The Easiest Way to Grasp Entropy

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Introduction

Despite its fundamental importance, the concept of entropy remains widely misunderstood. This article aims to clarify the concept simply and intuitively. The second law of thermodynamics, which asserts that entropy never decreases in an isolated system, is often regarded as a universal principle. In this work, we examine the physical processes underlying this law to reveal its true nature. With this understanding, it becomes evident that the second law is not as universally valid as commonly believed, since entropy can, in fact, decrease in many situations. Finally, we explore the distinction between the classical definition of entropy and that derived from statistical mechanics—two formulations long assumed to be equivalent.

An Intuitive Explanation of Entropy

In classical thermodynamics, the entropy change of a system is defined as an infinitesimal amount of heat transferred from the surroundings to the system during a reversible process divided by the instantaneous temperature of the system during the transfer:

$$dS = \frac{dQ}{T} \tag{1}$$

Here, T is the absolute temperature of the system, S denotes the entropy, dQ represents the heat transferred, and dS indicates the resulting change in entropy due to the heat transferred into the system. This definition only describes the change of entropy, but not the nature of entropy itself.

To understand the nature of entropy, let us consider a gaseous system of mass m with a constant specific heat capacity c over a small range of temperature to simplify the discussion. Under these assumptions, the entropy defined in Equation (1) can be expressed in terms of the temperature change resulting from heat input:

$$dS = \frac{dQ}{T} = \frac{mcdT}{T} \tag{2}$$

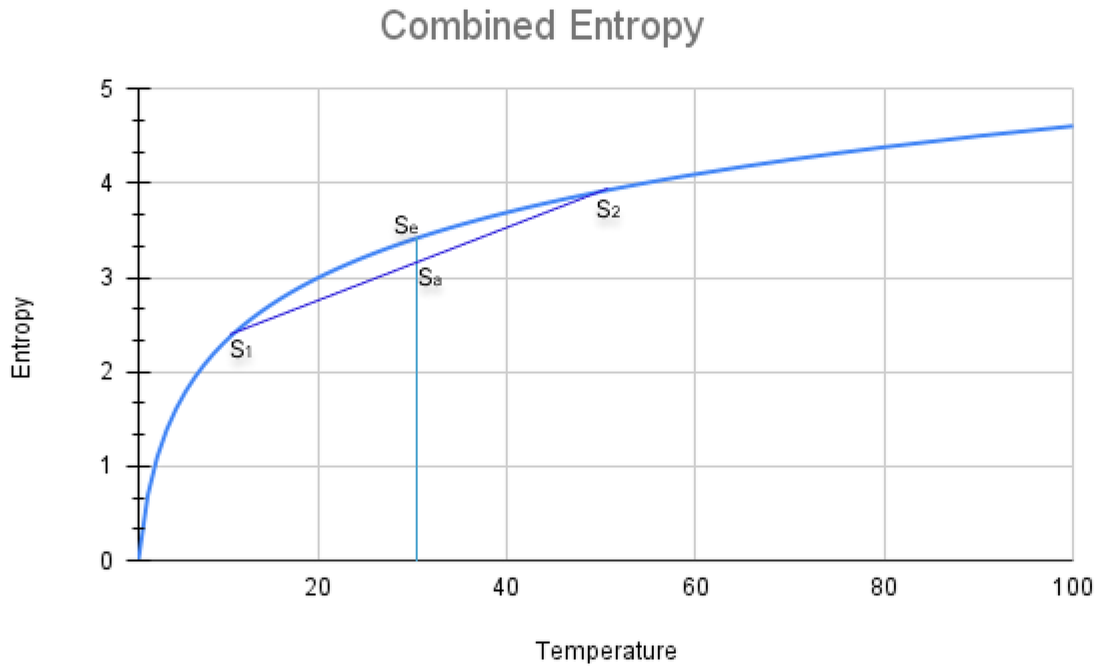
Integrating this equation over a temperature range from T_0 to T, we found:

$$S = mc\left(ln(T) - ln(T_0)\right) \tag{3}$$

Here, T_0 represents the starting temperature, which is treated as a constant in this example. By choosing the starting temperature at 1 K and combining the constant terms, the equation can be simplified as follows:

(4) $S = kln(T)$

In this equation, k is a constant. The expression shows that the system's entropy S at equilibrium increases in proportion to the logarithm of its temperature T as heat is added, as illustrated in the following figure.



In other words, as heat is added to a system, its temperature increases, and the entropy also rises—but, more importantly, this increase occurs only on the logarithmic scale of temperature when the system reaches equilibrium.

The Physical Nature Expressed by the Second Law of Thermodynamics

The simplified system discussed above offers valuable insight into the concept of entropy without sacrificing generality. Consider, for instance, two systems of equal mass but with different temperatures and initial entropies, S_1 and S_2. The average entropy, S_a, represents the initial entropy of the combined system. As the two systems interact and exchange heat over time, the total entropy at equilibrium becomes S_e. As illustrated in the figure, the entropy of the combined system at equilibrium is always greater than the average of the two initial entropies, demonstrating the directional evolution of a system as dictated by the second law of thermodynamics. In essence, entropy change within an isolated system is driven by the uneven distribution of energy, reflecting the natural tendency for energy to evolve toward a uniform distribution at equilibrium.

