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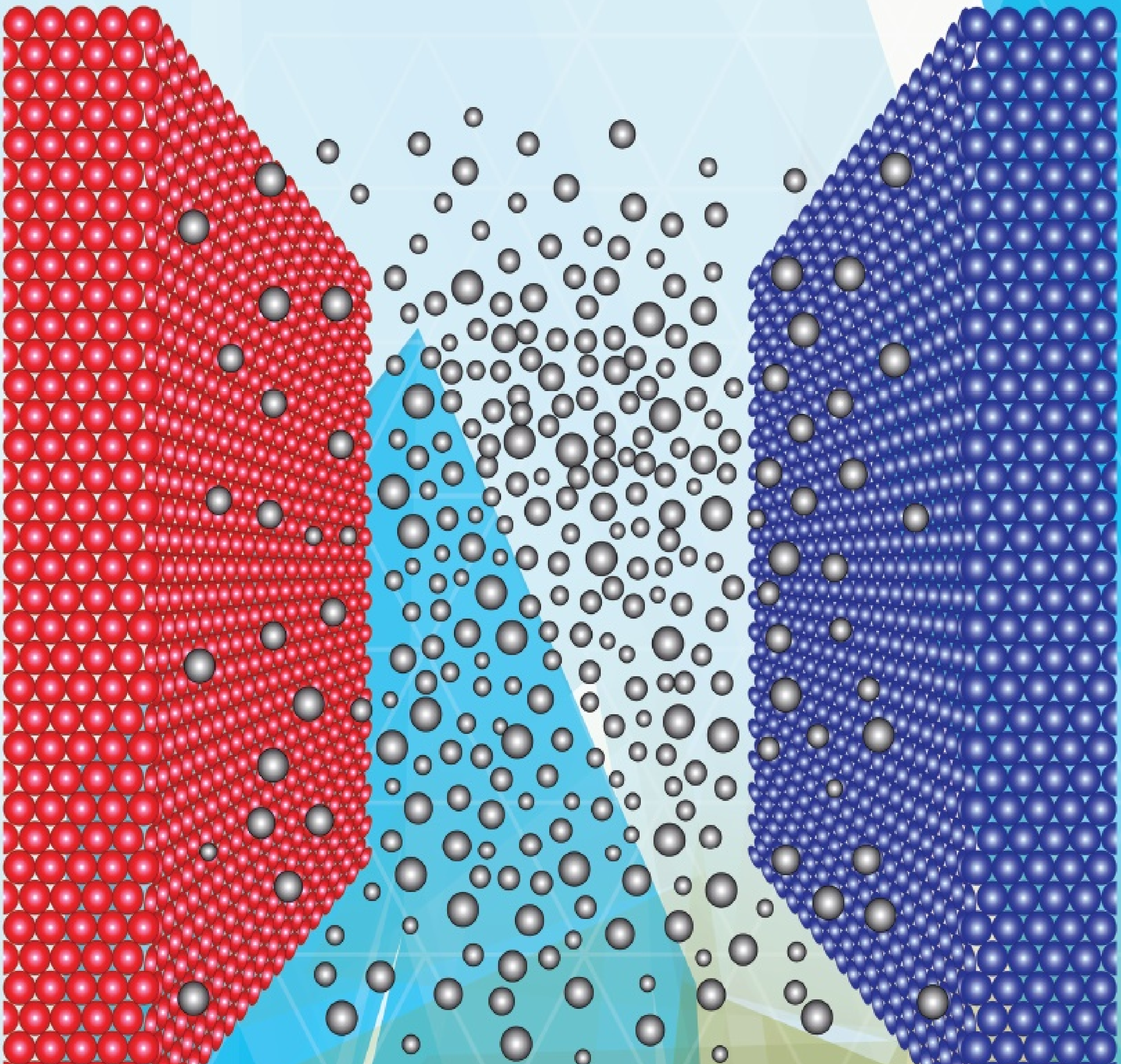
An Account of Thermodynamic Entropy



Alberto Gianinetti

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An Account Of Thermodynamic Entropy

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FOREWORD

As it is well established, the second law of thermodynamics is a cornerstone of natural sciences. However, its impressive consequences cannot be considered as a closed issue. Despite having been established more than one hundred years ago, it still surprises us with its extensive reach and profound results, many times associated with simple and elegant arguments. Indeed, it is probable that its actual form will not change in its essential meaning even within the context of new possible scientific paradigms that will emerge during the development of science. This is the reason why it has fascinated the greatest minds for over a century. Its reach spreads all over the sciences: in the diffusion of an ink drop in a glass of water, in the chemical reactions inside of living things, attached to evolutionary processes; it may even be connected with the answer to the question: why do we live in a 3-dimensional space? The reason behind the wide reach of thermodynamics is that almost all phenomena around us can be summarized as how energy is transformed. Nature is strongly related to equilibrium and optimization, and despite the particularities of every field of knowledge, these two ingredients, in one way or another, will remain present. In this sense, it is a relevant task to bring thermodynamics and specially the concept of entropy closer to all the disciplines of science. The actual technological and industrial needs, everyday more demanding, require the compromise of the scientific community to work together, within interdisciplinary efforts, to understand and look for the better way to deal with the environmental impact and the best energy management in the new technologies, as well as establishing linkages between theoretical models and the real world.

I applaud the diversity of approaches in which knowledge is transmitted, especially those, such as this work, that look for the integration of people from different fields and levels of expertise in the subject. In this text, you will find a broad discussion of the second law of thermodynamics and entropy, focusing on the concepts and their understanding, but without losing formality. I personally enjoyed the actual and fresh perspective of this text and I’m sure that, as a reader of this book, you will find out strong elements to deepen your understanding of entropy.

Dr. Julian Gonzalez-Ayala
Universidad de Salamanca
Salamanca, 2017

Preface

The second law of thermodynamics is one of the most fundamental laws that govern our universe and is relevant to every scientific field studying the physical world. Nonetheless, the second law's application makes constant reference to entropy, one of the most difficult concepts to work with, and this is the reason why they are discussed almost exclusively in highly specialized literature.

Thermodynamic entropy has been rigorously examined by classical, statistical, and quantum mechanics, which provide several mathematical expressions for calculating it under diverse theoretical conditions. However, the concept of entropy is still difficult to grasp for students and even more for educated laymen. As a scientist in plant biology, I fall into the second category with regards to this subject. Indeed, I first wrote this introductory book for myself; to approach my work with greater awareness about its physicochemical implications, I felt I needed better insight into the thermodynamic considerations that underpin spontaneous processes and allow plants, as well as humans, to achieve and improve the capability to exploit the environment to their benefit. When I consulted the literature on this topic, I found that although there are very many papers and books on the subject, the thorough explanation that I was looking for was scattered throughout them. I then began taking notes, and when I was finally satisfied I realized that, once organized and suitably presented, they were potentially interesting for other people looking for detailed, but not too advanced, clarifications on entropy and the second law of thermodynamics. I believe that a better understanding of these concepts requires a more satisfactory verbal explanation than is generally provided, since, in my opinion, a verbal approach is the one closer to the understanding capability of students and non-experts. This is why this book is focused on providing a verbal account of entropy and the second law of thermodynamics. In this sense, I deem that, beside to the basic mathematical formulations, a consistent explanation in verbal terms can be very useful for the comprehension of the subject by people who do not have a full understanding of it yet. Thus, I eventually came out with the present work, targeted to students and non-experts who are specifically interested into this matter and have a basic knowledge of mathematics and chemistry.

With this book I attempt to offer an account of thermodynamic entropy wherein verbal presentation is always a priority. Basic formal expressions are utilized to maintain a rigorous scientific approach to the matter, though I have always tried to explain their meaning. The essential outlines for a verbal account of thermodynamic entropy are summarized in the last chapter. Such an outline is how I wish I had been taught the core concepts of this matter when I was first introduced to it. Therefore, I hope it can be of help for a general introduction to the second law of thermodynamics and the basic concept of entropy. The main text of the present work aims to demonstrate the validity of the proposed verbal presentation from a rigorous, scientific point of view, but it also represents a resource for insights on specific topics since the verbal approach is adopted throughout the text. Several examples illustrate the concept of entropy in its different expressions. A number of notes provide further clarification or insight into the content in the main text and the reader may skip them on a first reading.

With regard to the contents of the this work, I have highlighted that the best way to conceive thermodynamic entropy that I found in the literature was that of a function of "energy spreading and sharing" as suggested by physicist Harvey S. Leff. Herein I try to take this line of thought further to verbally unravel the concept of thermodynamic entropy and to provide a better verbal account of it. I propose that a useful definition of entropy is "a function of the system equilibration, stability and inertness", and that the tendency to an overall increase of entropy set forth by the second law of thermodynamics should be meant as "the tendency to the most probable state", that is, to a macroscopic state whose distribution of matter and energy is maximally probable (according to the probabilistic distributions of matter and energy, and also considering the eventual presence of constraints). Thus, with time, an isolated system settles into the most equilibrated, stable, and inert condition that is actually accessible. I have provided a wide overview to introduce the rationale for these definitions and to show that they are consistent throughout the various levels and applications of the concept of entropy. The key idea is to extract from known formal expressions of entropy the essential verbal outlines of this concept and to use them to elaborate a verbal presentation of entropy that can be of general utility to non-experts, as well as to educators.

CONFLICT OF INTEREST

The authors confirm that they have no conflict of interest to declare for this publication.

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Declared none.

CHAPTER 1

Introduction

Abstract: Basic concepts are defined, such as what thermodynamics aims to, what a system is, which are the state functions that characterize it, what a process is.

Keywords: Adiabatic system, Boundaries, Classical thermodynamics, Classical mechanics, Closed system, Exchange of energy and matter, Heat transfer, Interactions, Isolated system, Macroscopic systems, Microscopic structure, Open system, Parcel, Processes, Quantum mechanics, Quantization of energy, State functions, Statistical mechanics, Surroundings, Thermal reservoir, Universe, Work.

Thermodynamics deals with the overall properties of macroscopic systems as defined by state functions (that is, physical properties that define the state of a body) such as: internal energy, E; temperature, T; volume, V; pressure, P; and number of particles[1], N. In addition to these properties, which are easy to understand, macroscopic systems are also characterized by specific values of entropy, a further state function that is more difficult to comprehend. Entropy can be calculated in many diverse theoretical conditions by several mathematical expressions; however, the concept of entropy is still difficult to grasp for most non-experts. A troublesome aspect of entropy is that its expression appears to be very different depending upon the field of science: in classical thermodynamics, the field where it was first defined, the conceptualization of entropy is focused on heat transfer; in classical mechanics, where many of the first studies were performed, entropy appears to be linked to the capability of an engine to produce work; its nature was then more precisely explained by statistical mechanics, which deals with the microscopic structure of the thermodynamic systems and studies

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how their particles affect the macroscopic properties of these systems; finally, quantum mechanics, by focusing on the quantization of energy and particles states, showed that the probabilistic nature of entropy, already highlighted by statistical mechanics, is closely dependent on the non-continuous nature of the universe itself. This works aims to show that, eventually, all these different aspects of entropy, which are necessarily linked to each other, can be better understood by considering the probabilistic nature of entropy and how it affects the properties of macroscopic systems, as well as the processes by which they interact.

A first exigency is then to define a macroscopic system. According to Battino *et al.* [2] a system is “any region of matter that we wish to discuss and investigate”. The surroundings consist of “all other matter in the universe that can have an effect on or interact with the system”. Thus, “the universe (in thermodynamics) consists of the system plus its surroundings”. The same authors notice that “there is always a boundary between the system and its surroundings and interactions between the two occur across this boundary, which may be real or hypothetical” [2]. In any case, a thermodynamic system, which typically includes some matter, is a part of the universe that is clearly defined and distinguishable from all the other parts of the universe. The presence of solid boundaries around the system is an obvious aid in the identification of the system, but it is not a necessary one. A gas inside a vessel is traditionally seen as a good, simple thermodynamic system. An aquarium can be another quite well defined thermodynamic system, although the presence of fish and other organisms would greatly complicate its thermodynamic properties and entropy in particular. The Earth, even though it is not surrounded by solid boundaries, represents a thermodynamic system too since it is something that is clearly defined and distinguishable by the remaining universe: beyond its stratosphere there is extended empty space that separates our planet from other systems. Although some energy and matter can move through the theoretical boundary that divides the Earth from empty space, these can be precisely identified as transfers of energy and matter from/to the Earth system, which maintains its identity. It can then be immediately noted that the identification of a system is essentially a theoretical step, since the Earth can contain innumerable smaller systems, *e.g.*

vessels containing fluid, like an aquarium, but also each cell of a fish in an aquarium is clearly an enclosed system with physical boundaries.

Hence, a system must be clearly delimited to be studied, but the rules that govern a system must also hold for any macroscopic parcel of matter with corresponding properties and conditions. Simply put, a system is just an identifiable parcel of the universe. It is worthy to note, therefore, that any parcel inside a system has, with the rest of the system, the same relationship that holds between an open system and its surroundings. So, for a system to be equilibrated it is necessary that all of its parcels, however sorted out, are equilibrated with the rest of the system, just like a thermodynamic system equilibrates with its surroundings if there is no insulating barrier between them.

What is particularly relevant to the study of entropy is that the system that is under consideration has to be macroscopic, that is, it must include a huge number of particles. This is because of the above-mentioned probabilistic nature of entropy, which can really be appreciated when, in the presence of a large number of particles, the probabilities become determining for every feature of the system; that is, the intensive state functions of the system (*i.e.*, those that do not depend on the system size, but, rather, on the distributions of particles and energy across the system), which emerge as overall properties from the statistical average behaviours of all the constituting particles, can be sharply defined and statistical fluctuations due to random effects of the particles are so small that they can be neglected. Of course, the concept of entropy holds true for every system, including very small ones consisting of only a few particles. However, some statistical approximations and mathematical simplifications that are ordinarily used for large systems, cannot be applied when dealing with very small ones. Notably, in every system, intensive state functions like temperature, density and pressure, which are widely used to characterize large systems, can undergo instantaneous fluctuations. However, whereas such fluctuations are negligible in large systems, as we will see, they become relevant for very small ones. In fact, in very small systems, intensive state functions can attain ample inhomogeneities across the system itself, or between the system and its external environment if they are connected, even at equilibrium. Hence, very small systems cannot be accurately described by single average values for these parameters, which, thus,

CHAPTER 2

Entropy in Classical Thermodynamics: The Importance of Reversibility

Abstract: The concept of entropy is introduced within the context of classical thermodynamics where it was first developed to answer the questions: What happens when heat spontaneously goes from hot bodies to cold ones? To figure out this change, the transfer process must have some peculiar features that make it reversible. First of all, to be studied, systems and processes must be conceptualised as occurring at equilibrium conditions, or in conditions close to equilibrium. A first description of equilibrium is provided.

Keywords: Balancing of forces, Classical thermodynamics, Clausius' equation, Dynamic equilibrium, Entropy, Equilibrium conditions, Friction, Heat capacity, Heat dissipation, Ideal gas, Infinitesimal change, Irreversible process, Isothermal process, Potentially available energy, Quasi-static process, Reversible process, Stationary state, Thermal energy, Transfer of heat, Turbulence.

