

## Preface

Ever since I heard the word “entropy” for the first time, I was fascinated with its mysterious nature. I vividly recall my first encounter with entropy and with the Second Law of Thermodynamics. It was more than forty years ago. I remember the hall, the lecturer, even the place where I sat; in the first row, facing the podium where the lecturer stood.

The lecturer was explaining Carnot’s cycle, the efficiency of heat engines, the various formulations of the Second Law and finally introducing the intriguing and mysterious quantity, named *Entropy*. I was puzzled and bewildered. Until that moment, the lecturer had been discussing concepts that were familiar to us; heat, work, energy and temperature. Suddenly, a completely new word, never heard before and carrying a completely new concept, was being introduced. I waited patiently to ask something, though I was not sure what the question would be. What is this thing called entropy and why does it always increase? Is it something we can see, touch or feel with any of our senses? Upon finishing her exposition, the lecturer interjected, “If you do not understand the Second Law, do not be discouraged. You are in good company. You will not be able to understand it at this stage, but you will understand it when you study statistical thermodynamics next year.” With these concluding

remarks, she had freed herself from any further explanation of the Second Law. The atmosphere was charged with mystery. I, as well as some of those present during the lecture were left tongue-tied, our intense craving for understanding the Second Law unsatisfied.

Years later, I realized that the lecturer was right in claiming that statistical mechanics harbors the clues to the understanding of entropy, and that without statistical mechanics, there is no way one can understand what lies beneath the concept of entropy and the Second Law. However, at that time, we all suspected that the lecturer had chosen an elegant way of avoiding any embarrassing questions she could not answer. We therefore accepted her advice, albeit grudgingly.

That year, we were trained to *calculate* the entropy changes in many processes, from ideal gas expansion, to mixing of gases, to transfer of heat from a hot to a cold body, and many other spontaneous processes. We honed our skills in *calculations* of entropy changes, but we did not really capture the essence of the meaning of entropy. We did the calculations with professional dexterity, pretending that entropy is just another technical quantity, but deep inside we felt that entropy was left ensconced in a thick air of mystery.

What is that thing called entropy? We knew it was *defined* in terms of heat transferred (reversibly) divided by the absolute temperature, but it was neither heat nor temperature. Why is it always increasing, what fuel does it use to propel itself upwards? We were used to conservation laws, laws that are conceived as more “natural.” Matter or energy cannot be produced out of nothing but entropy seems to defy our common sense. How can a physical quantity inexorably keep “producing” more of itself without any apparent feeding source?

I recall hearing in one of the lectures in physical chemistry, that the entropy of solvation of argon in water is large

and negative.<sup>1</sup> The reason given was that argon *increases* the *structure* of water. Increase of *structure* was tantamount to increase of order. Entropy was loosely associated with disorder. Hence, that was supposed to explain the *decrease* of entropy. In that class, our lecturer explained that entropy of a system *can* decrease when that system is coupled with another system (like a thermostat) and that the law of ever-increasing entropy is only valid in an isolated system — a system that does not interact with its surroundings. That fact only deepened the mystery. Not only do we not know the *source* which supplies the fuel for the ever-increasing entropy, but no source is permitted, in principle, no feeding mechanism and no provision for any supplies of anything from the outside. Besides, how is it that “structure” and “order” have crept into the discussion of entropy, a concept that was *defined* in terms of *heat* and *temperature*?

A year later, we were taught statistical mechanics and along side we learnt the relationship between entropy and the number of states, the famous Boltzmann relationship which is carved on Ludwig Boltzmann’s tombstone in Vienna.<sup>2</sup> Boltzmann’s relationship provided an interpretation of entropy in terms of disorder; the ever-increasing entropy, being interpreted as nature’s way of proceeding from order to disorder. But why should a system go from order to disorder? Order and disorder are intangible concepts, whereas entropy was *defined* in terms of heat and temperature. The mystery of the perpetual increment of disorder in the system did not resolve the mystery of entropy.

I taught thermodynamics and statistical mechanics for many years. During those years, I came to realize that the mystery associated with the Second Law can never be removed within classical thermodynamics (better referred to as the

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<sup>1</sup>This was another fascinating topic that was eventually chosen for my PhD thesis.

<sup>2</sup>A picture is shown on the dedication page of this book.

non-atomistic formulation of the Second Law; see Chapter 1). On the other hand, looking at the Second Law from the molecular point of view, I realized that there was no mystery at all.

I believe that the turning point in my own understanding of entropy, hence also in my ability to explain it to my students came when I was writing an article on the entropy of mixing and the entropy of assimilation. It was only then that I felt I could penetrate the haze enveloping entropy and the Second Law. It dawned on me (during writing that article) how two key features of the atomic theory of matter were crucial in dispersing the last remains of the clouds hovering above entropy; the large (unimaginably large) numbers and the indistinguishability of the particles constituting matter.

Once the haze dissipated, everything became crystal clear. Not only clear, but in fact obvious; entropy's behavior which was once quite difficult to understand, was reduced to a simple matter of common sense.

Moreover, I suddenly realized that one *does not* need to know any statistical mechanics to understand the Second Law. This might sound contradictory, having just claimed that statistical mechanics harbors the clues to understanding the Second Law. What I discovered was that, *all* one needs is the *atomistic formulation* of entropy, and nothing more from statistical mechanics. This finding formed a compelling motivation for writing this book which is addressed to anyone who has never heard of statistical mechanics.

While writing this book, I asked myself several times at exactly what point in time I decided that this book was worth writing. I think there were three such points.

First, was the recognition of the crucial and the indispensable facts that matter is composed of a huge number of particles, and that these particles are indistinguishable from each other. These facts have been well-known and well-recognized for almost a

century, but it seems to me that they were not well emphasized by authors who wrote on the Second Law.

The second point was while I was reading the two books by Brian Greene.<sup>3</sup> In discussing the entropy and the Second Law, Greene wrote<sup>4</sup>:

*“Among the features of common experience that have resisted complete explanation is one that taps into the deepest unresolved mysteries in modern physics.”*

I could not believe that Greene, who has explained so brilliantly and in simple words so many difficult concepts in modern physics, could write these words.

The third point has more to do with aesthetics than substance. After all, I have been teaching statistical thermodynamics and the Second Law for many years, and even using dice games to illustrate what goes on in spontaneous processes. However, I always found the correspondence between the dice changing faces, and the particles rushing to occupy all the accessible space in an expansion process, logically and perhaps aesthetically unsatisfactory. As you shall see in Chapter 7, I made the correspondence between dice and particles, and between the outcomes of tossing dice and the *locations* of the particles. This correspondence is correct. You can always name a particle in a right compartment as an R-particle and a particle in the left compartment as an L-particle. However, it was only when I was writing the article on the entropy of mixing and entropy of assimilation, that I “discovered” a different process for which this correspondence could be made more “natural” and more satisfying. The process referred to is deassimilation. It is a spontaneous process where the change in entropy is due solely to

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<sup>3</sup>Greene, B. (1999, 2004).

<sup>4</sup>Greene, B. (2004), p. 12.

the particles acquiring new identity. The correspondence was now between a die and a particle, and between the *identity* of the outcome of throwing a die, and the *identity* of the particle. I found this correspondence more aesthetically gratifying, thus making the correspondence between the dice-game and the real process of deassimilation a perfect one and worth publishing.

In this book, I have deliberately avoided a technical style of writing. Instead of teaching you what entropy is, how it changes, and most importantly why it changes in one direction, I will simply guide you so that you can “*discover*” the Second Law and obtain the satisfaction of unveiling the mystery surrounding entropy for yourself.

Most of the time, we shall be engaged in playing, or imagining playing, simple games with dice. Starting with one die, then two dice, then ten, a hundred or a thousand, you will be building up your skills in analyzing what goes on. You will find out what is that thing that changes with time (or with the number of steps in each game), and how and why it changes. By the time you get to a large number of dice, you will be able to extrapolate with ease whatever you have learned from a small number of dice, to a system of a huge number of dice.

After experiencing the workings of the Second Law in the dice world, and achieving full understanding of what goes on, there is one last step that I shall help you with in Chapter 7. There, we shall *translate* everything we have learned from the dice world into the real experimental world. Once you have grasped the evolution of the dice games, you will be able to understand the Second Law of thermodynamics.

I have written this book having in mind a reader who knows nothing of science and mathematics. The only prerequisite for reading this book is plain common sense, and a strong will to apply it.

One caveat before you go on reading the book; “common sense” does not mean easy or effortless reading!

There are two “skills” that you have to develop. The first is to train yourself to think in terms of big numbers, fantastically big numbers, inconceivably big numbers and beyond. I will help you with that in Chapter 2. The second is a little more subtle. You have to learn how to distinguish between a *specific* event (or state or configuration) and a *dim* event (or a state or configuration). Do not be intimidated by these technical sounding terms.<sup>5</sup> You will have ample examples to familiarize yourself with them. They are indispensable for understanding the Second Law. If you have any doubts about your ability to understand this book, I will suggest that you take a simple test.

Go directly to the end of Chapter 2 (Sections 2.7 and 2.8). There, you shall find two quizzes. They are specifically designed to test your understanding of the concepts of “specific” and “dim.”

If you answer all the questions correctly, then I can assure you that you will understand the entire book easily.

If you cannot answer the questions, or if you tried but got wrong answers, do not be discouraged. Look at my answers to these questions. If you feel comfortable with my answers even though you could not answer the questions yourself, I believe you can read and understand the book, but you will need a little more effort.

If you do not know the answers to the questions, and even after reading my answers, you feel lost, I still do not think that understanding the book is beyond your capacity. I would suggest that you read Chapter 2 carefully and train yourself in thinking

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<sup>5</sup>In statistical mechanics, these terms correspond to microstates and macrostates. In most of the book, we shall be playing with dice; and dice are always macroscopic. That is why I chose the terms “specific” and “dim” instead.

*probabilistically*. If you need more help, you are welcome to write to me and I promise to do my best to help.

Again, do not feel intimidated by the word “probabilistically.” If you are not surprised that you did not win the one million prize in the lottery, although you habitually buy tickets, you have been thinking “probabilistically.” Let me tell you a little story to make you comfortable with this formidable sounding word.

My father used to buy one lottery ticket every weekend for almost sixty years. He was sure that someone “up there” favored him and would bestow upon him the grand prize. I repeatedly tried to explain to him that his chances of winning the grand prize were very slim, in fact, less than one hundredth of one percent. But all my attempts to explain to him his odds fell on deaf ears. Sometimes he would get seven or eight matching numbers (out of ten; ten matches being the winning combination). He would scornfully criticize me for not being able to see the clear and unequivocal “signs” he was receiving from Him. He was sure he was on the right track to winning. From week to week, his hopes would wax and wane according to the number of matches he got, or better yet, according to the kind of signs he believed he was receiving from Him. Close to his demise, at the age of 96, he told me that he was very much disappointed and bitter as he felt betrayed and disfavored by the deity in whom he had believed all his life. I was saddened to realize that he did not, and perhaps could not, think *probabilistically*!

If you have never heard of the Second Law, or of entropy, you can read the brief, non-mathematical description of various formulations and manifestations of the Second Law in Chapter 1. In Chapter 2, I have presented some basic elements of probability and information theory that you might need in order to express your findings in probabilistic terms. You should realize that the fundamentals of both probability and information



theory are based on nothing more than sheer common sense. You need not have any background in mathematics, physics or chemistry. The only things you need to know are: how to count (mathematics!), that matter is composed of atoms and molecules (physics and chemistry!), and that atoms are indistinguishable, (this is advanced physics!). All these are explained in non-mathematical terms in Chapter 2. From Chapters 3–5, we shall be playing games with a varying number of dice. You watch what goes on, and make your conclusions. We shall have plenty of occasions to “experience” the Second Law with all of our five senses. This reflects in a miniscule way the immense variety of manifestations of the Second Law in the real physical world. In Chapter 6, we shall summarize our findings. We shall do that in terms that will be easy to translate into the language of a real experiment. Chapter 7 is devoted to describing two simple experiments involving increase in entropy; all you have to do is to make the correspondence between the number of dice, and the number of particles in a box, between different outcomes of tossing a die, and the different states of the particles. Once you have made this correspondence, you can easily implement all that you have learned from the dice-game to understand the Second Law in the real world.

