

How physicists disagree on the meaning of entropy

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Discussions of the foundations of statistical mechanics, how they lead to thermodynamics, and the appropriate definition of entropy have occasioned many disagreements. I believe that some or all of these disagreements arise from differing, but unstated assumptions, which can make opposing opinions difficult to reconcile. To make these assumptions explicit, I discuss the principles that have guided my own thinking about the foundations of statistical mechanics, the microscopic origins of thermodynamics, and the definition of entropy. The purpose of this paper will be fulfilled if it paves the way to a final consensus, whether or not that consensus agrees with my point of view. © 2011 American Association of Physics Teachers.

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I. INTRODUCTION

“Nobody really knows what entropy really is.”

—John von Neumann¹

Since I began speaking and publishing on the relation between statistical mechanics and thermodynamics in general and the meaning of entropy in particular,²⁻⁷ I've encountered a diversity of opinion among experts that is remarkable for a field that is well over a century old. Most colleagues with whom I have discussed the matter have indicated that they believe their views are essentially the same as those of the majority of physicists. However, when we discuss details, opinions turn out to be quite diverse and, at times, contentious.^{4,8}

The following is a partial list of opinions I have encountered in the literature and in discussions with other scientists:

- The theory of probability has nothing to do with statistical mechanics.
- The theory of probability is the basis of statistical mechanics.
- The entropy of an ideal classical gas of distinguishable particles is not extensive.
- The entropy of an ideal classical gas of distinguishable particles is extensive.
- The properties of macroscopic classical systems with distinguishable and indistinguishable particles are different.
- The properties of macroscopic classical systems with distinguishable and indistinguishable particles are the same.
- The entropy of a classical ideal gas of distinguishable particles is not additive.
- The entropy of a classical ideal gas of distinguishable particles is additive.
- Boltzmann defined the entropy of a classical system by the logarithm of a volume in phase space.
- Boltzmann did not define the entropy by the logarithm of a volume in phase space.
- The symbol W in the equation $S=k \log W$, which is inscribed on Boltzmann's tombstone, refers to a volume in phase space.
- The symbol W in the equation $S=k \log W$, which is inscribed on Boltzmann's tombstone, refers to the German word “Wahrscheinlichkeit” (probability).
- The entropy should be defined in terms of the properties of an isolated system.

- The entropy should be defined in terms of the properties of a composite system.
- Thermodynamics is only valid in the “thermodynamic limit,” that is, in the limit of infinite system size.
- Thermodynamics is valid for finite systems.
- Extensivity is essential to thermodynamics.
- Extensivity is not essential to thermodynamics.

This remarkable diversity of opinion has an interesting consequence. When people discuss the foundations of statistical mechanics, the justification of thermodynamics, or the meaning of entropy, they tend to assume that the basic principles they hold are shared by others. These principles often go unspoken, because they are regarded as obvious. It has occurred to me that it might be good to restart the discussion of these issues by stating basic assumptions clearly and explicitly, no matter how obvious they might seem. This paper is a start in that direction.

There are two possible reactions to the principles I put forward. A reader might agree with them. In that case, we would have a firm basis on which to proceed. Or, a reader might take issue with one or more. In that case, we would know where the conflict lies, which would give us a good chance of resolving points of disagreement. In either case, we should be able to make progress toward arriving at a consensus, which is the goal of this paper.

Because my topic is limited to macroscopic measurements of macroscopic systems, I will discuss what I understand those terms to mean in Sec. II. In this paper I will put forward 12 principles based on the concept of macroscopic measurements that have led me to advocate the use of Boltzmann's 1877 definition of the entropy¹¹ over other definitions that are often found in textbooks.

II. MACROSCOPIC SYSTEMS

In this paper I am concerned with the question of how to describe the observed behavior of macroscopic systems. The concept of macroscopic frames all of my arguments, so it is important to make clear at the outset how I define it. A macroscopic system contains a large number of particles, and a macroscopic measurement is limited in its resolution. These two features are closely related, in that what can be regarded as a large number depends on the resolution of the macroscopic measurements.

The reason for specifying a large number of particles is

that the quantities of interest in thermodynamics are collective variables, such as the energy or the number of particles in a system. The *relative* statistical fluctuations of such quantities are generally inversely proportional to the square root of the number of particles. If the statistical fluctuations are much smaller than the resolution of the macroscopic measurements, they can be ignored; the average values obtained from statistical mechanics then give a description of the expected results of the experiment.