THE FOUNDING DEFINITION OF ENTROPY

In classical thermodynamics, entropy was originally defined by Clausius' equation [3]:

$$dS = \delta Q/T$$

where dS is an infinitesimal change in the entropy[2] (S) of a closed system at an absolute temperature T, consequent to a transfer of heat (δQ) that occurs at equilibrium conditions. This definition was prompted by the observation, among others, that heat is spontaneously transferred from hot to cold bodies and the direction and universality of this phenomenon could be explained by some change in the involved bodies. So, the transfer of heat has to result in a change in the

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bodies that necessarily drives heat transfer from hot to cold and not the reverse. Although theoretically correct, the adoption of heat transfer as a definition of entropy is troublesome for our intuitive comprehension, since it requires that the transfer has to be at a defined temperature, *i.e.* the temperature of the entire system has not to change, in other words, the transfer has to be isothermal. This is unfortunate because what typically happens when something is heated is just that its temperature increases. In fact, a transfer of heat is commonly expected to occur from a hot body to a cold one, but in the simple heat to temperature ratio pointed out by the Clausius' equation only one temperature is considered. Which one should be used, the temperature of the hot body or that of the cold body? As we are presently using the Clausius' equation to define the entropy of a system, if the temperature is diverse in the two bodies, or systems, their entropy changes are different as well, as we will see soon, and the entropy changes are separately calculated for each body, even though the amount of heat transferred from one system to the other is one and the same. However, what is relevant here is that the temperature of each body is changing. So, the question could be whether the initial temperature, the equilibrium temperature, or perhaps their mean should be used. Actually, when the process is not isothermal and therefore the overall transfer of heat is discrete rather than infinitesimal, infinitesimal transfers of heat can nevertheless be imagined to occur at each subsequent instant, that is, instantaneous transfers of heat can be considered, which are infinitesimal as well. Although this approach is theoretically correct, and it will be used later in this chapter to show what generically happens to the total entropy when the transfer is not isothermal, in this case the problem is that the temperature at which each heat transfer occurs is changing for the system itself and is therefore unknown, unless further assumptions can be done for modelling it. As these assumptions depend on the specific bodies, it is not desirable to consider them when dealing with the general principle of equivalence between heat transfer and entropy change. In addition, if the initial temperatures of the bodies are diverse, a gradient of thermal energy forms during the equilibration process (unless it is extremely or, better, infinitely slow, as we'll see), thus generating inhomogeneities across the system itself, a problem that has already been remarked when discussing the size of the system and that greatly complicates the analysis of instantaneous changes. So, the problem with a non isothermal heat transfer is that the value of the Clausius' equation is different for the two bodies, and it is indeterminate inasmuch the instantaneous temperatures of the bodies are unknown, or indefinable. Obviously, for each body the equation holds true at every instant, it is just a problem of not being able to calculate it for a generic body if its temperature changes during the heat transfer. This is bothering, since the differential Clausius' equation just cannot be experimentally tested, or directly applied, in this situation. A theoretical solution to this methodological difficulty is based on the fact that the amount of transferred heat becomes smaller and smaller as the temperatures of the two bodies get closer. In the limit of the difference between the two temperatures becoming infinitesimal, even the amount of transferred heat becomes infinitesimal. If the difference of temperature that drives the transfer of heat is infinitesimal, the process is actually isothermal. Thus, the Clausius' equation is always true, but it provides a definable and exact measure of the change of entropy of a body, or system, when it is generated at a given, unchanging, temperature of the system, and this condition is unfailingly guaranteed by considering an infinitesimal transfer of heat.

A discrete version of the Clausius' equation is even more problematic: for a discrete heat transfer, the T in the denominator of $\mathrm{d}S = \delta Q/T$ is not constant and, therefore, not only $\mathrm{d}S$ cannot be calculated using this simple ratio, but the Clausius' equation itself does not hold true unless the process is isothermal. The reason for the isothermal requirement is that entropy is a non-linear function of temperature (it is logarithmic, for an ideal gas, as can be found out by integrating the Clausius' equation) and therefore the actual instantaneous change of entropy is different at different temperatures[3]. Thus, since in many processes it is not possible for the temperature and thermal energy of an ideal gas, or other system, to change independently of one another, a change in the entropy of a system can be expressed properly in terms of the simple heat to temperature ratio only in differential terms, specifically, $\mathrm{d}S = \delta Q/T$ (and not $\Delta S = \Delta Q/T$, unless, as we are going to see, there is a way to buffer any change of T) or its equivalent [4].

HEAT CAPACITY IS REQUIRED TO CALCULATE THE ENTROPY CHANGE IN DISCRETE HEAT TRANSFERS

The classical kinetic theory of gases implies that the amount of thermal energy

CHAPTER 3

Heat *vs.* Work

Abstract: The idea of transferring energy from/to a system is expanded to include work in addition to heat. Work is an alternative form by which the energy of a system can be transferred.

Keywords: Boltzmann constant, Classical mechanics, Conservation of energy, Dissipation of energy, Entropy increase, First law, Heat, Intermolecular potential energy, Internal energy, Kinetic energy, Microscopic level, Thermal energy, Transfer of work, Waste heat, Work.

Whereas in classical thermodynamics the interest was focused on heat transfers, in classical mechanics the attention was shifted toward the potentially much more applicative theme of the relationship between heat and work, with particular regard to how thermal energy can be used to produce work.

It is useful, at this point, to examine in a more in-depth manner the concepts of heat and work as thermodynamic ways of transferring energy. The first law of thermodynamics is often formulated by stating that any change in the internal energy (*i.e.*, the energy contained within a system, excluding the kinetic energy of motion of the whole system and the potential energy of the system as a whole due to external force fields, and, with the exception of nuclear reactions even the rest energy of the matter, $E = \mathrm{m}c^2$, is not considered because in common systems there is a clear distinction between matter and energy [7]) for a closed system is equal to the amount of heat supplied to the system, minus the amount of work done by the system on its surroundings. In other words, the energy is additive and an exact balance can be calculated when it is exchanged. Thus, the first law of thermodyna-

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mics is essentially the statement of the principle of the conservation of energy for thermodynamic systems [6, 8]. The sum of the heat (Q) and work (W) associated with a process represents a change in the internal energy, which is a state function of a system, as defined by the First Law of thermodynamics:

$$\Delta E = \mathrm{Q} - \mathrm{W}$$

where Q is the heat received by the system and W is the work done by the system. This is equivalent to the expression: $\Delta E = \mathrm{Q} + \mathrm{W}$, wherein the work done on the system is considered (this is just a matter of definition). Thus, if an ideal gas expands reversibly (*i.e.* against an external pressure, to equilibrate the system pressure) and isothermally (*i.e.* in the presence of a thermal reservoir), work is done by the gas and such work is equal to the heat absorbed by the gas during expansion (Fig. **1A**). Hence, a certain quantity of heat is converted entirely into work. At the same time, the entropy of the system has increased by some amount while the entropy of the heat reservoir has decreased by the same amount (since the heat transfer is isothermal and the work expended by the system is the same received by the surroundings). Thus, this symmetric change of entropy is equivalent to the transfers of heat and of work. However, real processes are irreversible and a macroscopic feature of these processes is that they are associated with an overall entropy increase (Fig. **1B**). Indeed, any transfer of work in real systems always implies that some heat is also produced as by-product, that is, as waste heat. Specifically, when a process exploits a difference in temperature any transfer will be of heat or of heat plus some work (which reaches a maximum proportion for reversible processes). Any transfer of heat (through a temperature gradient) that does not occur at equilibrium conditions, *i.e.* that does not produce an equivalent amount of work to build up another equipollent modification that maintains unchanged the overall amount of available energy, evidently results in a dissipation of available energy (*i.e.* of the energy potentially available from the temperature gradient to do work) and inevitably into an increase of entropy.

A transfer of heat is a transfer of thermal (or kinetic) energy [5]. The thermal energy is the sum of all the translational, rotational, and vibrational energies of the particles in a system.

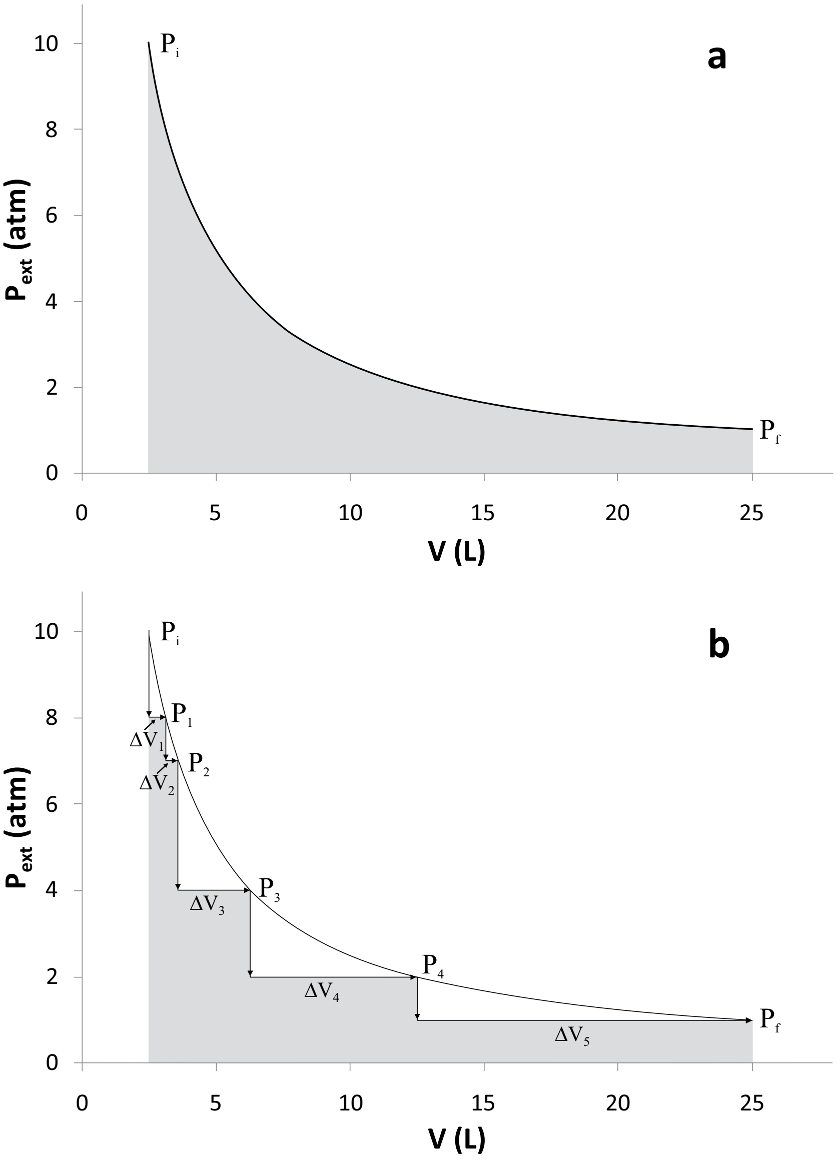

Fig. (1). An indicator diagram for the isothermal expansion of a closed system consisting of 1 mole of an ideal gas (at temperature $T = 304.66$ K). P_{ext}, the pressure exerted on the system by the surroundings (which also act as a constant-temperature thermal reservoir), is plotted against the volume V of the system [5]. For (**A**), in the reversible path, the gas is always pushing against the slowly decreasing external pressure, P_{ext}, which then remains equal to the pressure of the system. The PV work is done reversibly to the maximum possible level and is represented by the area under the curve, defined by the reversible isothermal equilibrium $PV = \mathrm{n}RT$, between the initial P_iV_i and final P_fV_f conditions; it is given by $W_{rev} = \mathrm{n}RT \cdot \ln(P_f / P_i) = -57.56$ L·atm. In (**B**) an irreversible path (stairstep plot) consisting of five steps of abrupt pressure drop, $-\Delta P_{ext}$, compared

CHAPTER 4

More on Reversibility

Abstract: Once the concept of work has been introduced, the concepts of reversibility, equilibrium, and entropy become clearer and can be better defined. This was the task undertaken by classical mechanics.

Keywords: Quasi-static process, Reversibility, Frictionless process, Local equilibrium, Maximum work, Overall increase of entropy, Irreversible process, Cyclical process, Carnot cycle, Maximum theoretical efficiency, Work accumulation, Engines, Real process, Particle motions, Balancing of forces, Energy levelling, Maximum entropy, Equilibrium, Stable state.

Now that the nature of work has been introduced, it can be noticed that reversible processes can also occur without any transfer of heat. In fact, for an ideal gas, an adiabatic reversible expansion occurs if the system is thermally insulated but its volume changes very slowly against an external pressure, so that there is always a quasi-static equilibrium between the pressure of the system and its surrounding environment (which restrains the system's expansion). In this way, the pressure and temperature of the system decrease while its volume increases. The temperature of the system decreases because reversible work is done by the expanding system on the surroundings (*e.g.*, some kinetic energy of the system's particles is transferred to the expanding wall to move it against the kinetic energy of the surroundings' particles), that is, in the system heat is converted into work (on the contrary, in an irreversible free adiabatic expansion the temperature of an ideal gaseous system remains constant because no work is done[6]). If the quasi-static process is frictionless, the gain in entropy due to the volume increase of the system is exactly balanced by the loss of entropy due to the decrease of temper-

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ature, as no exchange of heat occurs with the outside. Thus, the difference in the system's entropy at two temperatures can be measured in terms of volume change. The change in entropy of the surroundings is considered to be zero with the assumption that the slow drop in pressure is caused by some reversible process. Hence, no overall entropy change occurs. Whereas, in the irreversible free adiabatic expansion of an ideal gaseous system into vacuum, the entropy of the system increases with the increase in volume, as no work is done on the surroundings and therefore the system temperature does not decreases. No work is done because the gas is not pushing anything out of its way.

In general, for a process to be reversible it necessitates that [1]: (i) if heat is transferred, the temperatures must be equal; (ii) if volume is transferred, the pressures must be equal; (iii) if particles are transferred, the chemical potentials must be equal. In practice, this means that at each point in time the system is infinitely close to a local equilibrium [9]. If any of these conditions are missing, some work is lost and the process results in an overall increase of entropy (Fig. **1B**). In addition, to be virtually reversible, quasi-static processes (specifically those that involve a volume change) must be frictionless, so that no additional energy is dissipated as waste heat. If a process is not frictionless, then some work done by the system is no longer available in the surrounding environment, which can be described as [10]:

$$W_{sur} = (W_{sys} - \text{friction})$$

and then;

$$|W_{sur}| < |W_{sys}|$$

In other words, we obtain the maximum work from processes that generates no entropy in the universe. Putting everything together, reversible processes are always the most efficient. They represent the theoretical limit on the maximum work that can be performed by systems [9].

An overall increase of entropy is therefore always associated with an irreversible process since it occurs under non-equilibrium conditions (and, typically, is not frictionless). As originally noted by Clausius [3], an irreversible transfer of heat generates an equivalent change in the bodies involved that always drives the heat transfer from hot to cold and not the reverse. In general, an irreversible process occurs toward a spontaneous direction and such a process is spontaneous only if it increases the overall entropy of the system and the surrounding environment. Under equilibrium conditions, any change of entropy in the system is equal in magnitude, but opposed in sign to the change in the entropy of the surroundings, so that there is no overall change in entropy. In fact, the second law of thermodynamics points out that any process that would reduce the entropy of an isolated system is impossible. A process that could go in either direction without entropy change is possible and is said to be reversible. However, in an irreversible heat transfer the overall entropy is increased, that is, some energy is dissipated in the moving of the process toward its spontaneous direction.