By the time you finish reading Chapter 7, you will understand what entropy is and how and why it behaves in an apparently capricious way. You will see that there is no mystery at all in its behavior; it simply follows the rules of common sense.

By understanding the two specific processes discussed in Chapter 7, you will clearly see how the Second Law works. Of course, there are many more processes that are “driven” by the Second Law. It is not always a simple, straightforward matter to show how the Second Law works in these processes. For this, you need to know some mathematics. There are many more, very complex processes where we *believe* that the Second

Law has its say, but there is, as yet, no mathematical proof of how it does that. Biological processes are far too complicated for a systematic molecular analysis. Although I am well aware that many authors do use the Second Law in conjunction with various aspects of life, I believe that at this stage, it is utterly premature. I fully agree with Morowitz<sup>6</sup> who wrote: “*The use of thermodynamics in biology has a long history of confusion.*”

In the last chapter, I have added some personal reflections and speculations. These are by no means universally accepted views and you are welcome to criticize whatever I say there. My email address is given below.

My overall objective in writing this book is to help you answer two questions that are associated with the Second Law. One is: *What* is entropy? The second is: *Why* does it change in only one direction — in apparent defiance of the time-symmetry of other laws of physics?

The second question is the more important one. It is the heart and core of the mystery associated with the Second Law. I hope to convince you that:

1. The Second Law is *basically* a law of probability.
2. The laws of probability are *basically* the laws of common sense.
3. It follows from (1) and (2) that the Second Law is *basically* a law of common sense — nothing more.

I admit, of course, that statements (1) and (2) have been stated many times by many authors. The first is implied in Boltzmann’s formulation of the Second Law. The second has been expressed by Laplace, one of the founders of probability theory. Certainly, I cannot claim to be the first to make these statements. Perhaps I can claim that the relationship of

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<sup>6</sup>Morowitz (1992) page 69.

“basicity” is a transitive relationship, i.e., that statement (3) follows from (1) and (2), is original.

The first question is about the *meaning* of entropy. For almost a hundred years, scientists speculated on this question. Entropy was interpreted as measuring disorder, mixed-upness, disorganization, chaos, uncertainty, ignorance, missing information and more. To the best of my knowledge, the debate is still on going. Even in recent books, important scientists express diametrically opposing views. In Chapter 8, I will spell out in details my views on this question. Here I will briefly comment that entropy can be made *identical*, both formally and conceptually, with a specific measure of information. This is a far from universally accepted view. The gist of the difficulty in accepting this identity is that entropy is a physically measurable quantity having units of energy divided by temperature and is therefore an *objective* quantity. Information however, is viewed as a nebulous dimensionless quantity expressing some kind of human attribute such as knowledge, ignorance or uncertainty, hence, a highly *subjective* quantity.<sup>7</sup>

In spite of the apparent irreconcilability between an objective and a subjective entity, I claim that entropy *is* information. Whether either one of these is objective or subjective is a question that encroaches on philosophy or metaphysics. My view is that both are objective quantities. But if you think one is subjective, you will have to concede that the second must be subjective too.

There is trade-off in order to achieve this identity. We need to redefine temperature in units of energy. This will require the sacrifice of the Boltzmann constant, which should have been *expunged* from the vocabulary of physics. It will bring a few other benefits to statistical mechanics. For the purpose of this

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<sup>7</sup>More on this aspect of entropy may be found in Ben-Naim (2007).

book, absence of the Boltzmann constant will automatically make entropy dimensionless *and* identical with a measure information. This will, once and for all, “exorcise” the mystery out of entropy!

To the reader of this book, I dare to promise the following:

1. If you have ever learned about entropy and been mystified by it, I promise to unmystify you.
2. If you have never heard and never been mystified by entropy, I promise you immunity from any future mystification.
3. If you are somewhere in between the two, someone who has heard, but never learned, about entropy, if you heard people talking about the deep mystery surrounding entropy, then I promise you that by reading this book, you *should* be puzzled and mystified! Not by entropy, not by the Second Law, but by the whole ballyhoo about the “mystery” of entropy!
4. Finally, if you read this book carefully and diligently and do the small assignments scattered throughout the book, you will feel the joy of discovering and understanding something which has eluded understanding for many years. You should also feel a deep sense of satisfaction in understanding “*one of the deepest, unsolved mysteries in modern physics.*”<sup>8</sup>

## Acknowledgements

I want to express my sincerest thanks and appreciation to all those who were willing to read either parts, or the whole manuscript and offered comments and criticism.

I would like first of all to thank my friends and colleagues, Azriel Levy and Andres Santos for their meticulous reading and checking of the entire manuscript. They have saved me from

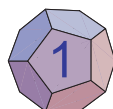
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<sup>8</sup>Greene, B. (2004).

what could have been embarrassing errors I did not, or could not detect. Thanks are also due to Shalom Baer, Jacob Bekenstein, Art Henn, Jeffrey Gordon, Ken Harris, Marco Pretti, Samuel Sattath and Nico van der Vegt, who read parts of the manuscript and sent me valuable comments. Finally, I would like to express my sincere thanks to my lifetime partner Ruby for her patience in struggling with my messy handwriting and correcting and re-correcting the manuscript. Without her gracious help this manuscript could not have seen the light of publication. The book's planning had a long period of incubation. The actual writing of the book began in Burgos, Spain and it was completed in La Jolla, California, USA.

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P.S. Just in case you wonder about the meaning of the little figures at the end of each chapter, let me tell you that since I undertook the responsibility of explaining to you the Second Law, I decided to do a little espionage on your progress. I placed these icons so that I can monitor your progress in grasping the Second Law. You are welcome to compare your state of understanding with my assessment. If you do not agree, let me know and I will do my best to help.



## Introduction, and a Short History of the Second Law of Thermodynamics

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In this chapter, I shall present some important milestones in the history of the Second Law of Thermodynamics. I shall also present a few formulations of the Second Law in a descriptive manner. In doing so, I necessarily sacrifice precision. The important point here is not to teach you the Second Law, but to give you a qualitative description of the types of phenomena which led the scientists of the nineteenth century to formulate the Second Law.

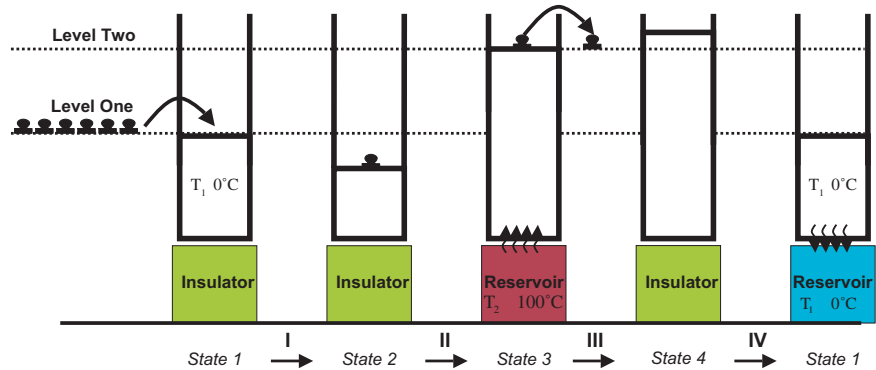
There are many formulations of the Second Law of Thermodynamics. We shall group all these into two conceptually different classes: Non-Atomistic and Atomistic.

### 1.1. The *Non-Atomistic* Formulation of the Second Law<sup>1</sup>

Traditionally, the birth of the Second Law is associated with the name Sadi Carnot (1796–1832). Although Carnot himself did

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<sup>1</sup>By “non-atomistic” formulation, I mean the discussion of the Second Law without any reference to the atomic constituency of matter. Sometimes, it is also said that this formulation views matter as a continuum. The important point to stress here is that these formulations use only macroscopically observable or measurable quantities without any reference to the atomic constituency of matter. It *does not* imply that the formulation applies to non-atomistic or continuous matter. As we shall see later, were matter really non-atomistic or continuous, the Second Law would not have existed.

2 *Entropy Demystified*

**Fig. (1.1)** Heat engine.

not formulate the Second Law,<sup>2</sup> his work laid the foundations on which the Second Law was formulated a few years later by Clausius and Kelvin.

Carnot was interested in heat engines, more specifically, in the efficiency of heat engines. Let me describe the simplest of such an engine (Fig. (1.1)). Suppose you have a vessel of volume  $V$  containing any fluid, a gas or a liquid. The upper part of the vessel is sealed by a movable piston. This system is referred to as a heat engine. The vessel is initially in State 1, thermally insulated, and has a temperature  $T_1$ , say  $0^\circ\text{C}$ . In the first step of the operation of this engine (Step I), we place a weight on the piston. The gas will be compressed somewhat. The new state is State 2. Next, we attach the vessel to a heat reservoir (Step II). The heat reservoir is simply a very large body at a constant temperature, say  $T_2 = 100^\circ\text{C}$ . When the vessel is attached to the heat reservoir, thermal energy will flow from the heat reservoir to the engine. For simplicity, we assume that the heat reservoir is immense compared with the size of the system or the engine. In Fig. (1.1), the heat reservoir is shown only at the bottom of the engine. Actually it should surround the entire engine. This

<sup>2</sup>This is the majority opinion. Some authors do refer to Carnot as the “inventor” or the “discoverer” of the Second Law.

ensures that after equilibrium is reached, the system will have the same temperature,  $T_2$ , as that of the reservoir, and though the reservoir has “lost” some energy, its temperature will be nearly unchanged. As the gas (or the liquid) in the engine heats up, it expands, thereby pushing the movable piston upwards. At this step, the engine did some useful work: lifting a weight placed on the piston from level one to a higher level, two. The new state is State 3. Up to this point, the engine has absorbed some quantity of energy in the form of heat that was transferred from the reservoir to the gas, thereby enabling the engine to do some work by lifting the weight (which in turn could rotate the wheels of a train, or produce electricity, etc.). Removing the weight, Step III, might cause a further expansion of the gas. The final state is State 4.

If we want to convert this device into an engine that repeatedly does useful work, like lifting weights (from level one to level two), we need to operate it in a complete cycle. To do this, we need to bring the system back to its initial state, i.e., cool the engine to its initial temperature  $T_1$ . This can be achieved by attaching the vessel to a heat reservoir or to a thermostat, at temperature  $T_1 = 0^\circ\text{C}$ , Step IV (again, we assume that the heat reservoir is much larger compared with our system such that its temperature is nearly unaffected while it is attached to the engine). The engine will cool to its initial temperature  $T_1$ , and if we take away the weight, we shall return to the initial state and the cycle can start again.

This is not the so-called Carnot cycle. Nevertheless, it has all the elements of a heat engine, doing work by operating between the two temperatures,  $T_1$  and  $T_2$ .

The net effect of the repeated cycles is that heat, or thermal energy, is pumped into the engine from a body at a high temperature  $T_2 = 100^\circ\text{C}$ ; work is done by lifting a weight and another amount of thermal energy is pumped out from the engine into a body at lower temperature  $T_1 = 0^\circ\text{C}$ . The Carnot



cycle is different in some details. The most important difference is that all the processes are done very gradually and very slowly.<sup>3</sup> We shall not be interested in these details here.

Carnot was interested in the *efficiency* of such an engine operating between two temperatures under some ideal conditions (e.g. mass-less piston, no friction, no heat loss, etc.).