This directional trend of entropy increase is not limited to the specific example above but reflects a more general phenomenon. Consider two systems with temperatures T_1 and T_2, where $T_2 > T_1$. When these systems interact, a quantity of heat dQ flows from the higher-temperature system to the lower-temperature one. According to Definition (1), the total change in entropy of the two systems is given by:

$$(5) \qquad dS = \frac{dQ}{T_1} - \frac{dQ}{T_2} = \frac{dQ}{T_1 T_2}\left(T_2 - T_1\right) > 0$$

Since $T_2 > T_1$, the total entropy of the combined system always increases, indicating that the system naturally evolves in the direction of increasing entropy. The system reaches its maximum entropy at equilibrium, where its energy—including the distribution of matter—is completely uniform. If the system has not yet reached this maximum, it will continue to undergo internal evolution until equilibrium is achieved. A system in equilibrium is not devoid of internal changes; rather, its entropy no longer increases. In other words, a system with an uneven energy distribution must be in a nonequilibrium state, with entropy below its maximum value. Conversely, a system that has reached maximum entropy must be in equilibrium. Therefore, the tendency toward entropy maximization describes the fundamental physical nature of a system's evolution toward equilibrium. At room temperature, the spontaneous melting of ice cubes in a glass of water—leading to a more uniform energy distribution—exemplifies this natural tendency.

The evolution of a system is driven by the exchange of energy. In systems governed by repulsive interactions, energy—manifested through temperature—tends to flow from regions of high density to low density. A similar dispersive tendency applies to both potential and kinetic energy. Consequently, such systems evolve toward a uniform spatial distribution at equilibrium. This behavior reflects the evolutionary nature captured in the second law of thermodynamics, where the direction of entropy increase aligns with the entropy formulation given in Definition (1).

Limitations of the Second Law of Thermodynamics

It is important to note that the derivation of Expression (5) relies on the intuitive assumption that heat always flows down a temperature gradient. This assumption generally holds for systems dominated by repulsive interactions—for example, gases in which electrostatic repulsion between valence electrons dictates molecular behavior. In such systems, particles tend to disperse, facilitating mixing and spontaneous heat transfer along the gradient. The notion that heat naturally flows from higher to lower temperatures has long been regarded as an intrinsic property of nature and is implicitly embedded in models of interacting systems. Under this premise, Expression (5) follows directly and often serves as the foundation for the assertion that entropy cannot decrease. This directional tendency is further reinforced by many everyday observations of systems governed primarily by repulsive interactions.

However, this assumption breaks down in systems where attractive forces dominate, particularly on large scales. While a small volume of gas tends to remain well mixed and uniformly distributed, a planetary atmosphere is typically stratified into distinct layers with different temperatures. Although temperature gradients can induce localized convection, the large-scale structure of Earth's atmosphere is primarily governed by gravity. In other words, without gravitational influence, the temperature and density of air molecules would eventually become uniformly distributed to maximize the entropy of the entire system. Yet, the entropy of the real atmosphere does not approach this maximum state, seemingly contradicting what one might expect based on the second law of thermodynamics.

The flow of energy near a black hole does not follow the conventional direction of an energy gradient. Due to the black hole's immense gravitational pull, surrounding radiation—including thermal energy—is drawn inward. Furthermore, surrounding matter, which represents a highly concentrated form of energy according to Einstein's mass–energy equivalence principle, is also pulled into the black hole. The average temperature of interstellar space is close to absolute zero, whereas the temperature of the black hole is considerably higher. In this scenario, energy effectively flows from a low-temperature environment to a high-temperature object, resulting in a net decrease in the total entropy of the combined system consisting of the black hole and its surrounding space.

Similarly, the evolution of the universe demonstrates the local aggregation of energy rather than its uniform dispersion, contrary to what might be expected from the second law of thermodynamics. Under the influence of gravity, stars, galaxies, and other celestial bodies are thought to form from vast cosmic gas clouds with low energy density. As these clouds collapse gravitationally, matter concentrates toward their centers of mass, giving rise to highly concentrated energy structures and more organized systems such as planets, stars, neutron stars, and black holes—processes that can be regarded as the inverse of those described by the second law.

Under sufficiently strong attractive forces, such as Coulomb interactions, this type of anti-gradient energy flow can also occur at small scales. One example is supercooled water—liquid water cooled below its freezing point that has not yet solidified. When disturbed, the water begins to freeze, even in an isolated container. As it transitions into ice, it releases heat associated with the formation of intermolecular bonds, which is absorbed by the container, warming it. In this case, heat flows from the colder water to the warmer container, illustrating energy transfer from a lower-temperature system to a higher-temperature one. This example demonstrates that the assembly of water into ice under certain conditions is not impossible. More generally, the energy exchange during crystallization processes represents a slow flow of energy from lower-temperature bodies to higher-temperature surroundings.