For a cyclical process, which is pertinent to engines as studied by classical mechanics, we have:

$$\Delta S_{\text{tot}} = \oint \delta Q/T \geq 0$$

that is, for an engine that undergoes a cyclical process, the sum of all instantaneous transfers of heat from the state at one point of the cycle to the same state at whatever subsequent cycle (this is indicated by the cyclic integral, $\oint$) is null (in fact, if the state is the same, the internal energy of the system, which is a state function, does not change, by definition, even though the internal energy changes during the course of the cyclic process), and therefore the entropy (which is a state function as well) of a cyclical engine (which is considered a system) does not change from one cycle to another (of course, considering the same point of the cycle). Thus, the net entropy change of a system subject to a cyclic process is always zero, whether the process is reversible or irreversible, as the state of a system is independent of which thermodynamic path was followed to reach it. However, whereas in a reversible cyclic process the entropy change of the surroundings is also zero (since the entropy change in the surroundings equals the change in the system and the surroundings themselves return to their initial state, or to one with the same entropy), in an irreversible cyclic process the entropy change of the surroundings (specifically, the thermal reservoirs) is always positive, and therefore the total change of entropy is positive too. In general, the

CHAPTER 5

More a Matter of Lost Work Than of Waste Heat

Abstract: It is further highlighted that the concept of work represents a more general way to see what entropy is. That is, the idea of work offers a better framework to understand entropy. A fundamental observation in classical mechanics is that a system is at equilibrium when no work can be done by it. The capability of a system to do work is inversely linked to its stability, which then can be considered to be equivalent to the inertness of the system. Thus, equilibration, stability and inertness are all aspects of the same feature of a system, and such feature is measured in terms of entropy. An equilibrated, stable, and inert system has the highest value of entropy it can reach, and any departure from these conditions results in a decrease of entropy. Therefore, work availability and entropy are inversely linked: the maximal entropy is attained when no work can be done.

Keywords: Classical mechanics, Constraints, Directional macroscopic displacement, Discontinuity, Disequilibrium, Energy availability, Energy dissipation, Free energy, Irreversible process, Levelling of gradients, Lost work, Macroscopic gradient, Overall entropy, Potential energy, Random microscopic motions, Reversible path, Spreading and sharing, Transfer of work, Wasted heat.

SHIFTING THE PERSPECTIVE FROM HEAT TO WORK

The concept of entropy was introduced by Clausius ([3] in English, see the accompanying notes therein for the original German publication; specifically, the word “entropy” was first introduced in 1865) to account for the dissipation of potentially available energy observed in real processes and notwithstanding the first law of thermodynamics implies that energy can neither be created nor disappear into nothing. Indeed, dissipation does not mean that the energy is lost, but, rather, that its availability is lost. In fact, dissipation of energy means that

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some energy has become no longer available to do work. This is because the system and/or its surroundings are subjected to some transformation that dissipates available energy. The equivalence between a transfer of heat and the production of work in a reversible cycle was indeed the basis of the idea of entropy [3].

In fact, the Carnot cycle shows that a net transfer of heat from hot to cold (where the cold reservoir typically is the environment, *i.e.*, the rest of the universe), which would seem to be a wasting of heat, can be associated with a reversible process. Therefore, a net transfer of heat from hot to cold is not necessarily linked to an overall entropy increase. An overall entropy increase always occurs if the transfer is direct, but if it is mediated by an opportune combination of other physical changes even a process that is ultimately a net transfer of heat from hot to cold can be reversible. It is the using the available energy in full to produce work (which must be used to accumulate some other form of available energy in a way that must be potentially usable to reverse the cycle) that makes the cycle reversible. Any dissipation of the available energy (*i.e.*, any direct, spontaneous transfer of heat) would increase the overall entropy and make the cycle irreversible.

In a reversible process, any change of entropy in the system is balanced by a corresponding, opposite change in the surroundings, typically mediated by a reversible transfer of heat or work. However, most real processes are irreversible and a macroscopic feature associated with an overall entropy increase is that some energy is transformed into a form that is less capable of producing work; it is said that energy is degraded or that available energy is lost. In other words, the energy is conserved (first law), but it undergoes qualitative changes that always decrease (second law) its capability to perform work. Thus, in a process that involves heat and work transfers between a closed system and its surroundings, the overall entropy change is:

$$\mathrm{d}S_{\mathrm{tot}} = \mathrm{d}S_{\mathrm{sys}} + \mathrm{d}S_{\mathrm{sur}}$$

and the entropy change in the system specifically is [12]:

$$\mathrm{d}S_{\mathrm{sys}} = \delta \mathrm{Q}_{\mathrm{actual}}/T_{\mathrm{eq}} + (\delta \mathrm{W}_{\mathrm{rev}} - \delta \mathrm{W}_{\mathrm{actual}})/T_{\mathrm{eq}}$$

where δQ_{actual} is the heat actually obtained by the system, δW_{rev} is the work theoretically obtainable by the system by a reversible process, δW_{actual} is the work actually obtained by that system, and T_{eq} is the temperature at equilibration with the environment. Notably, the difference $\delta W_{rev} - \delta W_{actual}$ represents lost work (δW_{lost}). If the process is reversible, the equation reduces to $dS_{tot} = 0$ because the change of entropy in the system is exactly opposite to that in the surroundings ($dS_{sys} = -dS_{sur}$), $\delta W_{lost} = \delta W_{rev} - \delta W_{actual} = 0$, and $dS_{sys} = \delta Q_{actual}/T_{eq}$. However, if the process is not reversible, less work is actually obtained by the system than in a reversible process ($\delta W_{rev} > \delta W_{actual}$), thus that $\delta W_{lost} > 0$ and then $dS_{sys} > \delta Q_{actual}/T_{eq}$. In fact, in an irreversible process, if the heat reservoir guarantees that the temperature of equilibration is the same the system had initially, the lost work is dissipated as heat to the surroundings and the net observed heat transfer to the system is less than the change of entropy of the system:

$$dS_{sys} = \delta Q_{actual}/T_{eq} + \delta W_{lost}/T_{eq}$$

and therefore:

$$\delta Q_{actual} = T_{eq} \cdot dS_{sys} - \delta W_{lost}$$

So, in an irreversible process the overall entropy is increased, that is, some energy is dissipated just in the moving of the process in a spontaneous direction. Therefore, if a transfer of heat occurs from the surroundings to the system, *i.e.* the latter was initially cooler, but the final equilibration temperature, T_{eq}, is considered in the calculations, then Clausius' equation provides an underestimation of the change of entropy in the system. As previously noted, there is a negative equivalence between accumulated work (actually, it is the energy available for doing work that is accumulated) and entropy, and it is now clear that entropy can be seen as lost work (lost in an irreversible process with respect to a reversible one), thus that in an irreversible heat transfer the overall entropy generated because of irreversibility is [12]:

$$dS_{tot} = dS_{sys} + dS_{sur} = \delta Q_{actual}/T_{eq} + \delta W_{lost}/T_{eq} - \delta Q_{actual}/T_{eq}$$

thus,

$$dS_{tot} = \delta W_{lost}/T_{eq}$$

CHAPTER 6

Entropy in Statistical Mechanics

Abstract: The systems we can directly see are composed of huge numbers of particles. So, the properties of these systems are obtained as statistical averages of the effects of their particles. This casts a conceptual bridge between the macroscopic world wherein we observe systems with their overall properties and the microscopic world where particles with their own properties dominate the scene. Statistical mechanics shows that the former world is determined by what happens in the latter, and this approach provides a better, finer understanding of what's going on at the macroscopic level and why.

Keywords: Accessible microstates, Boltzmann entropy, Constraints, Equilibration, Gibbs entropy, Inertness, Macroscopically stable equilibrium, Maximum entropy, Maxwell-Boltzmann distribution, Microstates, Microscopically dynamic equilibrium, Phase space, Second law, Spreading function, Stability, Statistical mechanics, Thermodynamic ensemble, Trajectory.

THE CONCEPT OF "MICROSTATES" AIMS TO DESCRIBE ENTROPY IN TERMS OF THE ACTUAL CHANGE THAT OCCURS IN THE SYSTEM WHEN SOME PROCESS MODIFIES IT

Although Clausius' equation is the working definition of entropy, even in classical mechanics, and the equivalence of entropy with lost work is very useful for measuring entropy changes, both these approaches do not provide a clear understanding of what entropy is by itself. Subsequent theoretical studies were therefore undertaken by statistical mechanics (which deals with the microscopic details of macroscopic systems) that showed entropy is an extensive property of a macroscopic system (*i.e.* a system that includes a large number of particles) that

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derives from the statistical features of the ensemble of microscopic states (microstates) the system can assume. Microstates are different states, detailed at the microscopic (particle) level, that a system can attain at given values of its macroscopic state functions (like N, E, and V, number of particles, energy, and volume, respectively; that is, the state functions that characterize isolated systems, which are the most fundamental thermodynamic systems to study). Each microstate is defined by both the way N particles are physically arranged in the system volume and how their different levels of thermal energy (which are exactly proportional to their velocities if all the particles are identical) are distributed among the particles. Formally, the microstates are said to be points in a phase space, whose coordinates define the spatial localization and the energetic level of each single particle of the system [9, 17]. In other terms, we define the phase space of a system as the multidimensional space of all of its microscopic degrees of freedom [9]. Thus, for classical systems, the positions and momenta (*i.e.*, instantaneous movements) of all constituent particles describe each microscopic state. If the particles of the system are all ideal and spherical, the multidimensional phase space has a number of dimensions that is given by the number of particles multiplied by six (namely, three positional coordinates plus three momentum coordinates, one for each spatial direction). This can be thought of as specifying a point in a $6N$-dimensional phase space, where each of the axes corresponds to one of the momentum or position coordinates for one of the atomic particles [9].

An ensemble of microstates is a collection of the various microscopic states of a system that correspond to the single macroscopic state of that system, which is characterized by a given set of state functions. It should be noted that an ensemble is the theoretical set of microstates that the system can assume over time given its overall thermodynamic properties, which means that, in actuality, these microstates are not independent through time (as if they were coloured balls extracted from an urn). They necessarily constitute a time sequence because each microstate is causally determined by what the particles were doing in the microstate at the previous instant. In other terms, over time the system moves through accessible microstates along a trajectory in the $6N$ phase space that reflects the ceaseless changes at the microscopic level as particles continuously move, collide, and exchange energy. The trajectory is deterministic, that is, we are guaranteed that all systems that sit at the same coordinates in phase space will evolve in exactly the same way [9]. Nonetheless, in the long run, it is expected that all accessible microstates are visited with frequencies that are (approximately) equal because they have the same energy (in an isolated system) or approximately the same energy (in a system equilibrated at a fixed temperature). In fact, although we cannot exclude the fact that the deterministic trajectory is trapped in a vicious circle that leaves out some, or many, of the theoretically equiprobable microstates, the huge number of particles included in a macroscopic system and their consequently immense number of interactions makes this possibility very remote. Thus, an implicit assumption of statistical thermodynamics is that for any isolated system, devoid of physical constraints, there must be full actual access to all the theoretically accessible microstates having the same, given energy, E, and conforming to other thermodynamic constraints, like V, N and the probabilistic distributions of matter and energy across every macroscopic parcel of the system. In other words, eventually the trajectory in phase space must visit all the points in the region representing the accessible microstates of the system with equal frequency [17]. Actually, this is an assumption of perfect randomness of the accessible microstates in the very long run, which is expected to hold whether the universe is either deterministic (that is, the state of the universe along time is fully determined by its initial state) or not; the mixing of the particles is expected to be complete (*i.e.*, with no theoretically accessible combinatory arrangement left out) in any case.

On the other hand, since a microstate's occurrence is not independent through time, some microstates are most probably not accessed because they would require trajectories that lead toward levels of higher and higher available energy (that is, against the increasing intensity of a net force that tends to restore the equilibrium) and then these trajectories have a higher and higher probability of reverting to a uniform energy level. For example, consider the case where most of the particles of a gaseous system would happen to move toward an edge of the system space: this is an instantaneous event that can casually occur; even though it has a very low probability, it is equally probable with respect to other random microstates. If, however, this synchronous behaviour should last for many

CHAPTER 7

The Effect of Temperature

Abstract: Since the features of macroscopic processes derive from the microscopic behaviour of the system's constituent particles, it is shown that temperature, which appears to us as a simple property of macroscopic bodies, is indeed a complex effect of the movement of the body's particles.

Keywords: Boltzmann factor, Dominating distribution, Heat transfer, Increase of entropy, Maxwell-Boltzmann distribution, Non-uniform energetic distribution, Partition functions, Peaked probability distribution of thermal energy, Probabilistic equilibration, Redistribution of thermal energy, Reduction in entropy, Spontaneous change, Uniform spatial distribution.

The entropy of a system increases progressively more slowly (logarithmically) as the number of accessible microstates grows with temperature[17]. So, entropy shows smaller incremental increases as temperature grows. It is null at absolute zero, at least for perfect crystals, which is a common way to state the third law of thermodynamics.

A discrete, irreversible transfer of heat causes a change of temperature and then influences the distributions of thermal energies among the particles of a finite system and of its surroundings (unless they can be considered as infinite) and always results in entropy increase. Since entropy shows reduced increases as temperature grows, an increase in temperature of the coldest between the system and its surroundings determines that the increase of its entropy is greater than the reduction in entropy due to the decrease in temperature of the warmer one. As seen, in an irreversible heat transfer, Q directly flows from a hot body at T_H to a cold one at T_C and the respective gain and loss of entropy for the two bodies are -

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$\delta Q/T_H$ and $\delta Q/T_C$, respectively, and therefore, as $T_H > T_C$, the overall entropy change is:

$$dS_{tot} = \delta Q/T_C - \delta Q/T_H > 0$$

Thus, the transfer of heat from hot matter to cold is a redistribution of thermal energy among particles that can be seen as being driven by an overall increase of entropy. In classical thermodynamics this was the only way to account for the universality of the phenomenon by which heat transfers from hot to cold bodies. Indeed, it is precisely to justify why such a kind of process is spontaneous and irreversible[18] that the concept of entropy as a state function of a system was introduced. Thus, to assert that heat spontaneously transfers from higher- to lower-temperature bodies but never in the reverse direction is just another way to state the second law of thermodynamics. It turned out that an increase of entropy is the drive for any heat transfer as well as a natural tendency that determines many other thermodynamic features of the universe. Indeed, a common formulation of the second law of thermodynamics is "the entropy of an isolated system increases in the course of a spontaneous change: $\Delta S_{tot} > 0$" [25]. In other words, any spontaneous change is always associated with an increase of entropy, and the entropy change is therefore the natural function used to assess the spontaneity of every physical change[19].