At the time of the publication of Carnot's work in 1824,<sup>4</sup> it was believed that heat is a kind of fluid referred to as *caloric*. Carnot was mainly interested in the limits on the efficiency of heat engines. He found out that the limiting efficiency depends only on the ratio of the temperatures between which the engine operates, and not on the substance (i.e., which gas or liquid) that is used in the engine. Later, it was shown that the efficiency of Carnot's idealized engine could not be surpassed by any other engine. This laid the cornerstone for the formulation of the Second Law and paved the way for the appearance of the new term "entropy."

It was William Thomson (1824–1907), later known as Lord Kelvin, who first formulated the Second Law of Thermodynamics. Basically, Kelvin's formulation states that there could be no engine, which when operating in cycles, the *sole* effect of which is pumping energy from one reservoir of heat and completely converting it into work.

Although such an engine would not have contradicted the First Law of Thermodynamics (the law of conservation of the total energy), it did impose a limitation on the amount of work that can be done by operating an engine between two heat reservoirs at different temperatures.

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<sup>3</sup>Technically, the processes are said to be carried out in a quasi-static manner. Sometimes, this is also referred to as a reversible process. The latter term is, however, also used for another type of process where entropy does not change. Therefore, the term quasi-static process is more appropriate and preferable.

<sup>4</sup>"Reflections on the motive power of fire and on machines fitted to develop this power," by Sadi Carnot (1824).

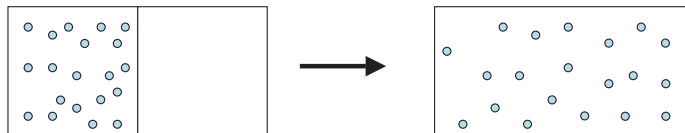
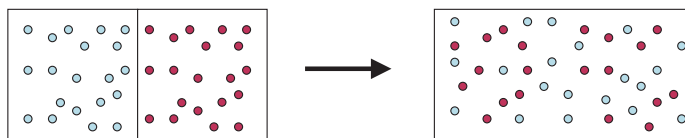
In simple terms, recognizing that heat is a form of energy, the Second Law of Thermodynamics is a statement that it is impossible to convert heat (thermal energy) completely into work (though the other way is possible, i.e., work can be converted completely into heat, for example, stirring of a fluid by a magnetic stirrer, or mechanically turning a wheel in a fluid). This impossibility is sometimes stated as “a perpetual motion of the second kind is impossible.” If such a “perpetual motion” was possible, one could use the huge reservoir of thermal energy of the oceans to propel a ship, leaving a tail of slightly cooler water behind it. Unfortunately, this is impossible.

Another formulation of the Second Law of Thermodynamics was later given by Rudolf Clausius (1822–1888). Basically, Clausius’ formulation is what every one of us has observed; heat always flows from a body at a high temperature (hence is cooled) to a body at a lower temperature (which is heated up). We never observe the reverse of this process occurring spontaneously. Clausius’ formulation states that no process exists, such that its net effect is only the transfer of heat from a cold to a hot body. Of course we can achieve this direction of heat flow by doing work on the fluid (which is how refrigeration is achieved). What Clausius claimed was that the process of heat transferred from a hot to a cold body when brought in contact, which we observe to occur spontaneously, can never be observed in the reverse direction. This is shown schematically in Fig. (1.2), where two bodies initially isolated are brought into thermal contact.

While the two formulations of Kelvin and Clausius are different, they are in fact equivalent. This is not immediately apparent.



**Fig. (1.2)**

6 *Entropy Demystified***Fig. (1.3)****Fig. (1.4)**

However, a simple argument can be employed to prove their equivalency, as any elementary textbook of thermodynamics will show.

There are many other formulations or manifestations of the Second Law of Thermodynamics. For instance, a gas in a confined volume  $V$ , if allowed to expand by removing the partition, will always proceed in one direction (Fig. (1.3)).<sup>5</sup> The gas will expand to fill the entire new volume, say  $2V$ . We never see a spontaneous reversal of this process, i.e., gas occupying volume  $2V$  will never spontaneously converge to occupy a smaller volume, say  $V$ .

There are more processes which all of us are familiar with, which proceed in one way, never in the reverse direction, such as the processes depicted in Figs. (1.2), (1.3), (1.4) and (1.5). Heat flows from a high to a low temperature; material flows from a high to a low concentration; two gases mix spontaneously; and a small amount of colored ink dropped into a glass of water will spontaneously mix with the liquid until the water

<sup>5</sup>The Second Law may also be formulated in terms of the spontaneous expansion of a gas. It can also be shown that this, as well as other formulations, is equivalent to the Clausius and Kelvin formulations.

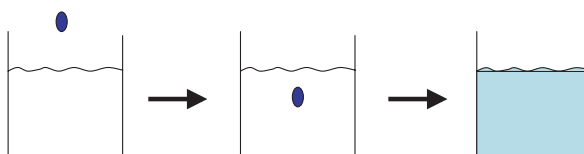


Fig. (1.5)

is homogeneously colored (Fig. (1.5)). We never see the reverse of these processes.

All these processes have one thing in common. They proceed in one direction, never proceeding *spontaneously* in the reverse direction. But it is far from clear that all these processes are driven by a common law of nature. It was Clausius who saw the general principle that is common in all these processes. Recall that Clausius' formulation of the Second Law is nothing but a statement of what everyone of us is familiar with. The greatness of Clausius' achievement was his outstanding prescience that all of these spontaneous processes are governed by one law, and that there is one quantity that governs the direction of the unfolding of events, a quantity that always changes in one direction in a spontaneous process. This was likened to a one-way arrow or a vector that is directed in one direction along the time axis. Clausius introduced the new term *entropy*. In choosing the word "entropy," Clausius wrote:<sup>6</sup>

*"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*

<sup>6</sup>Quoted by Cooper (1968).

*analogous in their physical significance, that an analogy of denominations seems to me helpful.”*

In the Merriam-Webster Collegiate Dictionary (2003), “entropy” is defined as: “change, literary turn, a measure of the unavailable energy in a closed thermodynamic system... a measure of the system’s degree of order...”

As we shall be discussing in Chapter 8, the term *entropy* in the sense that was meant by Clausius is an inadequate term. However, at the time it was coined, the molecular meaning of entropy was not known nor understood. In fact, as we shall see later, “entropy” is not *the* “transformation” (nor the “change” nor the “turn”). It is something else that *transforms* or *changes* or *evolves* in time.

With the new concept of entropy one could proclaim the general overarching formulation of the Second Law. In any spontaneous process occurring in an isolated system, the entropy never decreases. This formulation, which is very general, embracing many processes, sowed the seed of the mystery associated with the concept of entropy, the mystery involving a quantity that does not subscribe to a conservation law.

We are used to conservation laws in physics. This makes sense:<sup>7</sup> material is not created from nothing, energy is not given to us free. We tend to conceive of a conservation law as “understandable” as something that “makes sense.” But how can a quantity increase indefinitely and why? What fuels that unrelenting, ever-ascending climb? It is not surprising that the Second Law and entropy were shrouded in mystery. Indeed, within the context of the macroscopic theory of matter, the Second Law of Thermodynamics is unexplainable. It could have stayed

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<sup>7</sup>Here we use the term “makes sense” in the sense that it is a common *experience* and not necessarily a consequence of logical reasoning.

a mystery forever had the atomic theory of matter not been discovered and gained the acceptance of the scientific community. Thus, with the macroscopic formulation we reach a dead end in our understanding of the Second Law of Thermodynamics.

## 1.2. The Atomistic Formulation of the Second Law

Before the development of the kinetic theory of heat (which relied on the recognition of the atomistic theory of matter), thermodynamics was applied without any reference to the composition of matter — as if matter were a continuum. Within this approach there was no further interpretation of entropy. That in itself is not unusual. Any law of physics reaches a dead end when we have to accept it as it is, without any further understanding. Furthermore, the Second Law was formulated as an absolute law — entropy *always* increases in a spontaneous process in an isolated system. This is not different from any other law, e.g. Newton's laws are *always* obeyed — no exceptions.<sup>8</sup>

A huge stride forward in our understanding of entropy and of the Second Law of Thermodynamics, was made possible following Boltzmann's statistical interpretation of entropy — the famous relationship between entropy and the total number of microstates of a system characterized macroscopically by a given energy, volume, and number of particles. Take a look at the cover illustration or at the picture of Boltzmann's statue. Ludwig Boltzmann (1844–1906),<sup>9</sup> along with Maxwell and many others, developed what is now known as the kinetic theory of gases, or the kinetic theory of heat. This not only led to the identification of temperature, which we can feel with

<sup>8</sup>“Always” in the realm of phenomena that were studied at that time, and which are now referred to as classical mechanics.

<sup>9</sup>For a fascinating story of Boltzmann's biography, see Broda (1983), Lindley (2001), and Cercignani (2003).

our sense of touch, with the motions of the particles constituting matter, but also to the interpretation of entropy in terms of the number of states that are accessible to the system.

The atomistic formulation of entropy was introduced by Boltzmann in two stages. Boltzmann first defined a quantity he denoted as  $H$ , and showed that as a result of molecular collisions and a few other assumptions, this quantity always decreases and reaches a minimum at equilibrium. Boltzmann called his theorem “the minimum theorem”, which later became famous as Boltzmann’s *H-theorem* (published in 1872). Furthermore, Boltzmann showed that a system of particles starting with any distribution of molecular velocities will reach thermal equilibrium. At that point,  $H$  attains its minimum and the resulting velocity distribution will necessarily be the so-called Maxwell distribution of the velocities (see also Chapter 7).

At that time, the atomistic theory of matter had not yet been established nor universally accepted. Although the idea of the “atom” was in the minds of scientists for over two thousand years, there was no compelling evidence for its existence. Nevertheless, the kinetic theory of heat did explain the pressure and temperature of the gas. But what about entropy, the quantity that Clausius introduced without any reference to the molecular composition of matter?

Boltzmann noticed that his  $H$ -quantity behaved similarly to entropy. One needs only to redefine entropy simply as the negative value of  $H$ , to get a quantity that always *increases* with time, and that remains constant once the system reaches thermal equilibrium.

Boltzmann’s *H-theorem* drew criticisms not only from people like Ernst Mach (1838–1916) and Wilhelm Ostwald

(1853–1932), who did not believe that atoms existed, but also from his colleagues and close friends.<sup>10</sup>

The gist of the criticisms (known as the reversibility objection or the reversibility paradox), is the seeming conflict between the so-called time-reversal<sup>11</sup> or time symmetry of the Newtonian's equations of motion, and the time asymmetry of the behavior of Boltzmann's  $H$ -quantity. This conflict between the reversibility of the molecular motion, and the irreversibility of the  $H$ -quantity was a profound one, and could not be reconciled. How can one derive a quantity that distinguishes between the past and the future (i.e. always increasing with time), from equations of motions that are indifferent and do not care for the past and future? Newton's equations can be used to predict the evolution of the particles into the past as well as into the future. Woven into the  $H$ -Theorem were arguments from both mechanics and probability, one is deterministic and time symmetric, while the other is stochastic and time asymmetric. This conflict seems to consist of a fatal flaw in the Boltzmann  $H$ -theorem. It was suspected that either something was wrong with the  $H$ -theorem, or perhaps even with the very assumption of the atomistic nature of matter. This was clearly a setback for Boltzmann's  $H$ -theorem and perhaps a (temporary) victory for the non-atomists.

Boltzmann's reaction to the reversibility objection was that the  $H$ -theorem holds most of the time, but in very rare cases,

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<sup>10</sup>For instance, Loschmidt wrote in 1876 that the Second Law cannot be a result of purely mechanical principle.

<sup>11</sup>It should be noted as Greene (2004) emphasized that "time-reversal symmetry" is not about time *itself* being reversed or "running" backwards. Instead, time reversal is concerned with whether events that happen *in* time in one particular temporal order can also happen in the reverse order. A more appropriate phrase might be "*event reversal* or *process reversal*".



it can go the other way, i.e.  $H$  might increase, or the entropy might decrease with time.