In the late 19th century, when Boltzmann and Gibbs did their seminal work, the existence of atoms had not been proven. The idea of experimentally observing atomic behavior was scarcely considered. Now, it is possible to obtain images of microscopic structure with atomic resolution. Nevertheless, I am restricting my attention in this paper to macroscopic measurements that cannot discern microscopic behavior in order to discuss the emergence of a thermodynamic description from statistical mechanics.

In the remainder of the paper I will give the rationale for each of the principles I have followed, and I will show how they lead to the adoption of Boltzmann's 1877 definition of the entropy in terms of the logarithm of the probability of macroscopic states for a composite system.

III. PROBABILITY OF MACROSCOPIC STATES

Principle 1: Probability theory is necessary for a theoretical description of macroscopic behavior.

The first—and most fundamental—principle is that the basis for obtaining a description of a macroscopic system from microscopic laws of motion is given by probability theory. In any experiment (real or *gedanken*), the system is in some specific microscopic state (quantum or classical) at any given instant. That microscopic state is a property of the system, independent of measurement.

The most immediate consequence of the limited resolution of macroscopic measurements is that it severely restricts our knowledge of the microscopic state of a system. We cannot determine the microscopic state experimentally—we can only eliminate microscopic states that are not consistent with our macroscopic observations.

The limitations on our knowledge bring us to the distinction between reality and our knowledge of reality. The reality is the microscopic state of the system at any given time. Our knowledge of reality consists of the information we obtain from macroscopic measurements and the conclusions we are able to draw from that information. We can only construct a representation or description of the behavior of the system; we cannot know the microscopic state of a system from macroscopic measurements.

In quantum systems our knowledge is even more limited. For example, except for eigenstates, which have probability zero, the energy is not even determined uniquely by the microscopic state, so it cannot be a property of the system independent of measurement.

The most useful method I know for describing limited knowledge is Bayesian probability theory,⁹ which led me to the first principle.

After deciding to use probability theory, there remains the choice of which probability distribution to use. The most reasonable choice would seem to be the simplest that is consistent with what we know from macroscopic observations. Therefore, I take the probability distribution (a Bayesian prior or model probability) to be uniform in phase space for iso-

lated classical systems (subject to constraints on the total energy and the restriction of the particles to certain volumes), and correspondingly uniform over microscopic states of quantum systems. The logical consequences of such probability distributions are known to lead to predictions that agree with experiment, which is comforting.

Principle 2: Probability theory is sufficient for a theoretical description of macroscopic states.

In one sense, the introduction of probability distributions very nearly completes the theory of many-body systems. Little else is essential. The concepts of entropy, free energy, etc. are extremely convenient, but they are not absolutely necessary. We could calculate anything and everything about the behavior of macroscopic systems without ever mentioning them.

This principle is very important because it implies that however we define concepts like entropy and free energy in statistical mechanics, the consequences of the definitions must be consistent with the predictions of probability theory if they are to have the properties required by thermodynamics.

IV. COMPOSITE SYSTEMS

Principle 3: Statistical mechanics and thermodynamics must predict the properties of composite systems.

An essential part of statistical mechanics and thermodynamics is the analysis and prediction of the behavior of composite systems. A simple isolated system in equilibrium does not do anything macroscopically measurable. You can't even make an experimental determination of its temperature without putting a thermometer in contact with it, and then you have a composite system.

A simple container full of gas must also be regarded as a composite system if we want to investigate questions such as whether the density of the gas is uniform. Without conceptually dividing the system into smaller subsystems, we cannot discuss density variations.

An important feature of a composite system is that it can have internal constraints between its subsystems. The release of internal constraints can lead to measurable changes, which can be predicted by statistical mechanics and thermodynamics.

Although I don't expect serious disagreement on this principle, it does lead to a different emphasis than the usual textbook discussion. It is common to define thermodynamic functions for isolated systems and only much later consider equilibrium in composite systems. I believe that because of the crucial importance of composite systems, they should play a leading role in the development of statistical mechanics and thermodynamics.