Nonetheless, a non-intuitive point in interpreting entropy as a "spreading function" is precisely the increase of entropy with temperature. On the one hand, spatial spreading is an easily comprehensible concept, since diffusion commonly acts to smooth gradients, and this fits well with the idea that maximum entropy of an isolated system occurs when all the microstates have the same probability (that is, they are probabilistically equilibrated to a uniform spatial distribution [8]). On the other hand, however, it is far less clear why the spreading over quantum states of higher energy that occurs when temperature is increased should be a natural tendency. In this case, the idea of "spreading function" appears especially puzzling because, at the equilibrium (at a given temperature), the system does not have a uniform distribution through quantum states (that is, they are probabilistically equilibrated to a non-uniform energetic distribution). In fact, in the case of thermal energy, the equilibration is not to a uniform distribution of the frequencies of particles among energetic levels, but to the Maxwell-Boltzmann distribution, which is peaked. Thus, explaining entropy in terms of spreading and sharing [19, 20] turns out to be a very efficacious metaphor for spatial interpretations, whereas it is more difficult to convey when more nuanced and circumstantial interpretations of “spreading” and “sharing” are intended [26].

In contrast with space, over which a uniform distribution of the particles seems evidently the most probable condition (although gravity affects the spatial distribution of matter), the average thermal energy is constrained to $k_B T$ and therefore its distribution among molecules has to have an average of $k_B T$. This is a key constraint and is related to the first law, as it implies that the internal energy of a system is conserved and the average kinetic energy of the particles is therefore fixed. In addition, the distribution of energy is established by how it can be partitioned over the particles, *i.e.* using the thermal, or momentum, partition function. In statistical mechanics, partition functions are equations that assign probabilities to microstates, in relation to space and energy, and normalize such probabilities so that they sum to one over all microstates [9]. The momentum partition function is the denominator of the Maxwell-Boltzmann distribution:

$$\Sigma_j \, e^{-\beta \varepsilon j}$$

where $\varepsilon j = \varepsilon 0 \leq \varepsilon 1 \leq \varepsilon 2 \ldots$, is the energy of thermal state j = 1, 2, 3, ..., and $\beta = 1/(k_B T)$. This expression defines the way the thermal energy of the system, $k_B T$, is probabilistically partitioned over the different possible thermal states and energy levels[20] in terms of the fraction of particles that occur at each given thermal state[21]. As the momentum partition is a negative exponential function of the energy of the thermal states, it assigns decreasing probabilities to levels of higher energy. This is a second, fundamental restraint on the energy distribution. On the other hand, higher temperatures mean a more even distribution across thermal states, particularly at higher ones. Thus, there is a competition between the number of thermal states, which tends to grow as the state's energy grows, and the probability of higher-energy quantum states, given by Boltzmann factor $\exp(-\varepsilon j/(k_B T))$, which decreases at higher energies of these quantum states (*i.e.*, these states tend to be less populated because of their high energy). In other words, the fundamental distribution of particles to thermal levels is not equal, but

CHAPTER 8

From Nature's Tendency To Statistical Mechanics

Abstract: Some processes happen spontaneously. What, at a macroscopic level, appears as a nature's tendency, is an effect of the complex statistical behaviour of the microscopic particles: their overall net effect emerges at the macroscopic level as a spontaneous force that determines if and how a system can spontaneously change, and if and toward which direction a process is therefore started.

Keywords: Canonical ensemble, Canonical partition function, Crossproduct, Momentum partition function, Phase space, Positional partition function, System configuration, Tendency.

A couple of questions that arise from referring to the entropy increase as a "tendency" are: (i) a tendency toward what?, and (ii) what causes the tendency? As already established, the tendency is toward a more equitable states (however, since the Gibbs expression specifically deals with probabilities, I shall use "equiprobable", *i.e.* equally probable, instead of equitable), but what thrusts matter and energy to reach the condition of equiprobable states? To get the answer to this question requires further delving into the meaning of entropy, and particularly, of microstates. Each microstate is defined by both the way the N particles are physically arranged in the system volume and how their different levels of thermal energy (which are exactly proportional to their velocities, if all the particles are identical) are distributed among the particles. In other words, they are points in a multidimensional phase space, whose coordinates define the spatial localization and the energetic level of each single particle of the system [9, 17]. The phase space is therefore the crossproduct (*i.e.* the mathematical intersection) of a positional partition function (a function that describes the physical arrangement of the particles in the system volume) by a momentum partition

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function (a function that describes the distribution of the particles over the accessible momenta, in practice, their thermal levels). In the overall partition of energy and space the number of microstates is therefore:

$$\Omega = \Omega_m \cdot \Omega_p$$

where Ω_m is the number of accessible momenta and Ω_p is the number of accessible positional, *i.e.* physical, arrangements of the particles [9]. Together, the thermal and positional distributions define what is called the (microscopic) configuration of the system. A configuration is the set of microstates that have (approximately) identical distributions of energy. We will see that this definition is important because the assumption of equal *a priori* probability (approximately) holds even for a canonical ensemble, that is, when just the temperature, rather than the energy, of the system is fixed.

It is worth noting that the mathematical intersection of the positional and energy distributions makes always reference to the most probable distributions for both aspects, that is, the uniform spatial distribution of particles (eventually modified according to a gravitational field or other constraint) and the Maxwell-Boltzmann distribution of particles over levels of thermal energy. Microstates that deviate from these distributions represent, by definition, less probable microstates (as expressed by the Boltzmann factor in the respective partitions). Hence, the probabilities of the Ω_m accessible momenta are not uniform, but are given by the Maxwell-Boltzmann distribution. Correspondingly, the number of accessible momenta, Ω_m, and therefore the overall number of accessible microstates, $\Omega = \Omega_m \cdot \Omega_p$, are always constrained, and therefore limited, by the Maxwell-Boltzmann distribution. In fact, the momentum of each particle is not independent of that of the other particles as altogether they are constrained to E in an isolated system (or to E^*, if T is fixed, as we'll see). Simultaneously, the arrangements of the particles must ensure a uniform density distribution across the system volume. In other words, the crossproduct $\Omega = \Omega_m \cdot \Omega_p$ does not include the complete set of all the mathematically possible combinations. It should also be reminded that, at each instant, the distribution of particles among thermal levels can eventually move away from the Maxwell-Boltzmann distribution, just as the spatial arrangement of the particles can deviate from a uniform distribution, but the overall amount of thermal energy is in any case constrained to $k_B T$ (given the system temperature), just like the number of particles is constrained to N, at least in an isolated system.

Specifically, three possible kinds of deviations from the most probable configuration can occur, for every kind of system: (i) deviations from a uniform distribution of the particles throughout the system (like differences in the pressure of a gas over the internal space of its container), *i.e.* non-uniform positional arrangements; (ii) deviations from the Maxwell-Boltzmann distribution (like an increase of the frequencies of particles at low and high energy levels, which must anyway be symmetrically weighted to leave $k_B T$ unchanged); (iii) an interaction effect, that is, a non-uniform distribution of energy levels throughout the system volume (like inhomogeneities in the temperature of a gas over the internal space of its container). These deviations can either be casual fluctuations or they can be due to constraints. In any case they affect the entropy of the system and therefore, for a system at a given temperature, are considered in the canonical partition function.

The canonical partition function assumes that the microstates over which the macrostate of a system can fluctuate are constrained to T, V, and N, that is, the temperature, the volume, and the number of particles are exactly defined. It is typically assumed that the system is closed, *i.e.* there is no exchange of particles, but it is in contact with a very large bath (the surroundings) that keeps the temperature constant and with which the system can exchange thermal energy. Hence, there can be some fluctuations in the energy of the system that derive from ephemeral transfers from/to the surroundings (so, the macrostate of the system is considered to have temperature T, but it can instantaneously fluctuate over microstates that can deviate from the thermal energy strictly corresponding to T). Actually, the idea is that the surroundings (the bath) is fixed at a given temperature T (and small transfers of energy from/to the system do not affect its temperature because the bath is very large with respect to the system), whereas the system has its energy at equilibrium with the surroundings, but its temperature is not perfectly fixed. The temperature of the system is just kept at T by the equilibration consequent to the exchange of thermal energy with the bath. Indeed, these theoretical conditions are aimed at studying thermal equilibrium. In this sense, it can be useful to remind the reader that whereas the energy of the system

CHAPTER 9

Distributions of Particles and Energy

Abstract: The stability of a system is determined by the overall behaviour of the system's particles. In turn, this behaviour is established on the basis of the natural distributions the particles themselves spontaneously tend to assume. They tend to distribute across space according to a uniform spreading as the most probable outcome, and they also tend to share their energies according to a complex, non-uniform function that is nevertheless probabilistically equilibrated.

Keywords: Accessible states, Boltzmann factor, Classical Hamiltonian, Classical approximation, Configurational integral, Dominating configuration, Energy variance, Indistinguishable permutations, Levelling down energy, Macrostate fluctuation, Microstate probability, Minimum energy, Molecular partition function, Parcels equilibration, Sequence of microstates.

THE PHYSICAL ARRANGEMENT OF INDEPENDENT PARTICLES

To appreciate the probabilities of the distributions of particles and energy it is necessary to consider how energy distributes among particles and how particles actually distribute throughout space. The distribution of energy among particles occurs according to the Maxwell-Boltzmann equation, as we've seen. We are therefore going to see how particles actually distribute throughout space. To this end, it needs to be considered how the space over which particles distribute can be partitioned. Although the partitioning of energy is typically objective since the amount of energy of each particle has been long known to be quantized, that is, it can assume only a series of discrete values defined by Schrödinger's equation [9], the partition of particles over space is commonly approximated in a someway subjective manner and is mostly dependent upon the size of the particles (although, it will be mentioned, an objective quantization of space does seem to

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exist, and should then be a preferable framework for the calculation of the entropy).

It is first useful to consider the positional partition function, even called conformational partition function, in the case of macromolecules, or translational partition function, if we consider it as representing all the positions where the particles can translate to. This function is based on the partition of the system space into small units (typically, they should include only one particle each and therefore they should be of the size of the particles[26]). The positional partition function then considers the positional arrangement of the particles within the partition units in terms of combinatory calculus (as particle present/absent in each spatially localized partition unit, if the particles are all the same, or as permutations of empty/particle A/particle B/… particle Z, if there are more than one kind of particles[27]). In the most simplest approach, we can have a partition function for each given particle: the molecular (positional) partition function, q, which considers all the possible localizations of that particle throughout the system space[28]. If such particle is free to move throughout the system, the partition function for motion in three dimensions is $\mathrm{q} = V/\Lambda^3$, where q is the total number of accessible positional states and Λ is the de Broglie thermal wavelength of the particles, which represents the space occupied by a particle[29] and which, incidentally, decreases with increasing particle mass and system temperature[30] [24]. For the whole ensemble of independent[31] and distinguishable N particles[32], the overall positional partition function[33] can initially be assumed to be just the product of the molecular partition functions of all the particles:

$$Q = \mathrm{q}^N$$

which is the combination of the positional states of all the molecules[34]. However, if all the particles are identical and free to move through space, we cannot distinguish them (or, better, there is no objective reason to distinguish them) and therefore the relation $Q = \mathrm{q}^N$ provides an overestimation of the possible distinct positional microstates (arrangements). In fact, it must be corrected for the number of indistinguishable positional microstates the system can assume[35] (which are indistinguishable because they are obtained by exchanging the positions of identical particles), thus, for indistinguishable independent atoms or molecules, the positional partition function of the ensemble can be better calculated as [24]:

$$Q = \mathrm{q}^N/N! = (V/\Lambda^3)^N/N!$$

The nature of this partition function is evidently probabilistic[36]. It can be envisioned that even if we could, hypothetically, list and track the identical particles in the system so that we could keep a record at every subsequent instant of where each annotated particle is positioned, such a distinguishability would not be based on some objective distinction that systematically and persistently affects the individual properties of the particles; hence, all the microstates that appear identical though they are obtained by, for example, different permutations of the tracked particles, are indeed objectively identical. So, the $N!^{-1}$ correction is necessary because of the indistinguishable permutations that produce objectively identical microstates [17, 24]. It is not due to our incapacity to track particles. Things are very different if, instead, there is objective diversity among some particles that we are incapable of noting. An objective distinction does affect the probabilistic distribution of particles and, therefore, our incapacity of noting it would cause us to underestimate the value of the partition function, and, consequently, the real entropy.

NON-INDEPENDENT PARTICLES: THE CONFIGURATIONAL INTEGRAL

In reality, the positional partition function for the whole system, Q, is directly derivable from the products of the molecular partition functions of each of the single particles only if there are no interactions or joint effects, but this is typically an invalid assumption [25]. Thus, quite often, the statistical properties of the system are not simply the sum of the properties of all its constituent particles (*i.e.* the product of their molecular partition functions)[37], but they must be properly calculated as an average over all the microstates that the whole system can really assume[38] considering all its particles and their momenta together. The Q calculated in this way takes into account all the physical interactions occurring among the particles (such as electrostatic interactions, if the particles have a charge, or weak bonds like hydrogen bonds and van der Waals' interaction, if the particles are permanent or induced dipoles), as well as the effects the molecular partition functions can generate when they are considered jointly rather than

CHAPTER 10

Boltzmann Entropy & Equilibrium in Non-Isolated Systems

Abstract: The microscopic approach of statistical mechanics has developed a series of formal expressions that, depending on the different features of the system and/or process involved, allow for calculating the value of entropy from the microscopic state of the system. This value is maximal when the particles attain the most probable distribution through space and the most equilibrated sharing of energy between them. At the macroscopic level, this means that the system is at equilibrium, a stable condition wherein no net statistical force emerges from the overall behaviour of the particles. If no force is available then no work can be done and the system is inert. This provides the bridge between the probabilistic equilibration that occurs at the microscopic level and the classical observation that, at a macroscopic level, a system is at equilibrium when no work can be done by it.

Keywords: Approximate equiprobability, Approximate isoenergeticity, Boltzmann entropy, Boltzmann factor, Canonical ensemble, Canonical partition function, Dominating configuration, Energetic (im)probability, Equal probabilities, Equilibrium fluctuations, Fundamental thermodynamic potential, Gibbs free energy, Grand canonical ensemble, Helmholtz free energy, Maximization of entropy, Microcanonical partition function, Microcanonical system, Minimization of energy, Temperature, Thermostatic bath.