This was untenable. The (non-atomistic) Second Law of Thermodynamics, like any other laws of physics, was conceived and proclaimed as being absolute — no room for *exceptions*, not even rare exceptions. No one had ever observed violation of the Second Law. As there are no exceptions to Newton's equations of motion,<sup>12</sup> there should be no exceptions to the Second Law, not even in rare cases. The Second Law must be absolute and inviolable. At this stage, there were two seemingly different views of the Second Law. On the one hand, there was the classical, non-atomistic and absolute law as formulated by Clausius and Kelvin encapsulated in the statement that entropy never decreases in an isolated system. On the other hand, there was the atomistic formulation of Boltzmann which claimed that entropy increases “most of the time” but there are exceptions, albeit very rare exceptions. Boltzmann proclaimed that entropy could decrease — that it was not an *impossibility*, but only *improbable*.<sup>13</sup> However, since all observations seem to support the *absolute* nature of the Second Law, it looked as if Boltzmann suffered a defeat, and along with that, the atomistic view of matter.

In spite of this criticism, Boltzmann did not back down. He reformulated his views on entropy. Instead of the *H-theorem* which had one leg in the field of mechanics, and the other in the realm of probability, Boltzmann anchored both legs firmly on the grounds of probability. This was a radically

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<sup>12</sup>Within classical mechanics.

<sup>13</sup>As we shall see in Chapters 7 and 8, the admitted non-absoluteness of the atomists' formulation of the Second Law is, in fact, more absolute than the proclaimed absoluteness of the non-atomists' formulation. On this matter, Poincaré commented: “...to see heat pass from a cold body to a warm one, it will not be necessary to have the acute vision, the intelligence, and the dexterity of Maxwell's demon; it will suffice to have a little patience” quoted by Leff and Rex (1990).

new and foreign way of reasoning in physics. Probability, at that time, was not part of physics (it was not even a part of mathematics). Boltzmann proclaimed that entropy, or rather atomistic-entropy, is equal to the logarithm of the total number of arrangements of a system. In this bold new formulation, there were no traces of the equations of motion of the particles. It looks as if it is an ad-hoc new definition of a quantity, devoid of any physics at all, purely a matter of *counting* the number of possibilities, the number of states or the number of configurations. This atomistic entropy had built-in provisions for exceptions, allowing entropy to decrease, albeit with an extremely low probability. At that time, the exceptions allowed by Boltzmann's formulation seemed to *weaken* the validity of his formulation compared with the absolute and inviolable non-atomist formulation of the Second Law. In Chapter 8, I shall return to this point arguing that, in fact, the built-in provision for exceptions strengthens rather than weakens the atomistic formulation.

There seemed to be a state of stagnation as a result of the two irreconcilable views of the Second Law. It was not until the atomic theory of matter had gained full acceptance that the Boltzmann formulation won the upper hand. Unfortunately, this came only after Boltzmann's death in 1906.

A year earlier, a seminal theoretical paper published by Einstein on the Brownian motion provided the lead to the victory of the atomistic view of matter. At first sight, this theory seems to have nothing to do with the Second Law.

Brownian motion was observed by the English botanist Robert Brown (1773–1858). The phenomenon is very simple: tiny particles, such as pollen particles, are observed to move at seemingly random fashion when suspended in water. It was initially believed that this incessant motion was due to some tiny living organism, propelling themselves in the liquid. However,

Brown and others showed later that the same phenomenon occurs with inanimate, inorganic particles, sprinkled into a liquid.

Albert Einstein (1879–1955) was the first to propose a theory for this so-called Brownian motion.<sup>14</sup> Einstein believed in the atomic composition of matter and was also a staunch supporter of Boltzmann.<sup>15</sup> He maintained that if there are very large numbers of atoms or molecules jittering randomly in a liquid, there must also be fluctuations. When tiny particles are immersed in a liquid (tiny compared to macroscopic size, but still large enough compared to the molecular dimensions of the molecules comprising the liquid), they will be “bombarded” randomly by the molecules of the liquid. However, once in a while there will be asymmetries in this bombardment of the suspended particles, as a result of which the tiny particles will be moving one way or the other in a zigzag manner.

In 1905 Einstein published as part of his doctoral dissertation, a theory of these random motions.<sup>16</sup> Once his theory was corroborated by experimentalists [notably by Jean Perrin (1870–1942)], the acceptance of the atomistic view became inevitable. Classical thermodynamics, based on the *continuous* nature of matter, does not have room for fluctuations. Indeed, fluctuations in a macroscopic system are extremely small. That is why we do not observe fluctuation in a macroscopic piece of matter. But with the tiny Brownian particles, the fluctuations

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<sup>14</sup>It is interesting to note that the founders of the kinetic theory of gases such as Maxwell, Clausius and Boltzmann never published anything to explain the Brownian motion.

<sup>15</sup>It is interesting to note that Einstein, who lauded Boltzmann for his probabilistic view of entropy, could not accept the probabilistic interpretation of quantum mechanics.

<sup>16</sup>A well-narrated story of Einstein’s theory of Brownian motion may be found in John Rigden (2005). A thorough and authoritative discussion of the theory of Brownian motion, including a historical background, has been published by Robert Mazo (2002).

are magnified and rendered observable. With the acceptance of the atomic composition of matter also came the acceptance of Boltzmann's expression for entropy. It should be noted that this formulation of entropy stood fast and was not affected or modified by the two great revolutions that took place in physics early in the 20th century: quantum mechanics and relativity.<sup>17</sup> The door to understanding entropy was now wide open.

The association of entropy with the number of configurations and probabilities was now unassailable from the point of view of the dynamics of the particles. Yet, it was not easily understood and accepted, especially at the time when probability was still not part of physics.

Almost at the same time that Boltzmann published his views on the Second Law, Willard Gibbs (1839–1903) developed the statistical mechanical theory of matter based on a purely statistical or probabilistic approach. The overwhelming success of Gibbs' approach, though based on probabilistic postulates,<sup>18</sup> has given us the assurance that a system of a very large number of particles, though ultimately governed by the laws of motion, will behave in a random and chaotic manner, and that the laws of probability will prevail.

The mere relationship between entropy and the number of states in a system is not enough to explain the behavior of

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<sup>17</sup>Perhaps, it should be noted that within the recent theories of black holes, people speak about the "generalized Second Law of Thermodynamics" [Bekenstein (1980)]. It seems to me that this generalization does not affect Boltzmann's formula for the entropy.

<sup>18</sup>Today, any book on physics, in particular, statistical mechanics, takes for granted the atomic structure of matter. It is interesting to note in Fowler and Guggenheim's book on *Statistical Thermodynamics* (first published in 1939, and reprinted in 1956), one of the first *assumptions* is: "Assumption 1: The *atomistic constitution of matter*." They add the comment that "Today, this hardly ranks as an assumption but it is relevant to start by recalling that it is made, since any reference to atomic constitutions is foreign to classical thermodynamics." Today, no modern book on statistical mechanics makes that *assumption* explicitly. It is a universally accepted fact.

entropy. One must supplement this relationship with three critically important facts and assumptions. First, that there is a huge number of particles and an even “huger” number of microstates. Second, that all these states are equally likely i.e. have equal probability of occurrence, hence are equally likely to be visited by the system. Third, and most importantly, that at equilibrium, the number of *microstates* that are consistent with (or belonging to) the *macrostate* that we actually observe, is almost equal to the *total* number of possible microstates. We shall come back to these aspects of a physical system in Chapters 6 and 7.

With these further assumptions that would crystallize into a firm theory of statistical thermodynamics, the atomistic formulation of entropy has gained a decisive victory. The non-atomistic formulation of the Second Law is still being taught and applied successfully. There is nothing wrong with it except for the fact that it does not, and in principle cannot reveal the secrets ensconced in the concept of entropy.

Boltzmann’s heuristic relation between entropy and the logarithm of the total number of states<sup>19</sup> did open the door to an understanding of the meaning of entropy. However, one needs to take further steps to penetrate the haze and dispel the mystery surrounding entropy.

There are several routes to achieve this end. I shall discuss the two main routes. One is based on the interpretation of entropy in terms of the extent of disorder in a system;<sup>20</sup> the second involves

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<sup>19</sup>For simplicity and concreteness, think of  $N$  particles distributed in  $M$  cells. A full description of the state of the system is a detailed specification of which particle is in which cell.

<sup>20</sup>The association of entropy with disorder is probably due to Bridgman (1941;1953). Guggenheim (1949) suggested the term “spread” to describe the spread over a large number of possible quantum states. A thorough discussion of this aspect is given by Denbigh and Denbigh (1985).

the interpretation of entropy in terms of the missing information on the system.<sup>21</sup>

The first, the older and more popular route, has its origin in Boltzmann's own interpretation of entropy: a large number of states can be conceived of as having a large degree of disorder. This has led to the common statement of the Second Law of Thermodynamics that "Nature's way is to proceed from order to disorder."

In my opinion, although the order-disorder interpretation of entropy is intuitively clear in many examples, it is not always valid. In a qualitative way, it can answer the question of *what* is the thing that changes in some spontaneous processes, but not in all. However, it does not offer any answer to the question of *why* entropy always increases.

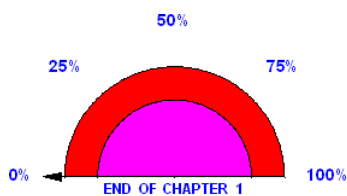
The second route, though less popular among scientists is, in my opinion, the superior one. First, because *information* is a better, quantitative and objectively *defined* quantity, whereas order and disorder are less well-defined quantities. Second, information, or rather the missing information, can be used to answer the questions of *what* is the thing that changes in *any* spontaneous process. Information is a familiar word; like energy, force or work, it does not conjure up mystery. The measure of information is defined precisely within information theory. This quantity retains its basic meaning of *information* with which we are familiar in everyday usage. This is not the case when we use the concept of "disorder" to describe *what* is the thing that changes. We shall further discuss this aspect in Chapters 7 and 8. Information in itself does not provide an answer to the question of *why* entropy changes in this particular way. However, information unlike disorder, is defined in terms of probabilities

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<sup>21</sup>Information theory was developed independently of thermodynamics by Claude Shannon in 1948. It was later realized that Shannon's informational measure is identical (up to a constant that determines the units) with Boltzmann's entropy.

and as we shall see, probabilities hold the clues to answering the question “*why*.”

For these reasons, we shall devote the next chapter to familiarizing ourselves with some basic notions of probability and information. We shall do that in a very qualitative manner so that anyone with or without a scientific background can follow the arguments. All you need is sheer common sense. Once you acquire familiarity with these concepts, the mystery surrounding entropy and the Second Law will disappear, and you will be able to answer both the questions: “What is the thing that is changing?” and “Why is it changing in this particular manner?”





## Reflections on the Status of the Second Law of Thermodynamics as a Law of Physics

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If you have followed me so far and have reached this last chapter, you must feel comfortable with the concept of entropy and with the Second Law. If you throw a pair of (real) dice many times, and find that the *sum* = 7 appears on the average more than any other sums, you should not be surprised. If you throw one hundred simplified dice (with “0” and “1”), you should not be puzzled to find out that the sum of the outcomes will almost always be about 50. If you throw a million simplified dice, you should not be mystified to find out that you will “never” get the *sum* = 0 or the *sum* = 1,000,000. You know that both of these results are *possible* outcomes, but they are so rare that you can play all your life and will not witness even once that particular result. You will not be mystified because you have thought about that and your common sense tells you that events with high probability will be observed more frequently, while events with extremely low probability will “never” occur.

