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.[1] 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.[2] 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

[1] This was another fascinating topic that was eventually chosen for my PhD thesis.
[2] 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.[3] In discussing the entropy and the Second Law, Greene wrote[4]:

> *"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

[3]Greene, B. (1999, 2004).
[4]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.[5] 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

[5] 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[6] 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

[6]Morowitz (1992) page 69.

"basicality" 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.[7]

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

[7] 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*."[8]

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[8] Greene, B. (2004).

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Arieh Ben-Naim
Department of Physical Chemistry
The Hebrew University
Jerusalem, Israel
Email: arieh@fh.huji.ac.il and ariehbennaim@yahoo.com

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.