RELATIONSHIP BETWEEN THE MICROCANONICAL (ISOENERGETIC) AND CANONICAL (ISOTHERMAL) ENSEMBLES

The classical Ω is calculated, for a system at equilibrium defined by given *N*, *E*, and *V* (*i.e.* a microcanonical system), by counting, among all the possible micro-

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states (*i.e.* every possible combination of positions, orientations, and velocities for all of the particles), only the number of microstates whose energy equals E, that is, those that belong to the microcanonical ensemble [9]. In fact, in the microcanonical ensemble, there are absolutely no fluctuations in energy, since it assumes that N, E, and V are constant, so that, by hypothesis, no fluctuations of E can occur over microstates. These microstates are assumed to be equiprobable, and $\Omega(E, V, N)$ represents the microcanonical partition function associated with such a condition [9]. In most real systems, however, the assumption that no fluctuations of E can occur over microstates cannot be guaranteed, because they are not isolated. This is why, in practice, the canonical partition/ensemble, which assumes that N, T, and V, are constant for a system, appears more realistic, since it is quite easy to guarantee the stability of the system temperature by, for example, a large thermostatic bath. In the canonical ensemble the probability of each microstate m is proportional to $\exp(-\beta E_m)$, where E_m is the energy of that microstate, that is, in the canonical ensemble the system visits each microstate with a frequency proportional to its Boltzmann factor [9]. The energy fluctuates in the canonical ensemble, even if only by very small amounts, while it is the temperature that is kept constant by coupling with an infinite heat bath [9]. Note, in fact, that, whereas the internal energy of a system, E, is an exact quantity (whatever the size of the system is) that can be theoretically kept perfectly constant if the system is perfectly insulated, the system's temperature, T, is an overall property that emerges from the statistical average behaviours of all the particles. So, temperature becomes increasingly reliable as a macroscopic property as the number of particles that contribute to determine it gets larger and relative deviations from this average value get smaller. Ultimately, temperature can be considered an exact property only in the limit of an infinite number of particles, that is, in the presence of an infinite thermal reservoir (the heat bath) with which the system (even a small one) is thermally equilibrated.

The fact that, in actuality, the microstates of every non-isolated system are not necessarily all equiprobable would suggest that the original Boltzmann equation, which assumes Ω as the number of microstates the system can access at equilibrium, provides a biased estimation of the maximum entropy outside microcanonical conditions. Specifically, it would seem to underestimate its value since there are many possible (although very improbable) microstates that are excluded [9] because they have higher energies than the one theoretically assumed for the microcanonical ensemble of the system. Indeed, the Boltzmann equation requires that entropy is calculated as $S(E, V, N)$ for an isolated system at equilibrium, that is, the energy, the volume, and the number of particles are exactly defined. However, E can be truly considered constant only if the insulation of the system is really perfect, which is a very difficult task to accomplish. On the other hand, real systems can easily be kept at a given temperature by means of a thermostatic bath, that is, it is easy to keep them in canonical conditions, wherein T, V, and N are fixed, but it is not really possible to guarantee that every microstate of a system has a given, exact energy level, as the microcanonical assumptions would require, since microscopic fluctuations in the system (resulting from microscopic transfers of thermal energy between the system and the bath, or the surroundings, which are in dynamic thermal equilibrium) can alter, even if passingly, this condition. In other words, strictly speaking, microcanonical conditions would seem quite imaginary for most ordinary systems. Nonetheless, it is important from a theoretical point of view to consider entropy under microcanonical assumptions, as $S(E, V, N)$ is a fundamental thermodynamic potential (*i.e.*, all the thermodynamic properties of the system can be derived from it, specifically in terms of its derivative, given the values of the fixed state functions), whereas $S(T, V, N)$ is not [9]. This means that the microcanonical entropy is a much more meaningful parameter than the canonical one, and, for this reason, it should be preferentially adopted for thermodynamic interpretations when possible.

An excellent compromise to these contrasting exigencies (have E theoretically fixed, so that entropy has a deep thermodynamic value, and to fixing the temperature as an actual possibility) is actually obtained thanks to the fact that the peak in the distribution of probabilities of energy levels over the microstates of the canonical ensemble (wherein T, instead of E, is fixed) is so sharp that the probability of energy $\wp(E)$ appears essentially to be one for only a single energy, and zero for all others [9], that is, in the canonical ensemble the system fluctuations occur almost entirely over microstates of energy E^*, the level of internal energy that is determined by the temperature of the system. In other

CHAPTER 11

Entropy Increase as Tendency: Drive and Effector

Abstract: A useful definition of entropy is "a function of the system equilibration, stability, and inertness", and the tendency to an overall increase of entropy, which is set forth by the second law of thermodynamics, should be meant as "the tendency to the most probable state", that is, to a state having the highest equilibration, stability, and inertness that the system can reach. The tendency to entropy increase is driven by the probabilistic distributions of matter and energy and it is actualized by particle motion.

Keywords: Entropy, Equilibration, Stability, Inertness, Most probable state, Spreading and sharing, Tendency.

Although it is clear that the entropy increase is the tendency of both particles and energy to spread spatially from less equitable to more equitable distributions [33], it also needs to be clear that such a tendency is not a teleological function, that is, spreading does not occur with the aim of suppressing non equitable distributions, even though that is a result. Deviations from the most probable distributions tend to be suppressed only because they are less probable, so that the system attains the most probable distributions of particles and energy, since they are most probable, and then tends to mostly fluctuate over the dominating energy configuration.

Thus, the most probable state of a system is determined by the uniform spatial distribution of particles (eventually modified by force fields or other constraints) and the Maxwell-Boltzmann distribution of thermal energies among particles, i.e. the most probable distributions of matter and energy, which are fully combined in the multidimensional phase space. These distributions are the drivers for the function of spreading and sharing, that is, of entropy. This is why, in addition to suggesting that a useful definition of entropy is "a function of the system equili-

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bration, stability and inertness", I also suggest that the tendency towards an overall increase of entropy set forth by the second law of thermodynamics should be meant as "the tendency to the most probable state", that is, to a macroscopic state whose distribution of matter and energy is maximally probable (according to the probabilistic distributions of matter and energy, and also considering the eventual presence of constraints), thus, with time, a system settles into the most equilibrated, stable, and inert condition that is actually accessible. Indeed, Ben-Naim [34] observed that a probabilistic interpretation reduces the second law to a matter of mere commonsense by saying that any system will go from a relatively low probability state to a high probability state.

By these definitions, the fact that in the physical world there is a tendency towards a state that is most probable is at the basis of the concepts of equilibration, stability, and inertness. In turn, it is the existence of the latter (equilibration, stability, and inertness) that allows us to think about a function that measures them. In other words, the second law of thermodynamics is the fundamental, empirical fact from which the ideas of equilibrium and entropy arise. Even the definition of Ω, at the basis of the Boltzmann entropy, implies the concept of accessible microstates; but theoretical accessibility, in turn, implies that the accessible microstates are only those constrained to the dominating configuration, that is to an arrangement of the particles and particles' energies that conforms to the probabilistic distributions of matter and energy across every macroscopic parcel of a system, which corresponds to the condition of equilibration, stability and inertness. So, the statistical definition of entropy actually implies the maximization of entropy, that is, the second law. Indeed, Gibbs [35] noticed the not immediately intuitive nature of "the notion of entropy, the very existence of which depends on the second law of thermodynamics". To state the second law in terms of an universal increase of entropy seems then a circular definition (though it is a self-consistent statement, once its meaning is grasped), whereas stating it as "the tendency to the most probable state" overcomes this trouble.

Indeed, the Gibbs equation underscores that the entropy would be maximal if all the microstates had the same probability, thus that overall equal probability is the real end state toward which there is spreading of energy, as well as of particles. Thus, I suggest specifying that entropy is a function of the tendency for particles and energy to spread to attain equiprobable macrostates over connected systems, that is, macrostates fluctuating over equiprobable combined microstates, which have the most equilibrated probabilistic distributions of both particles and energy given N, V and E or T, and as affected by any eventual constraint. Saying that entropy is a function of the tendency to attain macrostates equiprobable between combined systems is equivalent to saying that every system tends to the most probable macrostate (which is reached at equilibrium), since, as seen, each system can be considered as the combination of its parcels, or parts. Analogously, to say that a system tends to the most probable macrostate is to state that, at equilibrium, it stays at the most probable macrostate, because it fluctuates over equiprobable microstates and therefore does not have any possibility of autonomously increasing its macrostate probability further. In fact, in this condition there is not a single more probable microstate that could be accessed or where the system would be trapped by a greater stability and inertness. The system stays in the most probable macrostate because there is not a better energetic accommodation available, and then there is no force to push it out of such equilibrium. As already seen, equilibration, stability, and inertness are all different aspects of the same physical condition.

Since every large system can be considered to be composed of parcels, if all the macroscopic parcels of the system are equilibrated to the same most probable condition, then they are also equiprobable (in energetic terms, as quantified by the Boltzmann factor), and the whole system is then equilibrated to the most probable state (as a consequence, at equilibrium, connected systems have equiprobable macrostates corresponding to the most probable state of the combined system). This implies the absence of differential effects between the intensive properties of the parcels of the system[52], which occurs only at equilibrium as affected by eventual constraints that can modify the most probable distributions in different parts of the system. Hence, every system that originates from the combination of previously separated systems tends to assume a most probable configuration that minimizes the energy of each of its parts and is uniform throughout all the parts (in terms of probability, and according to the eventual presence of constraints). As the most probable state is the equilibrium one, and therefore all microstates are practically equiprobable, the tendency towards the most probable macrostate

CHAPTER 12

The Probabilistic Driver and the Role of Restraints

Abstract: The probabilistic distributions of matter and energy give the direction toward which processes spontaneously tend to go. However, every existing process is presently in force because of some kinetic barrier or restraint that operated in the past: were it not for kinetic restraints (and constraints that were eventually removed by past processes), all the ongoing processes, and their causal antecedents, had already occurred billions of years ago. The role of constraints and restraints is therefore fundamental to establish the actual direction a real process can take, as well as its velocity.

Keywords: Absolute minimum, Activation free energy, Earth's thermal gradient, Free energy, Kinetic barrier, Local minimum, Metastable equilibrium, Restraints, Stable thermodynamic equilibrium, Thermodynamic equilibrium, Transition state.

Through every spontaneous process, a system ultimately reaches a more stable thermodynamic equilibrium, with an unchanging, maximally probable macrostate and fluctuating microstates, and it will spend a larger fraction of time in those microstates that have a larger probability [34, 37]. As seen, a real system at temperature T fluctuates over the microstates of the dominating configuration, the ones having larger probability, for approximately equal times and eventually over microstates outside of the dominating configuration but with probability that is then approximately equal to zero [9]. Indeed, a thermodynamic equilibrium exists and is reached just because it is the maximally probable macrostate. It is, in fact, implicit in the concept of probability that if a system can be in a microstate that is not very probable, that just means that the system will spend less time in that microstate, and if the system and its surroundings had macrostates with diverse

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overall probabilities, and were not isolated from each other, particles and/or energy would make them equiprobable by spreading[53].

It should be noted, however, that a system may stay for a very long time in a state of metastable equilibrium corresponding to a local minimum of G (the form of energy that is minimized at the stable equilibrium of a closed system at constant T and P and which maximizes the overall entropy), or of a different energy function appropriate for different conditions [9]. This may happen because the energy barrier separating this local minimum from the absolute minimum (corresponding to the most stable equilibrium) can be large enough to be almost insurmountable by random fluctuations in the system [38]. A system that resides at a local, but not global, free energy minimum is said "metastable". The existence of a free energy barrier (actually, a transient state with higher free energy) between a metastable and the globally stable state of the system enables the former to exist for periods of time that permit it to be investigated. Ultimately, however, metastable systems will attain global equilibrium if given infinite time [9]. In the case of rates of chemical reactions, commonly, there is a barrier in free energy (F, if the ensemble is not specified) the system must overcome. This barrier, addressed as $\Delta F^{\ddagger}$, determines how fast the reaction can proceed [9]. The barrier is often called the activation free energy. The state of the system when it is at the height of this barrier is called the transition state (which is the rate-limiting state for a reaction, since this state has the highest energy and therefore the lower probability of occurrence), and it is usually denoted with a superscript symbol "‡". After reacting, if the process is energetically favourable, there will be a net lowering in free energy at the product state [9].

It is even possible for a system to remain in a kinetically-arrested metastable configuration for very long times if the minimization of energy involves extremely slow particle motions (*e.g.*, the deformation of ordinary glasses under the influence of gravity takes centuries) [9, 38]. Every existing process is presently in force because of some kinetic barrier, or restraint, that operated in the past; were it not for kinetic restraints (and constraints that were eventually removed by past processes), all the ongoing processes, and their causal antecedents, had already occurred billions of years ago. Purposeful removal of kinetic barriers (*i.e.* restraints) and constraints is the means by which we can intervene with spontaneous processes (*i.e.*, processes granted by an entropy increase) for shepherding, steering, and channelling them into a desired direction. Indeed, constraints, like the walls delimiting a gaseous system (Figs. **1** and **2**), allow recovery of some energy from spontaneous processes, that is, from entropy increments. By itself, entropy is not a force; it just measures the probability of a state, and therefore the equilibrium of a system, that is, the unbalancing of forces. It is from the unbalancing of forces that we can obtain work.

In the long run, kinetic restraints are responsible of the fact that stars still shine; they will continue to glow until the nuclear reactions that keep them hot are exhausted. A kinetic restraint is also responsible for the persistence of a thermal gradient in the Earth's interior. Although some heat flows from the Earth's interior to the surface and is then irradiated to the atmosphere, the Earth's crust effectively acts as an insulating barrier, thus that quasi-steady-state conditions can be considered to occur for the Earth's thermal gradient [28]. Indeed, the vast majority of the heat generated in the Earth's interior is attributable to the decay of radioactive isotopes within the mantle, and the amount of heat produced by this radiation is almost the same as the total heat emanating from the Earth, which means that the Earth is cooling very slowly. Interestingly, although this radioactivity-linked heat is generated in the mantle, the core is hotter, *i.e.* there is a stationary thermal gradient between the hot mantel and the hotter core. This thermal inhomogeneity of the Earth's interior has been suggested to be linked to the pressure-induced freezing of the metallic fluid of the outer core (which is fluid because the high temperature dominates high pressure) on the inner solid core (which is solid because the very high pressure raises the fusion point above the actual temperature). This is a mechanism that provides latent heat that promptly diffuses through the metallic core and maintains hotter isothermal conditions in the Earth's deep interior [28]. The enlargement of the solid core is due to the fact that, although very slowly, with time the Earth cools and the surface of intersection between the geothermal gradient and the curve of the pressure-induced melting progresses farther from the Earth's centre, causing the inner solid core to grow outwards. The heat thusly generated diffuses much more rapidly throughout the metallic core, which has a higher thermal conductivity, compared to the mantel, which has a low thermal conductivity (*i.e.*, it acts as an insulator). So, apparently because of the different kinetics of thermal transfer in the core and

CHAPTER 13

The Motional Effector

Abstract: According to the second law of thermodynamics every spontaneous change, or process, is associated with an increase in entropy. Although the probabilistic distributions of particles and energy give the possible direction of a process, its occurrence is enabled by the motional energy of the particles. Even particles, however, are subjected to constraints of motion that slow down the attainment of some possible changes and thereby reduce their probability of occurrence, especially if alternative pathways to increase entropy are possible and can be accessed faster. Kinetic restraints are therefore key determinants of which processes are activated among the different possible ones.

Keywords: Average kinetic energy, Constraints of motion, Energy redistribution, Energy spreading, Particles collisions, Particle motion, Zeroth law.