If you have never heard of the atomic constituency of matter and you watch a colored gas initially contained in one compartment of a vessel flowing and filling up the two compartments of the vessel, as shown in Fig. (8.1a); or two compartments with two different gases, say yellow and blue, transformed into a blend of homogenous green, as shown in Fig. (8.1b); or a hot



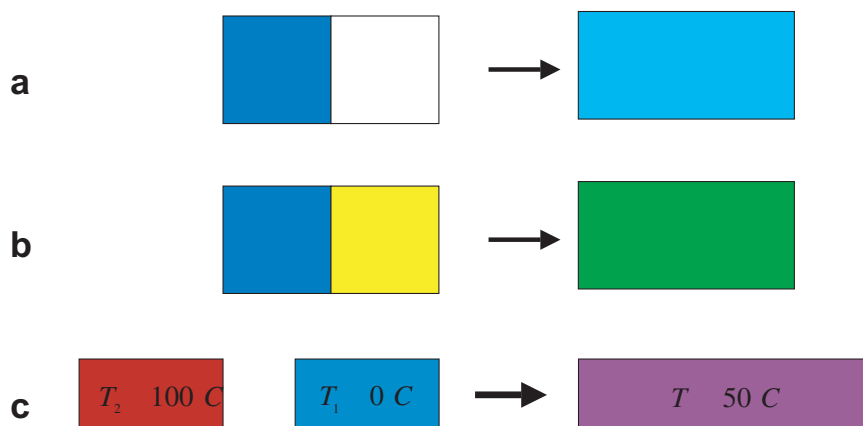


Fig. (8.1)

body at a temperature say  $T_2 = 100^\circ\text{C}$ , when brought into contact with a cold body, say at  $T_1 = 0^\circ\text{C}$ , cooled to a temperature somewhere in between  $T_1$  and  $T_2$ , as shown in Fig. (8.1c), you *should* be mystified. Why did the blue gas flow from one chamber to fill the other chamber? Why were the two colored gases transformed into a single color? Why did the temperatures of the two bodies change into a single temperature? What are the hidden forces that propelled all these phenomena, and always in these directions and never in the opposite directions? Indeed, for as long as the atomic theory of matter was not discovered and accepted,<sup>1</sup> all of these phenomena were shrouded in mystery.

Mystery might not be the right word. Perhaps “puzzlement” will describe the situation better. The only reason for you to be puzzled is that you do not have any understanding of why these phenomena happen in the particular direction. But that is the same for any law of physics. Once you accept the law as a fact,

<sup>1</sup>By “discovered and accepted,” I mean “*not yet* discovered and accepted.” If matter *did not* consist of atoms and molecules, then there would have been no mystery none of the phenomena would have occurred. The Second Law as formulated within classical thermodynamics would not have existed at all.

you will feel that it is natural, and that it makes sense.<sup>2</sup> The same is true for the Second Law; the fact that these processes are so common in daily life, means that they are slowly and gradually being perceived as “natural” and “make sense.”

If, however, you know that a gas consists of some  $10^{23}$  atoms or molecules, jittering and colliding incessantly millions of times a second, then you know that the laws of probability will prevail, and that there is no mystery. There is no mystery in all these processes as much as there is no mystery in failing to win the “one million” prize in the last lottery.

I would like to believe that even if you encountered the words “entropy” and the “Second Law” for the first time in this book, you would be puzzled as to why the word “mystery” was associated with these terms at all. You will have no more reasons to cringe upon hearing the word “entropy,” or to be puzzled by that unseen “force” that pushes the gas from one side to the other. There is also no need for you to continue reading this book. My mission of explaining the “mysteries of the Second Law” has ended on the last pages of Chapter 7, where you have reached a full understanding of the Second Law.

In this chapter, I take the liberty to express some personal reflections on the Second Law. Some of my views are not necessarily universally agreed upon. Nevertheless, I have ventured into expressing these views and taking the risk of eliciting the criticism of scientists whose views might be different and perhaps more correct than mine.

In this chapter, I shall raise some questions and shall try to answer them. I will begin with a relatively innocent question: “Why has the Second Law been shrouded in mystery for so long?” Is it because it contains a seed of conflict between

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<sup>2</sup>Here, “makes sense” is used in the sense of being a common and familiar experience, not in the logical sense.

the time-reversal symmetry of the equations of motion, and the observed irreversibility of natural processes? Then I shall discuss a few other questions, the answers to which are still controversial. Is entropy really a measure of “disorder,” and what does order or disorder of a system mean? How has “information” invaded a “territory” that used to harbor only physically measurable entities? Is the Second Law intimately associated with the arrow of time? What is the “status” of the Second Law of Thermodynamics *vis a vis* other laws of nature? Is it also possible that one day science will do away with the Second Law of Thermodynamics as it will be deemed a redundancy, a relic of the pre-atomistic view of matter that does not further enrich our knowledge of how nature works?

### **8.1. What is the Source of the Mystery?**

In my opinion, there are several reasons which gave rise to the mystery enveloping the Second Law. The first, and perhaps the simplest reason for the mystery is the very word “entropy.” Everyone is familiar with concepts like force, work, energy and the like. When you learn physics, you encounter the same words, although sometimes they have quite different meanings than the ones you are used to in everyday life. The amount of “work” that I have expended in writing this book is not measured in the same units of work (or energy) that are used in physics. Likewise, the “force” exerted on a politician to push for a specific law or a bill is not the same as the force used in physics. Nevertheless, the precise concepts of work and force as defined in physics retain some of the qualitative flavor of the meaning of these words as used in daily life. Therefore, it is not difficult to accommodate the new and more precise meaning conferred on familiar concepts such as force, energy or work. When you encounter, for the first time, a new word such as “entropy,”

it conjures up an air of mystery; it has a strange and uneasy effect on you. If you are not a student of physics or chemistry, and by chance hear scientists talking about “entropy,” you will certainly feel that this concept is beyond you and *a fortiori* so, when you hear the scientists themselves referring to “entropy” as a mystery.

Leon Cooper (1968), right after quoting Clausius’ explanation of his reasons for the choice of the word “entropy,” comments<sup>3</sup>

*“By doing this, 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**.”*

I generally agree with Cooper’s comment but I have two reservations about it. First, the word “entropy” is unfortunately a misleading word. This is clearly different than meaning “nothing.” Open any dictionary and you will find: “Entropy — Ancient Greek change, literary turn.” Clearly, the concept of entropy is not “transformation,” nor “change,” nor “turn.” As we have seen, entropy as defined in either the non-atomistic or the atomistic formulation of the Second Law is something that changes. But it is not the “transformation” that is transformed, nor the “change” that is changing, and certainly not the “turn” that is evolving.

My second reservation concerns the casual suggestion made by Cooper that “lost heat” could have been more appropriate. Of course, “lost heat” is a more meaningful term than “entropy.” It is also in accordance with the universal meaning

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<sup>3</sup>See Chapter 1, page 7. We again quote from Clausius’ writing on the choice of the word “entropy.” Clausius says: “*I propose, accordingly, to call  $S$  the entropy of a body after the Greek word “**transformation**.”*”

assigned to entropy as a “measure of the unavailable energy.”<sup>4</sup> I will revert to this meaning assigned to entropy in Section 8.3 below.

Besides the unfamiliarity with a new concept that creates an air of mystery, there is a second reason for the mystery. The very fact that many authors writing on entropy *say* that entropy *is* a mystery, *makes* entropy a mystery. This is true for writers of popular science as well as writers of serious textbooks on thermodynamics.

Take for example a very recent book, brilliantly written for the layman by Brian Greene. He writes<sup>5</sup>:

*“And among the features of common experience that have resisted complete explanation is one that taps into the deepest unresolved mysteries in modern physics, the mystery that the great British physicist, Sir Arthur Eddington called the arrow of time.”*

On the next pages of the book, Greene explains the behavior of entropy using the pages of Tolstoy’s epic novel *War and Peace*. There are many more ways that the pages of the said novel can fall out of order, but only one (or two) ways to put them in order.

It seems to me that the above quoted sentence contributes to perpetuating the mystery that is no longer there. In a few more sentences, Greene could have easily explained “entropy,” as he explained so many other concepts of modern physics. Yet to me, it is odd that he writes: “...the deepest unresolved mysteries in modern physics,” when I believe he should instead have written: “Today, the mystery associated with the Second Law no longer exists.” There are many authors who wrote on the Second Law

<sup>4</sup>Merriam Webster’s Collegiate Dictionary (2004).

<sup>5</sup>Greene (2004).

with the intention of *explaining* it, but in fact ended up propagating the mystery.<sup>6</sup>

Here is a classical example. Atkins' book on *The Second Law* starts with the following words<sup>7</sup>:

*“No other part of science has contributed as much to the liberation of the human spirit as the Second Law of Thermodynamics. Yet, at the same time, few other parts of science are held to be recondite. Mention of the Second Law raises visions of lumbering steam engines, intricate mathematics, and infinitely incomprehensible entropy.”*

What should one make of these opening sentences? I definitely do not agree with all the three quoted sentences. The first sentence is ambiguous. I failed to understand what the Second Law has got to do with “liberating the human spirit.” However, my point here is not to argue with Atkins' views on the Second Law. I quote these opening sentences from Atkins' book to demonstrate how each contributes to propagating the mystery. The first sentence elicits great expectations from the Second Law and presumably encourages you to read the book. However, these expectations are largely frustrated as you go on reading the book. The next two sentences are explicitly discouraging — “an infinitely incomprehensible entropy” does not whet your appetite to even try to taste this dish. In many textbooks on thermodynamics, the authors spend a lot of time discussing different manifestations of the Second Law, but very little on what is *common* to all these manifestations. Instead of selecting one or two simple examples of processes that are manifestations of the Second Law, the authors present a very large number of

<sup>6</sup>An exception is Gamov's book *One, Two, Three Infinity* that opens a section with the title *The Mysterious Entropy* but ends it with: “and as you see, there is nothing in it to frighten you.”

<sup>7</sup>Atkins (1984).

examples, some of which are too complicated to comprehend. Reading all these, you cannot see the forest for the trees.<sup>8</sup>

In Chapter 7, we have discussed two relatively simple examples that demonstrate the workings of the Second Law. In each of these examples only one parameter changes. In the first, the change we observed was in the *locational* information, i.e., particles that are initially confined to a smaller volume, disperse and fill a larger volume. In the second example, the *identities* of the particles were changed. In the experiment on heat transfer from a hot to a cold body, it is the distribution of velocities that was changed. There are, of course, more complicated processes that involve changes in many parameters (or degrees of freedom). Sometimes, it is difficult to enumerate all of them. For instance, the processes that occur following the splattering of an egg involve changes of location, identities of molecules, distribution of velocities, orientations and internal rotations within the molecules. All of these complicate the description of the process, but the principle of the Second Law is the same. To understand the *principle*, it is enough to focus on one simple process, and the simpler, the better and the easier to understand.

Atkins' book devotes a whole chapter to "see how the Second Law accounts for the emergence of the intricately ordered forms characteristic of life."<sup>9</sup> In my opinion, this promise is not delivered. I have read Atkins' entire book, cover-to-cover, and I failed to "see how the Second Law accounts for the emergence of the intricately ordered forms characteristic of life."

These kinds of promises contribute to the frustration of the readers and discourage them from getting to grips with the Second Law.

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<sup>8</sup>It is interesting to note that "entropy" and "the Second Law" feature in the titles of scores of books (see some titles of books in the bibliography). To the best of my knowledge, no other single law of physics has enjoyed that treat.

<sup>9</sup>Atkins (1984).

Life phenomena involve extremely complicated processes. Everyone “knows,” scientists as well as non-scientists, that *life* is a complex phenomenon, many aspects of which, involving the mind and consciousness, are still not well understood. Therefore, discussing *life* in a book which is supposed to *explain* the Second Law leaves the reader with the impression that entropy, like life, is hopelessly difficult to understand and very mysterious.

