entropy and the second law, and help to explain the indifferent and reticent response encountered by Snow (1959).

a) Disorder

The most popular description of entropy, and perhaps the oldest metaphor that has endured for the longest time, is disorder. Boltzmann was probably the first person to associate entropy with disorder (Unordnung), according to Kozliak and Lambert (2005), as seen from the following remarks by Boltzmann (1896):

... the initial state of the system ... must be distinguished by a special property (ordered or improbable) ...  
... this system takes in the course of time, states ... which one calls disordered.  
Since by far most of the states of the system are disordered, one calls the latter the probable states.  
... the system ... when left to itself, it rapidly proceeds to the disordered, most probable state.

However, it appears that Boltzmann (1896) did not equate entropy with disorder, as many people infer, but used disorder to describe what occurs “when (a system) is left to itself”; namely, that “it rapidly proceeds to the disordered, most probable state.” It is also notable that when Boltzmann (1896) describes what occurs in a spontaneous process, he uses the term “probable” state. This role of probability in driving the process might account for the idea that entropy is a measure of disorder.

Later scientists have also interpreted entropy in terms of the amount of disorder of a system. In the following account, Richard Feynman, a famous Nobel laureate, sets the scene in by considering the space inside a closed jar containing a gas:

So we now have to talk about what we mean by disorder and what we mean by order. ... Suppose we divide the space into little volume elements. If we have black and white molecules, how many ways could we distribute them among the volume elements so that white is on one side and black is on the other? On the other hand, how many ways could we distribute them with no restriction on which goes where? Clearly, there are many more ways to arrange them in the latter case. We measure “disorder” by the number of ways that the insides can be arranged, so that from the outside it looks the same. The logarithm of that number of ways is the entropy. The number of ways in the separated case is less, so the entropy is less, or the “disorder” is less.19

More formally, this is stating that each arrangement of molecules defines a unique microstate. If we swap the positions of two black molecules then the container looks the same from the outside, so both of these different microstates give rise to the same appearance or macrostate. Each macrostate is consistent with many equally probably microstates. So, macrostates with many microstates are more probable than macrostates with few microstates.

More recent accounts of thermodynamics also refer to entropy as a measure of disorder:

We shall identify entropy with disorder.  
With disorder in mind, we shall explore the implications of Clausius’s expression and verify that it is

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19 Feynman et al. (1964).
plausible in capturing the entropy as a measure of the disorder in a system.\textsuperscript{20}

More entropy means more disordered particles. This law ... established that disorder - entropy - increases over time.\textsuperscript{21}

Despite the fact that disorder is not a well-defined concept, it has prevailed in scientific literature as metaphor for entropy for over one hundred years. Seemingly, the need to visualise and explain entropy has compelled people to adhere to whatever metaphor seems qualitatively plausible.

b) Accessibility/Dispersion/Spreading

The notion that entropy is a measure of disorder is pervasive, but it is viewed as misleading by several authors who have objections to the old ‘doctrine of disorder’ (see Grandy 2008). Denbigh and Denbigh (1985: 43-44) refer to the disorder doctrine as “the prevailing mythology”, and infer that entropy cannot be interpreted in a reliable and comprehensive manner as increase of disorder. These and other scholars instead describe entropy as a measure of energy dispersion or spread.

The use of spread or dispersion as a descriptor of entropy was probably first suggested by Guggenheim (1949). He started with the Boltzmann definition of entropy in the form:

\[ S(E) = k \log \Omega(E) \]

where \( k \) is a constant and “\( \Omega(E) \) denotes the number of accessible independent quantum states of energy \( E \) for a closed system.” This is the correct definition of \( \Omega \).\textsuperscript{22} Subsequently, Guggenheim (1949) discusses the process of heat flow, in which an increase in entropy represents “an increase in the number of accessible states, more briefly an increase of accessibility or spread.” While the first part of this sentence is correct (i.e., the change in entropy in the spontaneous process of heat flow represents an increase in the number of accessible states), the second part - “increase of accessibility or spread” – is an incomplete, but acceptable, description of the change in \( \Omega \). However, elsewhere in the same paper, Guggenheim (1949) makes a further shortening of the description of \( \Omega \) as follows:

To the question what in one word does entropy really mean, the author would have no hesitation in replying ‘Accessibility’ or ‘Spread.’ When this picture of entropy is adopted, all mystery concerning the increasing property of entropy vanishes. The question whether, how and to what extent the entropy of a system can decrease finds an immediate answer.