The Maxwell-Boltzmann distribution, by defining the probability distribution of the particles among thermal states (or nondegenerate energy levels), also determines the average level of thermal energy of the particles, which is expressed as $k_B T$. In fact, a single parameter, $\beta = 1/(k_B T)$, determines the most probable distribution of the particle population over the thermal states of the system, and thus the thermodynamic temperature is the sole state function governing the most probable distribution of particles among energy levels of a system at thermal equilibrium [24]. Temperature (multiplied by k_B) represents the overall level of thermal energy that is redistributed throughout all the particle collisions (assuming that collisions are elastic, *i.e.* at each collision the total thermal energy of the colliding molecules is conserved) and is therefore a variable defining the state of the system. In the collisions, there is a tendency for energy to be transferred from

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the faster particles to the slower ones, so the energies even out [1]. In fact, collisions result in the ceaseless redistribution of energy not only between the molecules, but also between the quantum states that each molecule occupies, including their different modes of motion [29]. Temperature determines the motion of the particles and, therefore, it also determines the overall frequency of the collisions in the system. In fact, for a given type of particle, the thermal energy of these particles is exactly proportional to their translational energy (that is, the kinetic energy of the particles), and this energy is in turn proportional to their velocity, which thus is proportional to the thermal energy[58]. At a given (by the combination of N and V) overall density of particles, their average velocity determines the overall frequency of the collisions in the system. Indeed, in the configurational partition function the effect of temperature is included, but, differently from the thermal partition function, in this case the effect is not linked to the distribution of particles through thermal states (or nondegenerate energy levels), rather it has the peculiar role of affecting the probabilities of a system being in the various microstates [1]. Hence, the temperature determines the average translational energy of the particles, which diffuse throughout the space because they have translational energy. In addition, thermal energy causes motion, and particularly translation (at least in the case of fluids at low particle densities), which is the main reason why particles collide. In each collision, the colliding particles share their thermal energies, which are immediately redistributed in a probabilistic manner, thus assuring the transfer of thermal energy (energy spreading) as a function of the motion associated to that energy. Energy spreading is therefore strictly linked to energy sharing.

The collisions determine the sharing of thermal energies from the colliding particles; energies that are afterwards probabilistically divided among the particles that collided, according to the Maxwell-Boltzmann distribution, which is roughly mean-centred. That is, whatever the energies of two colliding particles were, their aggregated energy is redistributed according to a function that gives a maximum probability approximating an equitable repartition. In this way, the populations of states remain almost constant, but the precise identities of the molecules in each state may change at every collision [25]. This is the core mechanism of the tendency for the sharing/spreading of energy. Actually, the Maxwell-Boltzmann distribution is skewed toward higher energies, and therefore the mean speed of the particles is slightly higher than the most probable speed (and hence the most probable translational kinetic energy), but, anyway, the fractions of particles with very high and very low speeds will be very low [25].

Thermal energy, and particularly translational energy, therefore appears to be the cause of particles spreading throughout space and of energy spreading among particles (*i.e.*, sharing). Hence, thermal energy ($k_B T$), and particularly translational energy (at least in fluids, in solids, vibrational motions take a prominent role) is the effector (or enabler) of the tendency toward equiprobable macrostates. In fact, phase transitions from more constrained to less constrained states are accompanied by massive and discontinuous increases in the entropy because during the transition the molecules of solids, liquids, and gases rapidly gain greater freedom to move around, facilitating the spreading and sharing of thermal energy. Notably, in addition to atoms and molecules, spreading and sharing of energy can also be mediated by irradiating photons (electromagnetic waves) and other massless particles. In any case, it is the movement of particles that essentially causes energy spreading, and it is the interaction of particles, collisions, or emission/absorption, that determines energy sharing.

As a consequence to what was discussed above, the increase of entropy at higher temperature is not directly due to the higher average kinetic energy (a tendency to higher energy levels would be a tendency towards an increase in temperature, which is not the case), but it results from the fact that at higher temperatures: (i) the Maxwell-Boltzmann distribution of thermal energy is more spread (toward quantum states of both lower and higher energies); and (ii) the de Broglie thermal wavelength of the particles (Λ), which represents, for an ideal gas, the space occupied by a atom (intended, in quantum mechanics, as the spatial extent of the particle wave packet), decreases with increasing temperature. In fact, with increasing temperatures the wave-packet volume, Λ^3, decreases and the particles have a bit more space over which to spread and arrange in the system volume, and thus positional entropy is higher [19, 20]. So, an energy gain at fixed volume causes gas atoms to increase their possible arrangements (microstates) in the system [19]. This provides an alternative explanation for the work that is lost when the system settles into a new equilibrium state following an increase in

CHAPTER 14

Spreading & Sharing is a Common Outcome of a Physical Function Levelling Down Available Energy

Abstract: Entropy has been defined as a probabilistic function of energy spreading and sharing, and most often this description provides a straightforward way to conceptualize entropy. It is shown that, more in general, the spreading and sharing of energy is a common outcome of a physical function levelling down available energy. The latter, as formulated by a mathematical term called the "Boltzmann factor", originates from the equilibration of forces at the microscopic level and is effected by the net levelling force that results as statistical outcome of all the microscopic forces and that always pushes the system towards the dynamic equilibrium. This net levelling force is the rationale for which work can be done at a macroscopic level, and its derivation from the microscopic world explains why it is linked to equilibration and therefore to entropy increase.

Keywords: Energy dissipation, Free energy, Gradient equalization, Levelling function, Living organisms, Macroscopic homogeneity, Microstates equiprobability, Minimum possible level, Most probable distribution, Spreading and sharing, Unused heat, Work as change.

So far, entropy appears as a probabilistic phenomenon of sharing and spreading of energy, as underscored by Leff [19, 20], and we can therefore continue to use such a metaphor for now. Indeed, in each microstate of the dominating configuration the position and momentum of each particle are equilibrated according to the most probable distribution of matter and energy throughout the whole set of particles of the system. As seen, the fact that microstates with energy

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levels deviating from that of the dominating configuration are improbable is equivalent to the fact that the macrostate shows a distribution of matter and energy that, at a macroscopic level, is uniformly probable throughout the whole system. Any nascent inhomogeneity would be immediately prevented from developing further by the fact that either matter or energy, or both, would tend to flow or spread from/to that part to/from the others. Thus, the fact that the system fluctuates over microstates with probabilities strongly opposed to their energy levels (Fig. **3**) translates into a macroscopic homogeneity for the system in terms of probabilistic distribution of matter and energy, *i.e.* into equiprobability.

The fact that real processes are continuously observed demonstrates that equilibration is ongoing everywhere. Notably, it is exactly the existence of non-equilibrated conditions, or potentially improbable distributions of matter and energy, that allows for the obtaining of work (as stressed in classical mechanics) when (by dissipating some potentially available energy[62]) a constraint is removed. In other words, the tendency towards the most probable state (*i.e.* to equiprobable macrostates, if we consider the process of combining two systems) can be exploited to produce work when the degrees of freedom of a system are increased. If the removal of the constraint is casual, the produced work is aimless[63]; if, on the other hand, the removal of the constraint is purposeful, the obtained work can be functional to some aim. Indeed, an entropy increase is the material cause of any change, but whereas in many natural processes it is also the only cause, in purposeful processes, purposefulness implies that the process could be started or not, at a given time, by choosing the appropriate constraints upon which to act (that is, purposeful choice can be one of the causes of an event, if we assume that free will exists[64]). It is just by coupling opportune processes that can produce some work with other processes that can use at least part of that work, that purposeful changes can happen. Knowledge and choice are then key features of purposefulness, but an increase in thermodynamic entropy is always a fundamental requirement in the realization of every material purpose. Even single processes that, by themselves, are spontaneous can be reversed by coupling them with another process that increases the overall entropy more than the former reduces it. Everyday some fuel must be consumed: to remove heat that has leaked inside a refrigerator, or to put back on the shelf a fallen book, or to put air back into a tire once it has leaked out [1]. More generally, complex systems can exploit existing disequilibria to obtain work for carrying out some function, purposely or not.

It is indeed by this mechanism that, in the current era, living organisms proliferate on Earth[65]: life can be considered as a metastable condition associated with a reduction of the entropy on Earth, since living organisms maintain and multiply as constraints to the free spreading and sharing of their own molecules and energy (*i.e.*, they reduce the degrees of freedom of their matter and available energy). In fact, it has been argued that the source of all the complexity of life might just be nature's tendency to equalize things, and, accordingly, every living system is made to catch, store and degrade gradients [39]. Anyway, life is maintained essentially because of plants' capability to transform some high-energy radiation (sunlight) into low-energy radiation (Earth's infrared emission). Specifically, photosynthetic organisms intercept some sunlight and transform part of it into heat irradiating into the space, and obtain, in this irreversible process[66], some chemical work stored as potential energy in the usable bonds of organic compounds. So, until the sun will emit light, *i.e.* until it will guarantee non-equilibrated conditions, plants will have the opportunity to destabilize the local minimum of energy that constrains solar photons into their high-energy state, thereby producing a larger number of low-energy infrared photons [40]. By thus increasing the degrees of freedom for solar radiation, plants exploit the tendency to the most probable, low-energy state and manage to produce chemical work to maintain life. Increasing the degrees of freedom of solar radiation allows them to decrease the degrees of freedom for some of Earth's matter, although to a lesser extent.

It can be recalled that in classical mechanics the interest is focused on the production of work. Cyclical processes are typically used to this aim. These processes exploit macroscopic discontinuities of matter (*e.g.*, ΔP) or energy, for example ΔT and $\Delta \mathrm{h}$, the latter indicating some difference in the potential energy of an amount of matter subjected to a gravitational field, or other equivalent discontinuities or disequilibria. The maximum yield of work that can be obtained by these processes is proportional to the intensity of the discontinuity (and can be reached only under reversible conditions, assuming the discontinuity is unaffected during the process). An example is a heat engine where the maximum yield of

CHAPTER 15

Changes of Entropy: The Fundamental Equation and the Chemical Potential

Abstract: Any change in the physical world is consequent to a net force levelling down available energy. Different features of a system, or process, can determine on which properties of the system the levelling force eventually operates. Examples are the equilibration of the pressure of a gas, of the temperature of bodies, of the concentration of solutions, of the position of a body with respect to a fluid in the presence of a gravitational field, and so on. All these phenomena occur because of the levelling force and are associated with an entropy increase. The entropy increase can be calculated through specific relationships.

Keywords: Accessible microstates, Chemical potential, Colligative properties, Conjugate pairs, Equal multiplicity, Extensive variables, Fundamental equation, Intensive state functions, Lost work, Multiset permutations, Overall entropy increase, Particles concentration, Reversible change, Saturation, Spontaneous transfer, Standard conditions.

THE FUNDAMENTAL EQUATION FOR THERMODYNAMIC CHANGES IN THE MACROSCOPIC PROPERTIES OF OPEN SYSTEMS

Although the change of entropy in a system, following an interaction with its surroundings (a transfer of heat, of work, or of particles), might be theoretically computed by the change in the number of microstates at equilibrium (in terms of the Gibbs and Boltzmann entropies), it is much more practical to calculate it on the basis of the actual changes in those state functions that are linked to the effective transfer(s) of heat, work, or particles. Correspondingly, the spontaneity of a transfer, specifically, the overall change of entropy associated to it, can be computed in terms of the actual changes in the state functions of both the system

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and its surroundings. The change in the Gibbs entropy toward its maximal value at equilibrium would provide the direct calculation of the entropy increase in terms of the overall increase in accessible microstates, that is, from a microscopic point of view. However, calculating changes in the proper fundamental thermodynamic parameter (like the Helmholtz and Gibbs free energies for the canonical and isothermal-isobaric ensembles, respectively, or PV/T for the grand canonical ensemble) provides a much more comfortable approach to compute, from a macroscopic viewpoint, the entropy changes, since, as previously shown, the two approaches are mathematically linked.

As seen, any transfer of energy or matter is caused by particle motions and its net effect is directed by the probability of the actual distribution of energy and matter in the multidimensional phase space. Every spontaneous change moves toward a macrostate that is overall more equiprobable among its macroscopic parts, and therefore more equilibrated, stable, and inert. Hence, any spontaneous transfer is associated with an increase in entropy, *i.e.* a dissipation of energy, because the overall condition following the transfer shows a better probabilistic arrangement of the system(s). For example, when two isolated systems become connected, they exchange heat if their temperatures differ, exchange particles if their density is not homogeneous, and mix their particles if their compositions are not the same[67]. Thus, the two systems integrate with each other, increasing their overall stability[68] and thereby decreasing their capability of doing work, that is, some potential energy is dissipated. When this happens, the joint system has settled into a probabilistically more stable condition. This adjustment to the overall stability/inertness is what makes the system less capable of doing work, thus that the entropy increase is precisely what accounts for the dissipation of energy, as found by early studies in classical thermodynamics. Again, it must be reminded that various constraints, interactions, and force fields can affect the probabilistic outcome.

From a macroscopic point of view, the changes of the entropy (at a given temperature) of a large system occur because of changes in the macroscopic state functions of the system. For an open system under grand canonical conditions (wherein T, V, and μ are fixed, which can be considered as representative of many real systems), reversible changes occur at equilibrium according to the fundamental equation [9]:

$$\mathrm{d}S = \mathrm{d}E/T + P\mathrm{d}V/T - \mu\mathrm{d}N/T$$

which is based on the macroscopic state functions and summarizes the set of partial derivatives of the entropy changes occurring in a system due to thermal, mechanical, and diffusive processes, respectively[69] (note that the last term becomes $-\Sigma\mu_i dN_i/T$ if more chemical species are present). Likewise other expressions of entropy change, the fundamental equation is expressed in differential terms. As explained when discussing the Clausius' equation, this allows to render the relationships between state functions in a form that is as general as possible and it makes calculations and measurements more straightforward. The signs of the three terms depends on the fact that if heat is added, the temperature must rise, and entropy increases; or if the volume is increased, there are more possible spatial arrangements, and the entropy increases; or if particles are added into a given volume, the system's entropy changes in relation to the chemical potential. How, actually, the system's entropy changes in the latter case is quite complex and deserves some discussion. Nonetheless, since in many ordinary systems the chemical potential is negative[70], the minus sign in the third term of the fundamental equation assures that, in these systems, the higher the chemical potential (*i.e.*, the closer it is to zero and then the lower its absolute value is) the smaller is the increase in the entropy of the system that occurs when new particles are added. Notably, in discrete terms, if particles are added into a given volume, the chemical potential rises [1].

THE CHEMICAL POTENTIAL

It is commonly noted that chemical potential can be seen as the tendency of a substance to redistribute in space, or to react with other substances, or to change physical state, decompose, rearrange, or decay [42]; all these features are indeed derived from the fact that the chemical potential can be basically defined in terms of entropy (and then in terms of spontaneity of change). In fact, chemical potential can be defined as the partial derivative of the system entropy as a function of an infinitesimal change of N at a given T [9]:

$$(\delta S/\delta N)_{E,V} = -\mu/T$$

CHAPTER 16

Instances of Entropy Change

Abstract: Entropy is maximal at equilibrium. According to the fundamental equation this demands that there is equilibration for every specific interaction term, namely, thermal, mechanical, diffusive, and others. Relevant exemplifications are illustrated for a number of important processes.

Keywords: Chemical potential, Concentration, Diffusive interactions, Earth's life, Electron transport chain, Energy sharing, Equilibration, Hurricane heat engine, Intermolecular potential energy, Katabatic wind, Mechanical interactions, Mixability, Mixtures, Potential wells, Snowflakes, Thermal interactions.