It is true that many scientists believe that all aspects of life, including consciousness, are ultimately under the control of the laws of physics and chemistry, and that there is no such separate entity as the mind which does not succumb to the laws of physics. I personally believe that this is true. However, this contention is still far from being proven and understood. It might be the case that some aspects of life will require extension of the presently known laws of physics and chemistry, as was cogently argued by Penrose.<sup>10</sup> Therefore, in my opinion, it is premature to discuss life as just another example, fascinating as it may be, within the context of explaining the Second Law.

There are more serious reasons for the mystery that has befogged entropy. For over a century, the Second Law was formulated in thermodynamic terms and even after the molecular theory of matter has been established, the Second Law is still being taught in thermodynamics, employing macroscopic terms. This approach inevitably leads down a blind alley. Indeed, as my first lecturer correctly proclaimed (see Preface), there is no hope of understanding the Second Law *within* thermodynamics. To reach the light, you must go through the tunnels of statistical thermodynamics, i.e., the formulation of the Second Law in terms of a huge number of indistinguishable particles. If you go through the various different formulations of the Second Law within classical thermodynamics, you can prove the equivalence

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<sup>10</sup>Penrose (1989, 1994).



of one formulation to some other formulations; you can show that the entropy that drives one process, say the expansion of a gas, is the same entropy that drives another process, say the mixing of two different gases. It is somewhat more difficult to show that it is also the same entropy that drives a chemical reaction, or mixing of two liquids. It is impossible to prove that it is the same entropy that causes the mess created by the splattering of an egg (yet we do assume that it is the same entropy and that one day, when the tools of statistical thermodynamics shall have been more powerful, we will be able to prove it). However, no matter how many examples you work out and prove that they are driven by the inexorably and the ever-increasing entropy, you will reach a blind alley. You can never understand what the underlying source of this one-way ascent of the entropy is. Thermodynamics does not reveal to you the underlying molecular events.

Had the atomic theory of matter not been discovered and accepted,<sup>11</sup> we would have never been able to explain the Second Law; it would have forever remained a mystery.

That was the situation at the end of the nineteenth century and at the beginning of the twentieth century. Although the kinetic theory of heat had succeeded in explaining the pressure, temperature, and eventually also the entropy in terms of the motions of atoms and molecules, these theories were considered to be *hypotheses*. Important and influential scientists such as Ostwald and Mach thought that the concept of the atom, and the theories based on its existence, should not be part of physics. Indeed, they had a point. As long as no one had “seen” the atoms directly or indirectly, their incorporation in any theory of matter was considered speculative.

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<sup>11</sup>See footnote 1, page 187.

The situation changed dramatically at the beginning of the twentieth century. It was Einstein who contributed decisively to defeating the aether, and also paved the way for the atomists' victory. The acceptance of Boltzmann's molecular interpretation of entropy became inevitable (see Chapter 1).

But how come the mystery still did not vanish with the embracing of Boltzmann's interpretation of entropy? True, the door was then widely open to a full understanding of the ways of entropy and yet the mystery persisted.

I am not sure I know the full answer to this question. But I do know why, in my *own* experience, the mystery has remained floating in the air for a long time. The reason, I believe, involves the unsettled controversy which arose from the association of entropy with "disorder," with "missing information" and with the "arrow of time." I shall discuss each of these separately.

## **8.2. The Association of Entropy with "Disorder"**

The association of entropy with disorder is perhaps the oldest of the three, and has its roots in Boltzmann's interpretation of entropy. Order and disorder are vague and highly subjective concepts, and although it is true that in many cases, increase in entropy can be correlated with increase in disorder, the statement that "nature's way is to go from order to disorder" is the same as saying that "nature's way is to go from low to high entropy." It does not explain why disorder increases in a spontaneous process. There is no law of nature that states that systems tend to evolve from order to disorder.

In fact, it is not true that, in general, a system evolves from order to disorder. My objection to the association of entropy with disorder is mainly that order and disorder are not well-defined, and are very fuzzy concepts. They are very subjective,

sometimes ambiguous, and at times totally misleading. Consider the following examples:

In Fig. (8.2) we have three systems. On the left hand side, we have  $N$  atoms of gas in volume  $V$ . In the second, some of the  $N$  atoms occupy a larger volume  $2V$ . In the third, the  $N$  atoms are spread evenly in the entire volume  $2V$ . Take a look. Can you tell which of the three systems is the more ordered one? Well, one can argue that the system on the left, where the  $N$  atoms are gathering in one half of the volume, is more ordered than the system on the right, where  $N$  atoms are spread in the entire volume. That is plausible when we associate entropy with missing information (see below), but regarding order, I personally do not see either of the systems in the figures to be more ordered, or more disordered, than the other.

Consider next the two systems depicted in Fig. (8.3):

In the left system, we have  $N$  blue particles in one box of volume  $V$  and  $N$  red particles in another box of the same volume  $V$ . In the right, we have all the atoms mixed up in the *same* volume  $V$ . Now, which is more ordered? In my view, the left side is more ordered — all the blues and all the reds are

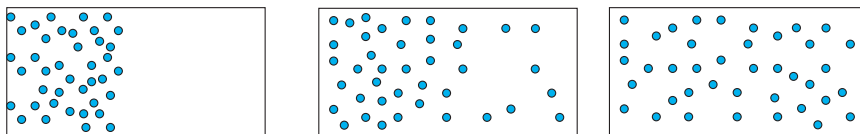


Fig. (8.2)

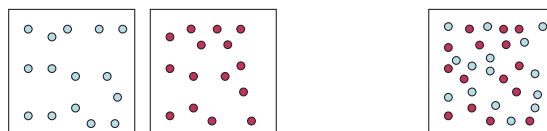


Fig. (8.3)

separated in two different boxes. On the right-hand side, they are mixed up in one box. “Mixed-up” is certainly a disordered state, colloquially speaking. In fact, even Gibbs himself used the word “mix-upness” to describe entropy. Yet, one can prove that the two systems mentioned above have *equal* entropy. The association of mixing with increase in disorder, and hence increase in entropy, is therefore only an illusion. The trouble with the concept of order and disorder is that they are not well-defined quantities — “order” as much as “structure” and “beauty” are in the eyes of the beholder!

I am not aware of any precise *definition* of order and disorder that can be used to validate the interpretation of entropy in terms of the extent of disorder. There is one exception, however. Callen (1985), in his book on thermodynamics, writes (p. 380):

*“In fact, the conceptual framework of “information theory” erected by Claude Shannon, in the late 1940s, provides a basis for interpretation of the entropy in terms of Shannon’s measure of **disorder**.”*

And further, on the next page, Callen concludes:

*“For closed system the entropy corresponds to Shannon’s quantitative measure of the maximum possible disorder in the distribution of the system over its permissible microstates.”*

I have taught thermodynamics for many years and used Callen’s book as a textbook. It is an excellent textbook. However, with all due respect to Callen and to his book, I must say that Callen misleads the reader with these statements. I have carefully read Shannon’s article “The Mathematical Theory of Communication,” word-for-word and cover-to-cover, and found out that Shannon neither defined nor referred to “disorder.” In my opinion, Callen is fudging with the definition of disorder in the quoted statement and in the rest of that chapter.

What for? To “legitimize” the usage of *disorder* in interpreting entropy. That clearly is not in accord with Shannon’s writings. What Callen refers to as Shannon’s definition of *disorder* is in fact Shannon’s definition of *information*. In my opinion, Callen’s re-definition of information in terms of disorder does not help to achieve the goal of explaining entropy. As we have seen in Chapters 2 and 6, the concept of information originated from a qualitative and highly subjective concept, has been transformed into a quantitative and objective measure in the hands of Shannon. As we have also seen, the distilled concept of “information” also retains the meaning of information as we use it in everyday life. That is not so for disorder. Of course, one can define disorder as Callen has, precisely by using Shannon’s definition of *information*. Unfortunately, this definition of “disorder” does not have, in general, the *meaning* of disorder as we use the word in our daily lives, and has been demonstrated in the examples above.<sup>12</sup>

To conclude this section, I would say that increase in disorder (or any of the equivalent words) can sometimes, but not always, be associated with increase in entropy. On the other hand, “information” can *always* be associated with entropy, and therefore it is superior to disorder.

### 8.3. The Association of Entropy with Missing Information

Ever since Shannon put forward his definition of the concept of information, it has been found to be very useful in interpreting entropy.<sup>13</sup> In my opinion, the concept of missing information has not only contributed to our understanding of what is

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<sup>12</sup>Furthermore, Shannon has built up the measure of information, or uncertainty, by requiring that this measure fulfill a few conditions. These conditions are plausible for *information*, but not for disorder. For further reading on this aspect of entropy see Ben-Naim (2007).

<sup>13</sup>See Tribus (1961) and Jaynes (1983) both dealing with the informational theoretical interpretation of entropy.

the *thing* that changes (which is called entropy), but it has also brought us closer to the last and final step of understanding entropy's behavior as nothing but common sense. This view, however, is not universal.

On this matter, Callen (1983, page 384) writes:

*“There is a school of thermodynamics who view thermodynamics as a subjective science of prediction.”*

In a paragraph preceding the discussion of entropy as disorder, Callen writes:

*“The concept of probability has two distinct interpretations in common usage. ‘Objective probability’ refers to a frequency, or a fractional occurrence; the assertion that ‘the probability of newborn infants being male is slightly less than one half’ is a statement about census data. ‘Subjective probability’ is a measure of expectation based on less than optimum information. The (subjective) probability of a particular yet unborn child being male, as assessed by a physician, depends upon that physician’s knowledge of the parents’ family histories, upon accumulating data on maternal hormone levels, upon the increasing clarity of ultrasound images, and finally upon an educated, but still subjective, guess.”*

As I have explained in Chapter 2 (in the section on “Conditional probabilities and subjective probability”), my views differ from Callen’s in a fundamental sense. Both examples given by Callen could be subjective or objective depending on the *given* condition or on the given relevant knowledge.

I have quoted Callen’s paragraph above to show that his argument favoring “disorder” is essentially fallacious. I believe Callen has misapplied probabilistic argument to deem information “subjective” and to advocate in favor of “disorder,” which in his view is “objective.”

An extraterrestrial visitor, who has no information on the recorded gender of newborn infants, would have no idea what the probabilities for a male or female are, and his assignment of probabilities would be totally subjective. On the other hand, given the same information and the same knowledge, including the frequencies of boys and girls, the reliability of all the statistical medical records, his assignment of probabilities will inevitably be *objective*.

It is unfortunate and perhaps even ironic that Callen dismisses “information” as subjective, while at the same time embracing Shannon’s definition of information, but renaming it as disorder. By doing that, he actually replaces a well-defined, quantitative and objective quantity with a more subjective concept of disorder. Had Callen not used Shannon’s definition of information, the concept of disorder would have remained an undefined, qualitative and highly subjective quantity.

In my view, it does not make any difference if you refer to *information* or to *disorder*, as subjective or objective. What matters is that order and disorder are not well-defined, scientific concepts. On the other hand, information is a well-defined scientific quantity, as much as a point or a line is *scientific* in geometry, or the mass or charge of a particle is *scientific* in physics.

Ilya Prigogine (1997) in his recent book *End of Certainty* quotes Murray Gell-Mann (1994), saying:

*“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 the degree of ignorance the microstate is in by counting the number of bits of additional information needed to specify it, with all the microstates treated as equally probable.”*<sup>14</sup>

<sup>14</sup>The microstates and macrostates referred to here are what we call *specific* and *dim*-configurations, or states, or events.

I fully agree with this quotation by Gell-Mann, yet Ilya Prigogine, commenting on this very paragraph, writes:

*“We believe that these arguments are untenable. They imply that it is our own ignorance, our coarse graining, that leads to the second law.”*

Untenable? Why?

The reason for these two diametrically contradictory views by two great Nobel prize winners lies in the misunderstanding of the concept of information.

In my opinion, Gell-Mann is not only right in his statement, but he is also careful to say “entropy *can* be regarded as a measure of ignorance... Entropy ... measures the degree of ignorance.” He does not say “*our own ignorance*,” as misinterpreted by Prigogine.