Guggenheim (1949) does not, however, define either accessibility or spread; he merely uses these terms to describe the “number of accessible quantum states of energy E for a closed system”, i.e., the quantity \( \Omega \) as it appears in the Boltzmann formula for entropy. Nor does he offer a proof of the contention that the meaning of entropy is either accessibility or spread.

Nevertheless, the terms spread and dispersion appear as descriptors of entropy in several more recent

\textsuperscript{20} Atkins (2007).
\textsuperscript{21} Greene (2011).
\textsuperscript{22} In other words, if there is no ambiguity in a system’s status, then only one state is available to it, that is, \( \Omega = 1 \), and, thus, the entropy is zero.
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works, most notably by Lambert (1996, 2002a,b, 2006, 2007), where they are lauded as a modern view of entropy to replace disorder, and helpful pedagogically for university students:

“Entropy is disorder” is an archaic, misleading definition of entropy dating from the late 19th century before knowledge of molecular behaviour, of quantum mechanics and molecular energy levels, or of the Third Law of thermodynamics. It seriously misleads beginning students, partly because “disorder” is a common word, partly because it has no scientific meaning in terms of energy or energy dispersal.23 Entropy change measures the dispersal of energy in a process: how much is spread out or how widely spread out that energy becomes. 24

Defining entropy change as a change from order to disorder is misleading at best and incorrect at worst. Although Boltzmann described it this way in 1898, he did so innocently in the sense that he had never calculated the numerical values of W... 25

Finally, Leff (1996, 2007) assigns properties of entropy to the idea of a spreading function, and suggested that the symbol S used for entropy should be viewed as shorthand for spreading.

c) Information

The earliest association between information and entropy was probably that of Lewis (1930).

In the simplest case, if we have one molecule which must be in one of two flasks, the entropy becomes less by $k\ln 2$, if we know which is the flask in which the molecule is trapped. Gain in entropy always means loss of information and nothing more.

In the second quotation, Lewis (1930) is using the term information in its colloquial meaning; when a gas expands we have a sense of losing some locational information. In this sense, information is a qualitative descriptor of the state of the system, rather than a quantitative description of entropy.

In an influential paper, Shannon (1948) used entropy as the term to describe information in his mathematical treatise on information theory (Shannon and Weaver, 1949), an idea prompted by an allegedly facetious suggestion from John von Neumann (1903-1957):26

You should call it entropy for two reasons: first, the function is already in use in thermodynamics under the same name; second, and more importantly, most people don’t know what entropy really is, and if you use the word entropy in an argument you will win every time.

Shannon’s information entropy is a measure of information, whereas thermodynamic entropy is a measure of the number of states a physical system (such as gas in a container) can adopt. These two different conceptualisations of entropy do not seem to be obviously related. However, thermodynamic entropy can be derived from Shannon’s measure of information; and the relationship between them matters because thermodynamic entropy can be used to measure the energy costs of Shannon’s information entropy.

Jaynes (1957a,b) and later Katz (1967) also identified entropy with information when deriving the fundamental distributions of statistical mechanics. Jaynes (1957a), for example, notes:

23 Lambert (2002a).
24 Lambert (2002b).
26 Tribus and McIrvine (1971).
Henceforth, we will consider the terms ‘entropy’ and ‘uncertainty’ as synonyms. The thermodynamic entropy is identical with information theory – entropy of the probability distribution except for the presence of Boltzmann’s constant.

Later, Gell-Mann (1994) suggested that entropy can be regarded as “a measure of ignorance”, seeing this term as a synonym for “measure of lack of information”:

Entropy and information are very closely related. In fact, entropy can be regarded as a measure of ignorance. When it is known only that a system is in a given macrostate, the entropy of the macrostate measures degree of ignorance about which the microstate is in, by counting the number of bits of additional information needed to specify it, with all the microstates in the microstate treated as equally probable.