EQUILIBRIUM IS THE REFERENCE FOR SPONTANEOUS CHANGES

The second law requires that "when interacting systems are at equilibrium, their total entropy is maximized" [1]. This demands that there is a complete equilibration between connected systems/parcels regarding their (a) thermal, (b) mechanical, and (c) diffusive interactions [1]. So, approaching equilibrium in the absence of specific constraints, as the changes δQ, dV, and dN can occur independently from each other, then the three terms of the fundamental equation must each individually obey entropy maximization and therefore they must equilibrate independently. Specifically, as two interacting systems/parcels approach equilibrium, three possible processes can occur [1]: "heat flows toward the system with the lower temperature, boundaries move toward the system with the lower pressure, and particles flow toward the system with lower chemical potential". That is, "all changes are in the direction that approaches equilibrium" (because of the net force that results from the overall particles motions), and this guarantees that "interacting systems will converge toward equilibrium rather than diverging away from it" [1]. Therefore, for interacting systems at equilibrium [1]:

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(a) their temperatures are equal, (b) their pressures are equal, and (c) their chemical potentials are equal. In addition, the macroscopic distribution of matter inside the system is stabilized according to both gravitational and electrical effects. In fact, at equilibrium, there is no net force to induce any further discrete change, and entropy (stability and inertness) is consequently maximized. This, of course, holds even for the different parcels of a system and therefore, for the different phases of an heterogeneous system [32]. In fact, "thermal equilibrium implies that all phases have the same temperature, mechanical equilibrium implies that all phases have the same pressure, and phase equilibrium implies that the chemical potential of every substance has the same value in every phase" [32]. In addition, when either heat, volume, or particles are transferred, with the other two state functions held constant, what typically happens is that [1]: (a) if heat is added, the temperature must rise, (b) if the volume is increased, the pressure must fall, or (c) if particles are added, the chemical potential must rise. Of course, if more than one term could change at the same time, that is, more types of interaction were allowed at once, there could be relevant interferences between these terms; if heat is added to ice, it melts and the temperature does not change; but it also contracts its volume, so it undergoes both thermal and mechanical interactions [1]. Some instances of entropy change occur independently for each term of the fundamental equation, as described below.

INDEPENDENT CHANGES IN THE EXTENSIVE STATE FUNCTION OF EACH TERM OF THE FUNDAMENTAL EQUATION

The first term of the fundamental equation considers the change in energy of the system for purely energetic interactions (*i.e.*, V and N are constant) and, since thermal energy is the component of internal energy transferred in ordinary processes, this term generally correspond to what we define as a heat transfer, δQ (either in terms of conduction, convection, or radiation). In addition to heat, other forms of energy can be transferred. One example that was already mentioned is the instance of light. High-energy radiation from the Sun to the Earth almost equates to the blackbody radiation of the Earth to space, but the two kinds of radiation differ in their entropy content, the former being a more concentrated form of energy, so that the overall entropy increases in consequence to the change. Assuming that the amount of life on the Earth is presently constant (thus that no new overall energy is becoming accumulated in the living organisms), the overall entropy increase occurring in the radiation is partially used to maintain the low level of entropy associated with Earth's life. So, whereas the evolutionary development of photoautotrophic life can be seen as an accumulation of potential energy obtained by exploiting an energy-density difference (partially analogous with the thermal difference between the hot reservoir and the cold reservoir used in a heat engine to produce work), the present dynamic equilibrium can be seen as a process where a local entropy minimum (life) is maintained at the expense of another local entropy minimum (high-energy photons). Hence, no net entropy change needs to occur on the Earth because of existing life, even though an overall entropy increase, through energy transfer from the Sun to the Earth and then to the space, is continuously needed to maintain the local Earth's life entropy minimum. A local decrease in entropy can instead occur when photosynthetic life spreads onto some dead environment, just like a global (*i.e.*, on our Earth globe) decrease of entropy was occurring while photoautotrophic life was expanding on the Earth, but was always coupled to an overall increase of entropy[75].

The second term of the fundamental equation shows that a change of volume (which corresponds to some work transfer, unless the process is completely free and irreversible) always affects the number of the possible arrangements of the particles, and therefore entropy. Any discontinuity in the equilibrium between the pressure of the system and of its surroundings corresponds to a loss of the work that could be obtained reversibly (Fig. **1**). This means that part of the potential energy associated with a pressure gradient is lost during the process. In general, this term considers processes wherein a mechanical equilibration occurs. In turn, this means that a macroscopic mechanical movement should correspond to a discrete PV work, and then it is only usually employed when the system is contoured by solid walls (either rigid or elastic) and that at least one of these walls moves. Anyway, the presence of walls is not always necessary; for example in the atmosphere, air circulates in large masses, and since it is a very poor conductor of heat, its temperature strongly depends on the altitude, as its pressure decreases with height and therefore, when moving upwards, it expands because of the reduced pressure and cools almost adiabatically. Thus, even though a large mass of air has no walls, it does PV work on its surrounding atmosphere, virtually

CHAPTER 17

The Limits of the Spreading and Sharing Metaphor

Abstract: Some phenomena, though representing instances of entropy change, appear to defy the description of entropy as a function of energy spreading and sharing. Despite its great utility such a description is sometimes difficult to apply because a function levelling down available energy not always exactly acts as a spreading and sharing function. The concept of a physical function levelling down available energy is therefore preferable to understand entropy and the second law of thermodynamics because it has a more general value.

Keywords: Basal energy level, Boltzmann factor, Dissipation of discontinuities, Energy levelling function, Free energy, Macrostate probability, Maximal state probability, Minimal ephemeral deviations, Most probable state, Spreading and sharing, System parcels, Tendency to levelling.

The spreading and sharing function [19, 20] is a useful metaphor that has been conveniently used throughout the previous parts of this discussion. It should nonetheless be clear that some spontaneous processes (*e.g.*, the various phenomena of phase separation, like the formation of a precipitate in saturated solutions, the equilibration of a system to a multiphase state, the genesis of snowflakes, as well as self-assembly processes, including the tendency of surfactants to form micelles, or the hybridization of complementary DNA strands into a double-helix structure) are associated with entropy changes that are not linked to an evident spreading and sharing function (at least in the common sense; spreading and sharing of matter and energy intended with an actual variable meaning according to the condition that for each specific instance turns out to maximize the entropy is always true, but this is a circular definition of entropy).

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So, the latter appears to be a metaphor that is generally good, but not always valid, although there is an implicit vagueness in meaning that allows it to conveniently be adjusted to different circumstances. Nevertheless, "spreading" and "sharing" are likely to be given primarily spatial interpretations [26]. On the other hand, what every process, included the ones eluding to the idea of a spreading and sharing function, spontaneously does, is to tend to equilibrate to the most probable macroscopic state, which is defined by the combination of probabilistic distributions of matter and energy. Our reliance on these distributions is derived from experience and is, in turn, empirically based on the assumption that the microscopic state of a macroscopic system, or parcel, tends to stabilize uniformly at the basal level of energy identified by the state functions of the system (Fig. **3**). In other words, entropy can also be seen as a function that maximizes the state probability by minimizing the ephemeral, local deviations in the energy of a system from the basal level of internal energy. In the same way, this function levels the energy of different systems when they are combined into a new, single one. In this sense, the Boltzmann factor operates as a function for levelling down the energy of any parcel of the system (Fig. **3**) as well as of any combined system, and therefore it is the fundamental operator that assigns a probabilistic weight to each possible microstate in the canonical partition function[79]. In fact, the second law implies that at equilibrium E is minimized throughout the system (at constant S, V, and N_i conditions) with respect to any internal perturbations of the system, or unconstrained internal degrees of freedom [9].

On this view, the maintenance of inhomogeneities in an equilibrated or quasi-static system, like the equilibration to a biphasic state of two chemical species or to a less dispersed state of a single species (from gaseous to liquid to solid, depending on the temperature), should be seen as a consequence to the maximization of the entropy (minimization of the deviations from the basal level of internal energy)[80]. In these cases, the minimization of the otherwise large potential energy for a uniform distribution of particles overpowers the increase in the potential energy associated with the inhomogeneities of the system.

Notably, as seen, minimizing the local, ephemeral deviations of the energy from its basal level of internal energy includes the dissipation of macroscopic discontinuities that can arise when a constraint is removed [34] (Fig. **2**), thus this definition provides a straightforward bridge between statistical and classical mechanics. Since the tendency to the most probable state is a tendency for energy levelling (this is how the Boltzmann factor works; (Fig. **3**)), the second law can be seen as saying that "any isolated system spontaneously tends to equilibrate at an uniform level of energy, saved the effect of constraints". In fact, it is just the levelling of the energy associated with a gradient that represents an increase in entropy and the wasting of potential work (intended as available energy) for any irreversible process (Figs. **1** and **2**). Correspondingly, in isolated systems the stability point is found at the maximum value of entropy or, for other kinds of thermodynamic systems, in configurations of minimum free energy, where the relevant free energy function has to be decided based on the state functions that have been hypothesized to be fixed in the studied system [9, 14]. As a matter of fact, more-probable macrostates are associated with lower free energy, whereas less-probable macrostates are associated with higher free energy [14]. Of course, that's true of the corresponding microstates.

It can be further noted that, once it is constrained within the limits of the system, the net effect of the levelling function (as shown in Fig. (**3**)) is levelling the internal energy of the system to its basal level. This is the effect picked up by the Boltzmann entropy in terms relative to the energy of the considered isolated system, that is, such an expression is focused on the equilibration inside the system. However, in absolute terms defined by the canonical partition function, the energy of the whole system is evidently still subjected to a levelling function (Fig. **3**) that can actually operate only if the system is no longer isolated. This highlights why changing the focus of the expression used to calculate the entropy also changes its calculated value. Actually, the Boltzmann entropy could be better understood by saying that $S \propto \ln \Omega$, which highlights that entropy, at equilibrium, is proportional to the number of microstates, *i.e.* it is an extensive property because it depends on the combinatory distribution of the particles in the available space, and, more generally, it is maximized by extending in phase space the region corresponding to the system's macrostate [46]. Indeed, Boltzmann did not even give thought to the possibility of carrying out an exact measurement of the proportionality constant [47], and therefore of the entropy. He rather meant to show entropy increases monotonically as an isolated gas evolves from non-

CHAPTER 18

Some Special Instances of Entropy Change

Abstract: A few particular phenomena are quite difficult to frame into the fundamental equation, nonetheless they can be interpreted to the light of the general idea of statistical mechanics that any system and any overall change tend to the most probable state, *i.e.*, a state that is microscopically equilibrated and then macroscopically stable.

Keywords: Correlational behaviour, Deassimilation, Distinguishability of particles, Isomers, Most probable state, Natural patterns, Spontaneous separation, Whirl.

Some reactions that increase entropy are difficult to frame in classical terms, although they are well described at the microscopic level by statistical mechanics. For example, a change in the extent to which molecules are distinguishable can be induced in a system [48] so that it increases the number of accessible positional microstates (*i.e.* the number of distinguishable spatial arrangements of the molecules): if, in a thought-experiment, a catalyst was introduced into a system and caused a spontaneous interconversion of the molecules from pure optical isomers into a racemic mixture [48], the reaction is driven by an increase of entropy that can be seen as an expansion of the phase space in terms of more positional coordinates, since the volume becomes available for two different species of particles in place of the single one previously present. Hence, doubling the chemical species doubles the dimensionality of the phase space, at constant total N. Since the catalyst[81], for which a negligible direct effect on the system entropy should be assumed, is expected to diffuse through the system, then the increase of entropy could be seen as a particular case of the second term of the fundamental expression for entropy changes, wherein an isobaric filling of the available volume occurs by the partial "deassimilation" [48], or appearance, of the

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new species from the original one, rather than by a more obvious increase in the volume. More exactly, it is the hyper-volume that increases; it depends on the greater combinatory distribution of the particles in the available volume.

Although in chemistry the studied particles are typically atoms and molecules, in high-temperature physics nuclear reactions are considered and the particles are sub-atomic. The highest temperatures occurred at the beginning of the Big Bang, and this made the initial entropy of the newborn universe already quite high. Nevertheless, the entropy of the universe is always increasing since those highest temperatures caused an expansion force that overwhelmed the gravitational force (although it was immense) in a practically adiabatic free expansion (explosion) that is still ongoing and that increases the volume and therefore the entropy of the universe. However, at the same time, the universe cooled off, dampening the entropy increase. The fact that stars and planets formed is just a consequence of the equilibration of matter distribution at the decreased temperatures, which are no longer enough to overcome local gravitational fields. At the same time, with the enormous distances that matter has spread, the overall gravitational effect seems to be too weak to be reverted, just like in a supernova the outer matter is expelled at a speed beyond the escape velocity and gravity cannot pull it back. Notably, the decrease in temperature for the expanding universe has not been caused by work counteracting an external pressure, in fact it is a free expansion, but rather it was consequent to the internal work necessary to overcome the immense gravitational force of its huge mass. In any gravitational field, work has to be done to move a mass outward from the centre of the field (like a weight that has to be lifted up). In this case, the whole mass of the universe was moving outward from its centre owing first to the translational motion of the particles and then to the centrifugal motion of galaxies, into which particles had condensed. So, the particles of the expanding universe gained gravitational potential energy and lost kinetic energy because they used work to drift away from the gravitational centre. In addition, it can be speculated that part of the very initial energy was converted into particle mass to form elementary particles, including quarks and then electrons and protons and, later, atoms and molecules. Since this was a spontaneous phenomenon, given the constraints of sub-atomic forces, it must have represented an increase in entropy as well. In addition, a kind of deassimilation occurred, that is, the appearance of many new species of particles. Even earlier, the second law of thermodynamics possibly selected the number of dimensions in the universe [49].

There are, however, processes that are probabilistically improbable and are therefore associated with negative changes in the overall entropy; for example, a whirl of particles typically does not occurs spontaneously because it would require the synchronous, correlated behaviours for particles to generate a macroscopic effect. After a cup of milk is mixed with a spoon, it spontaneously stops swirling in a relatively short time. Clearly, turbulences tend to dissipate some mechanical energy of the whirl as heat, and the centrifugal force causes a corresponding gradient of milk level in the cup that is levelled down under the force of gravity. For the same reason, in an ideal gas, the particles are expected to randomly deviate from a rotating flux if there is nothing to cause this behaviour. The value of energy to be included in the Boltzmann factor for microstates of this kind of configuration corresponds to the work reversibly obtainable from such a swirling. Something analogous would be the casual, spontaneous separation of hot and cold particles in the cup of milk, to generate a thermal gradient that could be exploited by a heat engine. These types of processes represent highly improbable events corresponding to the transformation of random motion/distribution into correlational, synchronous ones. If they should become macroscopically persistent, this would represent an actual reduction of the number of microstates of the system (maintaining a rotating whirl, or a temperature gradient, would require that some parcels of the system had less possible combinations of either motion direction or kinetic energy with respect to the whole set of combinations actually available if those parcels would have access to all the set of a particle's directionality and kinetic energy present in the system), and therefore to a decrease of overall entropy. As singularities, these phenomena would not be violations of the second law of thermodynamics; this law merely states that they are extremely improbable and ephemeral, so that, in the long run, they must be exceedingly rare and actually unobservable in practice. The assumption of *a priori* equal probability means we feel confident these phenomena are so improbable we can safely keep ignoring them.