Indeed, information, as we have seen in Chapter 2, is a measure that *is there* in the system (or in the game of Chapter 2). Within “information theory,” “information” is not a subjective quantity. Gell-Mann uses the term “ignorance” as a synonym of “lack of information.” As such, ignorance is also an objective quantity that belongs to the system and it is not the same as “*our own ignorance*,” which might or might not be an objective quantity.

The misinterpretation of the informational-theoretical interpretation of entropy as a subjective concept is quite common. I will quote one more paragraph from Atkins’ preface from the book *The Second Law*.<sup>15</sup>

*“ I have deliberately omitted reference to the relation between information theory and entropy. There is the danger, it seems to me, of giving the impression that entropy requires the existence of some cognizant entity capable of possessing “in formation” or of being to some*

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<sup>15</sup>Atkins (1984).



*degree “ignorant.” It is then only a small step to the presumption that entropy is all in the mind, and hence is an aspect of the observer.”*

Atkins’ rejection of the informational interpretation of entropy on grounds that this “analogy” might lead to the “presumption that entropy is all in the mind,” is ironic. Instead, he uses the terms “disorder” and “disorganized,” etc., which in my view are concepts that are far more “in the mind.”

The fact is that there is not only an “analogy” between entropy and information; the two concepts can also be made identical.

It should be stressed again that the interpretation of entropy as a measure of information cannot be used to *explain* the Second Law of Thermodynamics. The statement that entropy is an ever-increasing quantity in a spontaneous process (in an isolated system) is not *explained* by saying that this is “nature’s way of increasing disorder,” or “nature’s way of increasing ignorance.” All these are possible descriptions of the *thing* that changes in a spontaneous process. As a description, “information” is even more appropriate than the term “entropy” itself in describing the thing that changes.

Before ending this section on entropy and information, I should mention a nagging problem that has hindered the acceptance of the interpretation of entropy as information. We recall that entropy was *defined* as a quantity of heat divided by temperature. As such, it has the units of energy divided by  $K$  (i.e., Joules over  $K$  or  $J/K$ ,  $K$  being the units of the absolute temperature in Kelvin scale). These two are tangible, measurable and well-defined concepts. How is it that “information,” which is a dimensionless quantity,<sup>16</sup> a number that has nothing to do with either energy or temperature, could be associated with entropy,

<sup>16</sup>I used here “dimensionless” as unit-less or lack of units.

a quantity that has been *defined* in terms of energy and temperature? I believe that this is a very valid point of concern which deserves some further examination. In fact, even Shannon himself recognized that his measure of information becomes identical with entropy only when it is multiplied by a constant  $k$  (now known as the Boltzmann constant), which has the units of energy divided by temperature. This in itself does not help much in proving that the two apparently very different concepts are identical. I believe there is a deeper reason for the difficulty of identifying entropy with information. I will elaborate on this issue on two levels.

First, note that in the process depicted in Fig. (8.1c), the change in entropy does involve some quantity of heat transferred as well as the temperature. But this is only one example of a spontaneous process. Consider the expansion of an ideal gas in Fig. (8.1a) or the mixing of two ideal gases in Fig. (8.1b). In both cases, the entropy increases. However, in both cases, there is no change in energy, no heat transfer, and no involvement of temperature. If you carry out these two processes for ideal gas in an isolated condition, then the entropy change will be fixed, independent of the temperature at which the process has been carried out and obviously no heat transfer from one body to another is involved. These examples are only suggestive that entropy change does not *necessarily* involve units of energy and temperature.

The second point is perhaps on a deeper level. The units of entropy ( $J/K$ ) are not only unnecessary for entropy, but they *should not* be used to express entropy at all. The involvement of energy and temperature in the original definition of entropy is a historical accident, a relic of the pre-atomistic era of thermodynamics.

Recall that temperature was defined earlier than entropy and earlier than the kinetic theory of heat. Kelvin introduced the

absolute scale of temperature in 1854. Maxwell published his paper on the molecular distribution of velocities in 1859. This has led to the *identification* of temperature with the mean kinetic energy of atoms or molecules in the gas.<sup>17</sup> Once the identification of temperature as a measure of the average kinetic energy of the atoms had been confirmed and accepted, there was no reason to keep the old units of  $K$ . One should redefine a new absolute temperature, denoting it tentatively as  $\bar{T}$ , defined by  $\bar{T} = kT$ . The new temperature  $\bar{T}$  would have the units of energy and there should be no need for the Boltzmann constant  $k$ .<sup>18</sup> The equation for the entropy would simply be  $S = \ln W$ , and entropy would be rendered dimensionless!<sup>19</sup>

Had the kinetic theory of gases preceded Carnot, Clausius and Kelvin, the change in entropy would still have been defined as energy divided by temperature. But then this ratio would have been dimensionless. This will not only simplify Boltzmann's formula for entropy, but will also facilitate the *identification* of the *thermodynamic* entropy with Shannon's information.

In (1930), G. N. Lewis wrote:

*“Gain in entropy always means loss of information and nothing more.”*

This is an almost prophetic statement made eighteen years before information theory was born. Lewis' statement left no

<sup>17</sup>This identity has the form (for atomic particles of mass  $m$ )  $\frac{3kT}{2} = \frac{m\langle v^2 \rangle}{2}$  where  $T$  is the absolute temperature and  $\langle v^2 \rangle$ , the average of the squared velocity of the atoms, and  $k$ , the same  $k$  appearing on Boltzmann's tombstone.

<sup>18</sup>In doing so, the relation  $3kT/2 = m\langle v^2 \rangle/2$  will become simpler  $3\bar{T}/2 = m\langle v^2 \rangle/2$ . The gas constant  $R$  in the equation of state for ideal gases would be changed into Avogadro number  $N_{AV} = 6.022 \times 10^{23}$  and the equation state of one mole of an ideal gas will read:  $PV = N_{AV}\bar{T}$ , instead of  $PV = RT$ .

<sup>19</sup>Boltzmann's formula assumes that we know what configurations to count in  $W$ . To the best of my knowledge, this equation is not challenged within non-relativistic thermodynamics. In the case of Black-Hole entropy, it is not really known if this relation is valid. I owe this comment to Jacob Bekenstein.

doubt that he considered entropy as *conceptually* identical to information.

Shannon (1948) has shown that entropy is *formally* identical with information. There is a story<sup>20</sup> that John von Neumann advised Claude Shannon to use the term “entropy” when discussing information because:

*“No one knows what entropy really is, so in a debate you will always have the advantage.”*

Thus, without entering into the controversy about the question of the subjectivity or objectivity of information, whatever it is, I believe that entropy can be made *identical*, both conceptually *and* formally, to information. The identification of the two is rendered possible by redefining temperature in terms of units of energy.<sup>21</sup> This would automatically expunge the Boltzmann constant ( $k$ ) from the vocabulary of physics. It will simplify the Boltzmann formula for entropy, and it will remove the stumbling block that has hindered the acceptance of entropy as information for over a hundred years. It is also time to change not only the units of entropy to make it dimensionless,<sup>22</sup> but the term “entropy” altogether. Entropy, as it is now recognized, does not mean “transformation,” or “change,” or “turn.” It does mean *information*. Why not replace the term that means “nothing” as Cooper noted, and does not even convey the meaning it was meant to convey when selected by Clausius? Why not replace it with a simple, familiar, meaningful, and precisely

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<sup>20</sup>Tribus, M. and McIrvine, E. C. (1971), *Energy and Information*, Scientific American, 225, pp. 179–188.

<sup>21</sup>As is effectively done in many fields of Physics.

<sup>22</sup>Note that the entropy would still be an extensive quantity, i.e., it would be proportional to the size of the system.

defined term “information?” This will not only remove much of the mystery associated with the unfamiliar word entropy, but will also ease the acceptance of John Wheeler’s view to “*regard the physical world as made of information, with energy and matter as incidentals.*”<sup>23</sup>

Before concluding this section, I owe you an explanation of my second reservation regarding Cooper’s comment cited on page 190.

I agree that “lost heat” could be better than “entropy.” However, both the terms “lost heat,” and the more common term “unavailable energy,” are applied to  $T \Delta S$  (i.e., the product of the temperature with the change in entropy), and not to the change of entropy itself. The frequent association of entropy with “lost heat” or “unavailable energy” is due to the fact that it is the entropy that carries the energy units. However, if one defines temperature in terms of units of energy, then entropy becomes dimensionless. Therefore, when forming the product  $\bar{T} \Delta S$ , it is the *temperature* that carries the burden of the units of energy. This will facilitate the interpretation of  $\bar{T} \Delta S$  (not the change in entropy) as either “lost heat” or “unavailable energy.”

I should also add one further comment on nomenclature. Brillouin (1962) has suggested to refer to “information” as “neg-entropy.” This amounts to replacing a simple, familiar and informative term with a vague and essentially misleading term. Instead, I would suggest replacing entropy with either “neg-information,” “missing information,” or “uncertainty.”

Finally, it should be said that even when we identify entropy with information, there is one very important difference between the thermodynamic information (entropy) and Shannon’s information, which is used in communications or in any other branch

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<sup>23</sup>Quoted by Jacob Bekenstein (2003).

of science. It is the huge difference in order of magnitudes between the two.<sup>24</sup>

As we have seen, the association between entropy and probability not only removes the mystery, but also reduces the Second Law to mere common sense. Perhaps it is ironic that the atomic view of matter that has led to a full understanding of entropy had initially created a new and apparently deeper mystery. This brings us to the next question.

#### **8.4. Is the Second Law Intimately Associated with the Arrow of Time?**

Every day, we see numerous processes apparently occurring in one direction, from the mixing of two gases, to the decaying of a dead plant or animal. We never observe the reverse of these phenomena. It is almost natural to feel that this direction of occurrence of the events is in the right direction, consistent with the direction of time. Here is what Greene writes on this matter<sup>25</sup>:

*“We take for granted that there is a direction in the way things unfold in time. Eggs break, but do not unbreak; candles melt, but they don’t unmelt; memories are of the past, never of the future; people age, they don’t unage.”*

However, Greene adds: *“The accepted laws of Physics show no such asymmetry, each direction in time, forward*

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<sup>24</sup>A binary question gives you one bit (binary-unit) of information. A typical book, contains about one million bits. All the printed material in the world is estimated to contain about  $10^{15}$  bits. In statistical mechanics, we deal with information on the order of  $10^{23}$  and more bits. One can define information in units of cents, or dollars, or euros. If it costs one cent to buy one bit of information, then it would cost one million cents to buy the information contained in a typical book. The information contained in one gram of water, all the money in the world, will not suffice to buy!

<sup>25</sup>Greene (2004) page 13.

*and backward, is treated by the laws without distinction, and that's the origin of a huge puzzle."*

Indeed it is! For almost a century, physicists were puzzled by the apparent conflict between the Second Law of Thermodynamics and the laws of dynamics.<sup>26</sup> As Brian Greene puts it, "*Not only do known laws (of physics) fail to tell us why we see events unfold in only one order, they also tell us that, in theory, events can fold in the reverse order. The crucial question is Why don't we ever see such things? No one has actually witnessed a splattered egg un-splattering, and if those laws treat splattering and un-splattering equally, why does one event happen while its reverse never does?*"

Ever since Waddington associated the Second Law of Thermodynamics with the arrow of time, scientists have endeavored to reconcile this apparent paradox. The equations of motion are symmetrical with respect to going forward or backward in time. Nothing in the equations of motion suggests the possibility of a change in one direction and forbids a change in the opposite direction. On the other hand, many processes we see every day do proceed in one direction and are never observed to occur in the opposite direction. But is the Second Law really associated with the arrow of time?