This is analogous to the account by Greene (2011:251) of entropy as measuring “hidden information” - the “gap in information” between the data obtained from the macroscopic features of a system and the unknown data on a system’s particular microscopic arrangement:

Entropy measures the additional information hidden within the microscopic details of the system, which, should you have access to it, would distinguish the configuration at a micro level from all the macro look-alikes.

Denbigh (1981), however, took a different view and criticised the ‘informational’ interpretation of entropy, arguing that, if accepted, it leads us to the conclusion that entropy is an anthropomorphic concept.

d) Freedom

Nordholm (1997) suggested that freedom is a “fair translation of the concept of ‘entropy’ from thermodynamics of inanimate matter to thermodynamics of human life.” Styer (2000) also suggested the simile “entropy as freedom”, arguing that as “freedom” means a range of possible actions, “entropy” means a range of possible microstates.

The interpretation of freedom with entropy illustrates that it is easy to identify a concept, which in some sense happens to behave similarly to entropy, and conclude erroneously that it is the same as entropy.

6. Conclusion

As outlined above, the second law of thermodynamics has been quoted as the sine qua non of scientific enlightenment, rather as Shakespeare might be quoted to represent the arts or humanities. While the position of Shakespeare in our culture might be secure, the position of the second law of thermodynamics is perhaps less assured, as evidenced by the supercilious response of learned society to Snow’s (1959) question. This is lamentable because the exaltation of the second law is not unreasonable, as expressed by Eddington (1928: 74):

The law that entropy always increases – the second law of thermodynamics - holds, I think, the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations – then so much the worse for Maxwell’s equations. If it is
found to be contradicted by observation – well, these experimentalists do bungle things sometimes. But if your theory is found to be against the second law of thermodynamics I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Despite Snow’s (1959) rather jaundiced view of his peers in the humanities, one can understand their reticent response if we consider the many different interpretations of entropy – which still provoke debate to this day - and, indeed, the various depictions of the second law itself, the earliest of which were Clausius’s version, in terms of heat reservoirs, and Kelvin’s version, concerning the operation of a heat engine.

Snow (1963) later modified his position and acknowledged that the original motivating assumption of “dichotomous parsing of intellectual life into contrarian literary and scientific camps” was not a true representation, and that he had failed to recognise a third culture – one that combines aspects of the scientific and literary camps - in the continuous spectrum of intellectual life (see Kimball 1994). He also understood that education – or a more enlightened approach to it - was the route to this third culture, concluding as follows (Snow 1963):

The division of our culture is making us more obtuse than we need be: we can repair communications to some extent: but, as I have said before, we are not going to turn out men and women who understand as much of our world as Piero della Francesca did of his, or Pascal, or Goethe. With good fortune, however, we can educate a large proportion of our better minds so that they are not ignorant of imaginative experience, both in the arts and in science, nor ignorant neither of the endowments of applied science, of the remediable suffering of most of their fellow humans, and of the responsibilities which, once they are seen, cannot be denied.

This idea of a third culture, which attempts to combine and synthesise knowledge from the humanities and the natural sciences, has been advanced in a number of other works, too (e.g., Brockman 1995; Gould 2003; Wilson 1998). Nowadays, both camps of the two cultures are being challenged and shaped as never before by powerful exigencies: pressures on university autonomy and public funding; threats to academic freedom and integrity; increasing bureaucracy and centralisation; encroaching corporate mentality and the influence of business; ideology-driven research and compromised ethics.

In such an environment, it may be judicious to attempt to bridge the gap between the two cultures in order to improve intellectual discourse. On this point, Atkins (2007: 49) refers to the second law of thermodynamics in the following effusive terms, and sees it, not as some mark of division between the two cultures referred to by Snow (1959), but as that which underpins and unites the two cultures:

The second law is of central importance in the whole of science, and hence in our rational understanding of the universe, because it provides a foundation for understanding why any change occurs. Thus, not only is it a basis for understanding why engines run and chemical reactions occur, but it is also a foundation for understanding those most exquisite consequences of chemical reactions, the acts of literary, artistic, and musical creativity that enhance our culture.
References


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Chemical Educator, 10: 24-25.