Some systems show inhomogeneities that seem improbable, but are maintained by

CHAPTER 19

Quantization

Abstract: Entropy quantification can be performed under the assumption that both the position of a particle in space and its level of energy can be defined as corresponding to one among many enumerable states, even if their number is hugely high. This means that, if absolute values of entropy have to be computed, neither energy nor space should be continuous variables, even though entropy changes can be calculated in any case. Remarkably, quantum theory just says that's the case, because at a very short scale both energy and space seem to behave like discrete quantities rather than as continuous ones. So, a general string theory, which represents the evolution of quantum theory, appears to be the natural, preferable theoretical framework for the definition of entropy.

Keywords: Absolute entropy values, Continuous distributions, Classical approximation, Enumerability of microstates, Process directionality, Quantum mechanics, Reversible processes, String theory, Wasted work.

A further difficulty in conceptualizing entropy is that the expression for the value of the absolute entropy involves counting microstates through space and energy levels. As seen, the classical approximation to high-energy macroscopic systems that shows continuous distributions of matter and energy provides a valid estimation of the number of microstates supposedly present in the microcanonical ensemble that is theoretically associated with a system. Thus, the value of the classical, continuous canonical partition function is assumed to provide the value of entropy; however, this is strictly true only for the measures of changes in entropy, whereas the absolute value of entropy is only postulated to be that obtained by these calculations [1, 9]. Indeed, in the continuous terms of classical statistical mechanics, the entropy is indeterminate to the extent of an additive constant because of the arbitrariness associated with the calculation of Ω [6].

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If we consider that the Gibbs equation, like the Boltzmann equation, requires that the number of microstates is enumerable and finite, whereas the localization of a particle in a continuous space, and hence its velocity, can assume an infinitive series of values (independent of the fact that a measurement of the number of microstates can be in anyway computed by adopting an approximation of choice), it could be deduced that either the actual absolute entropy always has an infinite value (at $T > 0$ K), or that the space, as well as the states of thermal excitation, must be quantized. The latter option is just what is established by quantum physics, and string theory [52] provides an elegant interpretation of space quantization by considering it as a fabric of strings along which quantum energy waves spread (or clump in wavepackets, *i.e.* particles of matter), embedded in an empty nothingness (which is continuous and therefore inaccessible to quantized matter and energy). As remarked by Fermi [6], in a statistical theory based consistently on the quantum theory, all indeterminacy in the definition of Ω and therefore in the definition of entropy, disappears. So, a general string theory is expected to provide an objective quantization of space and then it would be the preferable framework for the definition of entropy. Indeed, the Gibbs entropy has extended to the field of quantum mechanics with the formulation:

$$S = -\mathrm{tr}(\rho \ln \rho)$$

known as the von Neumann entropy [53], which is essentially equivalent to Gibbs entropy, but introduces the density matrix, ρ, characterizing the quantum state of the system in the place of the classical probability, $\wp_m$, and quantifies the degree of mixing throughout the quantum states [53].

As mentioned, even if in classical thermodynamics we cannot have an absolute entropy, thus any measurement of the number of microstates involves an approximation of choice and therefore any calculated value of entropy includes an unknown reference entropy value (which is commonly assumed to be zero by convention, for the sake of simplicity), still we can compare relative numbers and hence obtain valid ratios between the number of microstates and therefore actual entropy differences. For example, if a system with volume V and containing a single particle is expanded to $2V$, the number of microstates doubles such that the entropy change of the system is [9]:

$$\Delta S = k_B \ln(2V/V) = k_B \ln 2$$

So, even if in quantum mechanics we can redefine the entropy to obtain an absolute value for this variable, no physical changes in the equilibrium behaviour of the studied systems would follow, nor would a single physical property or behaviour be affected. Indeed, there is no theoretical constraint preventing a definition for entropy that includes a nonzero value for the unknown reference entropy value [9].

It is worth noting that the quantization of matter, energy, and space also has an effect on the conceptualization of reversibility. Since, in reality, any transfer of matter or energy happens in tiny but discrete amounts (*e.g.*, one molecule at a time; (Fig. **2**)), rather than by mathematical infinitesimals, therefore any real equilibrium takes place in a finite time and even a truly reversible process can occur in a finite time (the infinite number of steps is just a mathematical exigency, since real numbers are not quantized). What really distinguishes reversible processes from irreversible ones is the directionality of the process: indefinite for the former and definite in the latter (and, of course, an overall change of entropy equal or greater than zero, respectively). Therefore, any process that has a direction involves some wasting of work. This is why two additional, equivalent versions of the second law are that "no real process can occur with a 100% efficiency", and that "any real process involves some transformation that reduces the overall available energy, that is, the potential work". Of course, both refer to a real process intended as something that has a given, spontaneous direction; any transformation that occurs at equilibrium conditions does not have a spontaneous direction and is therefore perfectly efficient (though doing nothing that is utilizable).

CHAPTER 20

The Role of Probability in Defining Entropy

Abstract: As a probabilistic law, the second law of thermodynamics needs to be conceptualized in terms of the probabilities of events occurring at the microscopic level. This determines the probability of occurrence for macroscopic phenomena. For the best comprehension of this approach, it is necessary to distinguish between "probabilities", which are subjective predictions of an expected outcome, and "frequencies", which are objective observations of that outcome. This distinction is of help to unravel some ambiguities in the interpretation of the second law of thermodynamics.

Keywords: Boltzmann factor, Equal probability, Equiprobability, Frequencies, Gibbs entropy, Isofrequency, Knowledge subjectivity, Maximum entropy, Observation of facts, Predictions, Probabilities, Quantized space, Subject's uncertainty, Temporal spreading.

Defining the tendency for an overall increase of entropy as the spontaneous tendency to the most probable macrostate implies, specifically, the adoption of the concept of probability in the explanation of a physical property of the universe. Since explaining is commonly intended as an effort to reduce a difficult concept to more primitive, elementary concepts, it is imperative that the idea of "probability" be adequately clarified, since, unfortunately, there is even some debate about its nature. In fact, there are at least two different ways to look at "probability": either as an objective feature of reality, or, rather, as a subjective formulation of the subject's uncertainty about reality [8, 43]. The former view is typically adopted by frequentists, who see probability as an actualized expression of the relative frequency over time of each element in a set of possible outcomes

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occurring in a given experiment, holding the overall conditions unchanged. It is immediately evident that, if the experiment is what happens in a closed system at equilibrium, probability is the relative frequency over time of each microstate out of the possible ensemble of microstates of that system. As for frequentism, however, a practical hindrance occurs immediately: frequencies can randomly fluctuate around a limit value, thus they are trustworthy only when they attain that limit, that is, only after an infinitely long time of observation. This means that we can be absolutely sure about the actual frequency of an outcome in our experiment/system at the end of the universe, perhaps. It appears to be a quite impracticable approach. Nonetheless, if we have an adequate knowledge of the experiment/system (typically including some observation of frequencies over a discrete time and a reasonable theoretical explanation of what's going on), we can feel able to predict the frequencies of occurrence for the different outcomes (microstates) over time. In other words, we feel we can actualize frequencies over time as present probabilities. This, yet, cannot be obtained without a price. Whereas frequencies would be physical events ascertainable by every competent observer, that is, they are objective facts, probabilities are a prediction of those still unobserved frequencies based on theoretical considerations. They are therefore valid estimations of frequencies if and only if our assumedly adequate knowledge of the experiment/system, and our theoretical considerations based on such knowledge, are really adequate to anticipate them[83]. It is easily recognizable that we cannot be absolutely sure if our knowledge is adequate; in fact, knowledge of experiments/systems widely varies among subjects and some of them can think their own knowledge is adequate while others think the former subjects are totally wrong for trusting in their own knowledge. In other words, knowledge is clearly subjective and certainty is even more so (this is especially evident for the correctness of theoretical considerations). Therefore, frequencies are observable facts about an experiment/system assumed as independent of any observer (apart from considering the Heisenberg's uncertainty principle when they are observed/measured), but probabilities are predictions and are therefore dependent on the experiment/system as much as on the predicting subject. By moving from frequencies to probabilities we gain the possibility of evaluating the experiment/system now, but we give up the full objectivity of the observations. In other words, we assume the risk of being wrong, inexact, or approximate.

However, it is an objective fact that probabilities provide a representation of the reality that is as much objective[84] as the assumptions we used to calculate them do correspond to reality and are exhaustive.

One of the most important assumptions we do in calculating the entropy is assuming the Boltzmann factor truly represents the probability of the corresponding microstate (or configuration) and in any circumstance, that is, either when spatial, thermal, concentration, or intermolecular effects are involved. That all these different aspects can be brought back to the same probabilistic term is a striking feature of our universe. At least, we feel very confident that it is.

As noted above, the subjective formulation sees probability as the subject's uncertainty about reality. Specifically, in statistical thermodynamics, assigning probabilities to the microstates seems not to be really linked with our uncertainty about the real occurrence of a specific microstate at present or at some future, or past, time, but it rather appears more a method to cope with uncertainty in the frequencies of microstates over time. Anyway, uncertainty about states through time (we feel it particularly for future time) is always a feature that characterizes probability. In fact, the uncertainty regarding a sequence of events occurring along time and the uncertainty about an event of the sequence occurring at a given future time are two equivalent instances: the uncertainty about what event occurs at each time is just what renders it impossible to know the sequence of events along time. This is always true, whether the universe is deterministic (that is, the state of the universe along time is fully determined by its initial state) or not. If it is deterministic, then our uncertainty about the exact state of a system at a given time means that we merely do not know, or we are not able to calculate, the exact state of the system and its evolution; if the universe is not deterministic, our uncertainty means that the change in the state of the system through time cannot be calculated at all.

Ultimately, a fully objective definition of the tendency towards an overall increase of entropy, and therefore to an equilibrium state, is "the spontaneous tendency to fluctuate almost only over isofrequent microstates"[85], that is, an isolated system is eventually moved to equilibrium by not-yet balanced forces, and then it essentially fluctuates over microstates that have very similar frequencies of

CHAPTER 21

Outlines of a Verbal Account of the Thermodynamic Entropy for a Pedagogical Approach

Abstract: Starting from the observation of spontaneous phenomena, it can be envisioned that, with time, every isolated system tends to settle into the most equilibrated, stable, and inert condition. In the very long term, this is the most probable state of a system. This can be shown to be a universal law, the second law of thermodynamics, defined as "the tendency to the most probable state". Thereafter, it is intuitive that "a function that measures the equilibration, stability, and inertness of a system" is maximized by the second law. This function is called entropy.

Keywords: Boltzmann factor, Deviation from equilibrium, Dissipation of energy, Energy conservation, Entropy, Free energy, Intensive state functions, Levelling of energy, Macroscopically available work, Meaning of expressions, Microscopic dynamic equilibration, Microscopic forces, Net statistical force, Particles motions, Potentially available work, Probabilistic distributions, Settlement of systems, Second law, Thermodynamic stability, Waste heat, Wasting of work.

Entropy, among other concepts in thermodynamics, is considered to be an abstract concept that is difficult for novices to grasp [26]. Indeed, students (as well as educated laymen) may have difficulties interpreting physical meaning from mathematical expressions [54]. On this regard, Sears [55] claimed that: "There is no concept in the whole field of physics which is more difficult to understand than is the concept of entropy, nor is there one which is more fundamental". Further-

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more, though thermodynamics is central to our understanding of physics, chemistry, and biology, in most cases these three disciplines treat the topic in distinctly different ways [56]. Therefore, at present, education research has come to focus on understanding how to better teach issues in thermodynamics, drawing across disciplinary boundaries [56]. A number of papers have addressed the teaching of thermodynamics and statistical mechanics, with some trying to spark more interdisciplinary interaction [56]. However, there is little evidence that the research is making progress in this arena [56].

I suggest that, in every context, the concept of entropy can be best introduced by first noting that with time every isolated system settles into the most equilibrated, stable, and inert condition (because of the overall effect of particle motions that tend to counteract any unbalancing of forces). Therefore, this can be shown to be a universal law, known as the second law of thermodynamics and defined as "the tendency to the most probable state", that is, to a macroscopic state whose actual distribution of matter and energy is maximally probable according to the theoretical probabilistic distributions of matter and energy, and also considering the eventual presence of constraints. The probabilistic distributions of matter and energy represent the direction and determine the intensity of the equilibration forces (they are the drive of the observed tendency), and the motions of the particles enable the equilibration forces (they are the effector of the tendency), and therefore they actually push the system into a state of microscopically dynamic equilibrium that corresponds to a macroscopically stable condition.

Since the Boltzmann factor identifies a universal function of energy levelling (which applies to all the intensive state function, namely temperature, pressure, chemical potential, and so on) that rules the state of every system and connects the microscopic and macroscopic levels of the system, then the most probable state is the most energetically equilibrated, stable, and inert state that is actually accessible at the given conditions. Such a macroscopic state implies the minimization, at the microscopic level of dynamic equilibrium, of the frequencies of the microstates wherein parcels (or subsystems) have energy higher than the basal, equilibrium energy. Emphasis should be given, here, to the fact that the overall level of energy is conserved throughout any process (first law of thermodynamics); what changes is rather the distribution of energy and matter (which, indeed, is a constrained form of energy as well).

The levelling function identified by the Boltzmann factor measures any overall unbalancing of microscopic forces, that is, differences in one or more intensive state functions between systems, as well as analogous inhomogeneities within a system. As any unbalance results in a net statistical force that is potentially available to do some kind of work, the levelling function corresponds to available energy (or free energy, that is, energy that is available, or free, for doing an equivalent amount of work). In fact, any unlevelled distribution of energy (like gradients, discontinuities, or inhomogeneities) represents an unconstrained difference of energy, ΔE, that can be subjected to "extraction", that is, the ΔE is potentially available for doing work and it is then called "available energy" (which, in the most common conditions is quantified as either Helmholtz free energy, Gibbs free energy, or PV/T). This available energy is always and only obtained as a deviation from equilibrium conditions, and therefore it represents, by definition, an imbalance in the microscopic forces, caused by the motions of the particles, that results in a net macroscopic force. If not used, or in proportion to the available energy that is not used, this force determines a spontaneous levelling of the internal energy (*i.e.*, the net force pushes the system toward equilibrium, minimizing itself), in any of its various forms (thermal, mechanical, chemical, and so on), and the previously potentially available energy is thereby dissipated. In other words, it can no longer be "extracted" (although the overall internal energy is, of course, conserved). As said, the motions of the system's particles are ultimately responsible for doing the work or dissipating the energy.

By identifying the causal connection between the macroscopic properties of a system and the microscopic particles that constitute it, the Boltzmann factor represents the key mathematical and conceptual function that links microscopic dynamic equilibration (statistical mechanics) with macroscopic equilibrium and available work (classical thermodynamics and mechanics), and also explains why they exist at all.

Quite often the loss, or dissipation, of available energy, which is a wasting of work, causes an increase in the thermal energy of the particles (typically by friction or turbulence), which diffuses to the surroundings as waste heat (which means energy is conserved, but transformed into a less utilizable form; it is less utilizable just because its distribution is more probable). Concomitantly, this

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SUBJECT INDEX

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