These examples demonstrate that entropy decreases are not uncommon in systems governed by attractive forces, particularly in large-scale systems dominated by gravity. By Einstein's mass–energy equivalence, matter is a concentrated form of energy; thus, gravitational attraction drives the aggregation of energy. Under gravity, all forms of energy—radiative, potential, and kinetic—tend to cluster, especially near massive objects such as black holes. Consequently, the commonly assumed dispersive tendency of energy to flow from high-density to low-density regions is not universal, but rather a characteristic of small systems dominated by repulsive interactions.

The second law of thermodynamics primarily characterizes a subset of phenomena in systems dominated by repulsive interactions. Furthermore, the evolution of systems in the universe does not always proceed along a single, unidirectional path as the second law implies; it can also display periodic or reversible behavior, such as the oscillation of a pendulum or reversible chemical reactions. Ultimately, the evolution of the universe arises from the continuous transformation of energy among different forms—a process more comprehensively described by the **Restoration Principle**.

Entropy of Statistical Mechanics

In addition to the classical thermodynamic definition (1), Ludwig Boltzmann introduced a statistical formulation of entropy based on the number of microstates accessible to a system and the probability associated with each state. For simplicity, if we assume that all microstates are equally probable, this definition can be expressed in the simplified form:

$$S = k_B ln(N) \tag{6}$$

In this formulation, k_B denotes the Boltzmann constant, and N represents the total number of possible microstates of the system. A microstate refers to a specific configuration of all components within the system. Despite its simplicity, this formulation provides sufficient insight to allow direct comparison with the classical definition of entropy.

Although Boltzmann is often credited with establishing the equivalence between the statistical and original definitions of entropy by analyzing the microscopic behavior of a system's components, the two definitions are fundamentally distinct—particularly when comparing the original definition (1) with the statistical definition (6). The former characterizes the macroscopic state of a system's energy distribution, while the latter describes the probabilistic distribution of its microscopic components. Under the statistical definition, a system evolves toward the most probable configuration of its components, whereas under the thermodynamic definition, it evolves toward a uniform distribution of energy. These two distributions may coincide in systems dominated by repulsive interactions, where components naturally tend to disperse. However, statistical entropy is a broader concept—it can, for example, quantify the disorder in a checkerboard pattern based solely on the randomness of piece placement, a measure entirely unrelated to energy and completely outside the thermodynamic context.

Furthermore, ambiguity presents a significant challenge to the statistical definition of entropy, as the concept of a microstate lacks a precise and universally accepted definition. Mathematically, for example, both a 1-meter and a 10-meter line segment contain the same number of points—an uncountably infinite set. Consequently, a volume of 1,000 cubic meters does not contain more points of spatial locations than a volume of 1 cubic meter. Therefore, it is not strictly valid to claim that a gas molecule has access to more microstates in a larger container based solely on spatial extent. This conceptual ambiguity limits the practical applicability of the statistical definition of entropy, which is why chemists often rely on the thermodynamic definition, grounded in measurable quantities such as temperature and heat.

The divergence between the two definitions becomes particularly evident as a system's temperature approaches 0 K. At this limit, the system occupies only a single accessible microstate—the ground state—corresponding to zero entropy according to Definition (6) and the original statistical formulation based on microstate probability. By contrast, the thermodynamic definition predicts a very different behavior: as temperature approaches 0 K, its reciprocal diverges, causing the entropy in Definition (1) to diverge as well. Specifically, in the example shown by Equation (4), the entropy tends toward negative infinity as the temperature approaches 0 K. Moreover, Equation (4) suggests that the entropy would reach zero at 1 K, rather than at 0 K as implied by the statistical definition (6). Because the number of accessible microstates must still exceed one at 1 K, the statistical definition requires the entropy to remain greater than zero. This discrepancy underscores a fundamental mismatch between the classical thermodynamic and statistical formulations of entropy.

Conclusions

Everything in the universe exists as energy in one form or another, including matter itself. The evolution of any system is driven by the tendency toward energy equilibrium through the continual transformation of energy among these forms. Such evolution manifests not only as irreversible, unidirectional changes but also as periodic and reversible dynamics—phenomena more comprehensively captured by the *Restoration Principle*. The second law of thermodynamics, articulated through the classical formulation of entropy, accounts for only part of thermodynamic behavior. Although the statistical definition of entropy describes the probabilistic redistribution of a system's constituents, and aligns well with the evolution typically observed in systems dominated by repulsive interactions, it does not, on its own, elucidate the fundamental physical mechanisms that drive these transformations.

Revision History

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- https://xenon.stanford.edu/~zjl/abstract.html, PDF
- https://doi.org/10.5281/zenodo.17967154, PDF

Further Literature

- Misconceptions in Thermodynamics (PDF: DOI) (中文: DOI)
- The Mechanism Driving Crookes Radiometers (PDF: DOI) (中文: DOI)
- The Cause of Brownian Motion (PDF: DOI) (中文: DOI)
- Can Temperature Represent Average Kinetic Energy? (PDF: DOI) (中文: DOI)
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