The classical answer given to this question is that if you are shown a movie played backwards, you will immediately recognize, even if not told, that the movie is going backwards. You will recognize, for instance, that a splattered egg scattered on the floor, suddenly and spontaneously collects itself into the pieces of the broken egg shell, the broken egg shell then becoming

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<sup>26</sup>Here, we refer to either the classical (Newtonian) or the quantum mechanical laws of dynamics. These are time-symmetric. There are phenomena involving elementary particles that are not time-reversible. However, no one believes that these are the roots of the second law. I owe this comment to Jacob Bekenstein.

whole again, and the egg flying upward and landing intact on the table. If you see that kind of movie, you will smile and invariably conclude that the movie is going backwards. Why? Because you know that this kind of process cannot proceed in this direction in time.

But what if you actually sit in the kitchen one day, look at a splattered egg scattered on the floor, and suddenly the egg gets back to its unbroken state, and then jumps back on top of the table?

Fantastic as it might sound, your association of the process of the splattering of the egg with the arrow of time is so strong that you will not believe what your eyes see, and you will probably look around to see if someone is playing a trick on you by running the film you are acting in backwards. Or, if you understand the Second Law, you might tell yourself that you are fortunate to observe a *real* process, in the *correct* direction of time, a process *that is extremely rare but not impossible*.

This is exactly the conclusion reached by the physicist in George Gamov's book *Mr. Tompkin's Adventure in Wonderland*.<sup>27</sup> When he saw his glass of whisky, suddenly and spontaneously, boiling in its upper part, with ice cubes forming on the lower part, the professor knew that this process, though extremely rare, *can* actually occur. He might have been puzzled to observe such a rare event, but he did not look for someone playing backwards the "movie" he was acting in. Here is that lovely paragraph from Gamov's book:

*"The liquid in the glass was covered with violently bursting bubbles, and a thin cloud of steam was rising slowly toward the ceiling. It was particularly odd, however, that the drink was boiling only in a comparatively small area*

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<sup>27</sup>Gamov (1940, 1999).



*around the ice cube. The rest of the drink was still quite cold.*

*‘Think of it!’ went on the professor in an awed, trembling voice. ‘Here, I was telling you about statistical fluctuations in the law of entropy when we actually see one! By some incredible chance, possibly for the first time since the earth began, the faster molecules have all grouped themselves accidentally on one part of the surface of the water and the water has begun to boil by itself.*

*In the billions of years to come, we will still, probably, be the only people who ever had the chance to observe this extraordinary phenomenon. He watched the drink, which was now slowly cooling down. ‘What a stroke of luck!’ he breathed happily.”*

Our association of the spontaneously occurring events with the arrow of time is, however, a mere illusion. An illusion created by the fact that in our lifetime we have never seen even one process that unfolds in the “opposite” direction. The association of the spontaneous, natural occurrence of processes with the arrow of time is almost always valid – almost, but not absolutely always.

George Gamov, in his delightful book *Mr Tompkins in Wonderland*, attempted to explain the difficult-to-accept results of the theories of relativity and quantum mechanics by narrating the adventures of Mr. Tompkins in a world where one can *actually see* and experience the difficult-to-accept results. He tried to imagine how the world would look if the speed of light was much slower than 300,000,000 meters per second, or conversely, how the world would appear to someone travelling at velocities near to the speed of light. In this world, one could observe phenomena that are almost *never* experienced in the real world.

Similarly, one can imagine a world where Planck's constant ( $h$ ) is very large and experience all kinds of incredible phenomena such as, for example, your car effortlessly penetrating a wall (tunneling effect), and similar phenomena which are *never* experienced in the real world where we live.

To borrow from Gamov's imagination, we can imagine a world where people will be living for a very long time, many times the age of the universe, say  $10^{10^{30}}$  years.<sup>28</sup>

In such a world, when performing the experiment with gas expansion, or with mixing of gases, we should see something like what we have observed in the system of 10 dice. If we start with all particles in one box, we shall first observe expansion and the particles will fill the entire volume of the system. But "once in a while" we will also observe visits to the original state. How often? If we live for an extremely long time, say  $10^{10^{30}}$  years, and the gas consists of some  $10^{23}$  particles, then we should observe visits to the original state many times in our lifetime. If you watch a film of the expanding gas, running forward or backward, you will not be able to tell the difference. You will have no sense of some phenomena being more "natural" than others, and there should not be a sense of the "arrow of time" associated with the increase (or occasionally decrease) of entropy. Thus, the fact that we do not observe the unsplattering of an egg or unmixing of two gases is not because there is a conflict between the Second Law of Thermodynamics and the equations of motion or the laws of dynamics. There is no such conflict. If we live "long enough" we shall be able observe

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<sup>28</sup>Perhaps, we should note here that as far as it is known, there is no law of nature that *limits* the longevity of people or of any living system. There might be however, some fundamental symmetry laws that preclude that. But this could be true also for the speed of light and Planck constant. If that is true, then none of Gamov's imaginations could be realized in any "world" where the speed of light or Planck's constant would have different values.

all these reverse processes! The connection between the arrow of time and the Second Law is not absolute, only “temporary,” for a mere few billion years.

It should be added that in the context of the association of the Second Law with the arrow of time, some authors invoke our human experience that distinguishes the past from the future. It is true that we remember events from the past, *never* from the future. We also feel that we can affect or influence events in the future, but *never* events in the past. I fully share these experiences. The only question I have is what have these experiences to do with the Second Law or with any law of physics?

This brings me to the next question.

### 8.5. Is the Second Law of Thermodynamics a Law of Physics?

Most textbooks on statistical mechanics emphasize that the Second Law is not absolute; there are exceptions. Though extremely rare, entropy can go downward “once in a while.”

Noting this aspect of the Second Law, Greene (2004) writes that the Second Law “is not a law in the *conventional sense*.” Like any law of nature, the Second Law was founded on experimental grounds. Its formulation in terms of the increasing entropy encapsulates, in a very succinct way, the common feature of a huge number of observations. In its thermodynamic formulation or, rather, in the non-atomistic formulation, the Second Law does not allow exceptions. Like any other law of physics, it proclaims a law that is absolute, with no exceptions. However, once we have grasped the Second Law from the molecular point of view, we realize that there can be exceptions. Though rare, extremely rare, entropy can go the other way. The Second Law is thus *recognized* as not absolute, hence Greene’s comments that it is not a law in the “conventional

sense.” Greene’s statement leaves us with the impression that the Second Law is somewhat “weaker” than the conventional laws of physics. It seems to be “less absolute” than the other laws of physics.

But what *is* a law in the conventional sense? Is Newton’s law of inertia absolute? Is the constancy of the speed of light absolute? Can we really claim that any law of physics is absolute? We know that these laws have been observed during a few thousand years in which events have been recorded. We can extrapolate to millions or billions of years by examining geological records or radiations emitted from the time near the Big Bang, but we cannot claim that these laws have *always* been the same, or will *always* be the same in the future, and that no exceptions will be found. All we can say is that within a few millions or billions of years, it is *unlikely* that we shall find exceptions to these laws. In fact, there is neither theoretical nor experimental reason to believe that any law of physics is absolute.

From this point of view, the second law is indeed “*not a law in the conventional sense,*” not in a *weaker* sense, as alluded to by Greene, but in a *stronger* sense.

The fact that we *admit* the existence of exceptions to the Second Law makes it “weaker” than other laws of physics only when the other laws are proclaimed to be valid in an *absolute* sense. However, recognizing the extreme rarity of the exceptions to the Second Law makes it not only stronger but the strongest among all other laws of physics. For any law of physics, one can argue that no exceptions can be expected within at most some  $10^{10}$  years. But exceptions to the Second Law can be expected only once in  $10^{10000000000}$  or more years.

Thus, the Second Law when formulated within classical (non-atomistic) thermodynamics is an *absolute* law of physics. It allows no exceptions. When formulated in terms of molecular events, violations are permitted. Though it sounds paradoxical,

the relative “weakness” of the atomistic formulation makes the Second Law the strongest among other laws of physics, including the Second Law in its thermodynamic (non-atomist) formulation. Putting it differently, the admitted *non-absoluteness* of the atomistic-Second-Law is in fact more absolute than the proclaimed *absoluteness* of the non-atomistic-Second-Law.<sup>29</sup>

In the context of modern cosmology, people speculate on the gloomy fate of the universe, which ultimately will reach a state of thermal equilibrium or “thermal death.”

Perhaps not?!

On the other end of the time scale, it has been speculated that since entropy always increases, the universe must have started in the “beginning” with a lowest value of the entropy.

Perhaps not?!

And besides, the last speculation is in direct “conflict” with the Bible:

“1. *In the beginning God created the heaven and the earth.*

2. *And the earth was unformed, and void.” Genesis 1:1*

א בְּרֵאשִׁית, בָּרָא אֱלֹהִים, אֶת הַשָּׁמַיִם, וְאֶת הָאָרֶץ.  
ב וְהָאָרֶץ, הִיְתָה תֹהוּ וָבֹהוּ, וְחָשֶׁךְ, עַל-פְּנֵי תְהוֹם; וְרוּחַ אֱלֹהִים, מְרַחֶפֶת עַל-פְּנֵי הַמַּיִם.

The original Hebrew version includes the expression “Tohu Vavohu,” instead of “unformed” and “void.” The traditional interpretation of “Tohu Vavohu,” is total chaos, or total *disorder*, or if you prefer, highest entropy!

Having said these, I would venture a provocative view that the Second Law of Thermodynamics is neither “weaker” nor

<sup>29</sup>Although my knowledge of cosmology is minimal, I believe that what I have said in this section is applicable also to the “generalized second law,” used in connection with black hole entropy, see Bekenstein (1980).

“stronger” than the other laws of physics. It is simply not a law of physics at all, but rather a statement of pure common sense.

This brings me to the last question.

### 8.6. Can We Do Away with the Second Law?

If the Second Law of Thermodynamics is nothing but a statement of common sense, do we have to list it and teach it as one of the laws of Physics? Paraphrasing this question, suppose that no one had ever formulated the Second Law of Thermodynamics? Could we, by purely logical induction and common sense *derive* the Second Law? My answer is probably yes, provided we have also discovered the atomic nature of matter and the immense number of indistinguishable particles that constitute each piece of material. I believe that one can go from the bottom up and deduce the Second Law.<sup>30</sup> We can certainly do so for the simple example of expansion of gas or mixing two different gases (as we have done at the end of Chapter 7). If we develop highly sophisticated mathematics, we can also predict the most probable fate of a falling egg.<sup>31</sup> All of these predictions would not rely, however, on the laws of physics but on the laws of probability, i.e., on the laws of common sense.

You can rightly claim that I could make this “prediction” because I have benefited from the findings of Carnot, Clausius, Kelvin, Boltzmann and others. So it is not a great feat to “predict” a result that you know in advance. This is probably true. So I will rephrase the question in a more intriguing

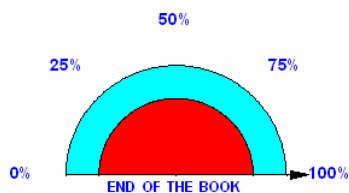
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<sup>30</sup>Here, I do not mean one can deduce the Second Law by solving the equations of motion of particles, but from the statistical behavior of the system. The first is impractical for a system of  $10^{23}$  particles.

<sup>31</sup>Again, I do not mean to predict the behavior of the falling egg by solving the equations of motion of all the particles constituting the egg. However, knowing all the possible degrees of freedom of all the molecules comprising an egg, we could, in principle, predict the most probable fate of a falling egg.

form. Suppose that all these great scientists, who founded the Second Law, never existed, or that they did exist but never formulated the Second Law. Would science arrive at the Second Law purely through logical reasoning, presuming the currently available knowledge of the atomic nature of matter and all the rest of physics?

The answer to this question might be NO! Not because one could not *derive* the Second Law from the bottom up even if no top-down derivation has ever existed. It is because science will find it unnecessary to formulate a law of physics based on purely logical deduction.







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