Section V will discuss the measurement of extensive parameters, which are quantities that are proportional to how much of something there is in a system. Examples include the energy and the number of particles. The prediction of the measured values of extensive parameters is a key step in linking statistical mechanics to thermodynamics.

V. PREDICTIONS OF THERMODYNAMIC QUANTITIES

Principle 4: The values of extensive parameters that maximize the probability predict the results of measurements of those parameters for composite systems in equilibrium.

This principle provides the key link between statistical mechanics and thermodynamic measurements.

When a constraint in a composite system is released, measurable quantities can change. As an example, consider a composite system consisting of two subvolumes separated by a partition, each containing some amount of the same type of ideal gas. Each subvolume contains on the order of 10^{20} particles, and our measurement apparatus can resolve the density of the gas to an accuracy of about 10^{-5} . If a hole is punched in the partition, the density of the gas in each subvolume will go to approximately the same value, within fluctuations of the order of 10^{-10} . Because the fluctuations are much smaller than the resolution of our measurement apparatus, we can take the location of the maximum of the probability distribution to predict the experimental outcome. This feature strongly supports Principle 2; probability theory is sufficient to predict macroscopic behavior.

Similar examples can be given for releasing constraints on the energy (using walls that conduct heat) or volume (using a freely moving piston to separate the subvolumes). In each case the probability distribution is very narrow, so that the fluctuations cannot be observed by macroscopic measurements. The extremely small relative fluctuations of macroscopic observables are so universal that, in the 19th century, many of Boltzmann's opponents didn't believe in their existence.

Although nonequilibrium behavior after the release of constraints is both interesting and important, the discussion here is limited to equilibrium states, which are discussed in Sec. VI.

VI. EQUILIBRIUM

Principle 5: A macroscopic equilibrium state is defined by two properties: the probability of macroscopically observable changes is extremely small, and there is no macroscopically observable flux of energy or particles. (This property distinguishes equilibrium from steady state.)

There might be some disagreement on this point. There is a substantial literature in statistical mechanics that makes the fundamental assertion that equilibrium is defined by a particular "equilibrium probability distribution" in phase space (or Hilbert space).

In my opinion, such a view is a serious error, primarily because the probability distribution of the microscopic states is not macroscopically observable. We use probability theory because we cannot discern microscopic states; we certainly cannot measure the relative frequency with which they occur.

If we limit the definition of equilibrium to behavior that can be observed, it follows that there are many probability distributions that all make the same predictions.¹⁰ The simplest probability distribution is the uniform distribution, but it is not unique.

It is traditional to define a number of thermodynamic functions to facilitate the analysis of macroscopic systems in equilibrium. Although Principle 2 implies that these functions are not absolutely necessary, they are such convenient descriptions of macroscopic behavior that it would be unreasonable to do without them. Their general nature is discussed in Sec. VII.

VII. THERMODYNAMIC PREDICTIONS

Principle 6: The predictions of statistical mechanics and thermodynamics are representations or descriptions of a system based on the extent of our knowledge.

This principle again reflects the distinction between reality and our knowledge of reality, between properties of a system and a description or representation of measurable quantities based on our limited knowledge.

As an example of this distinction, consider again a composite system consisting of a box containing a gas, with a partition dividing the box into two equal subvolumes. The partition has a small hole in it, so that molecules of the gas can move between the two subvolumes. At any instant of time, there is some specific number of particles on each side of the partition. Thermodynamics predicts a number of particles that give the same density on both sides of the partition. The predicted number turns out to agree with experiment to within the limited resolution of macroscopic measurements. For this reason, thermodynamics provides a very useful description of the behavior of a macroscopic system.

In contrast, the actual number of particles on each side of the partition at any instant cannot be the number that is predicted. The actual number is not determined for quantum systems without measurement, and even for classical systems, it fluctuates with time. The predicted number is a description based on our knowledge and is constant in time. It is very useful for human purposes, but it is not a real property of the system.

It is sometimes claimed that the predicted number of molecules in each subvolume is a real property of the system if we regard it as an average over the course of an experiment. How long would the observation time have to be for such a claim to be true? Consider an open system with about 10^{20} particles in equilibrium and a corresponding statistical uncertainty of about 10^{10} particles. To reduce the statistical uncertainty of the mean to about one particle, we would need at least 10^{20} independent observations. If the correlation time for the system is about 1 ms, this would take 10^{17} s, which is comparable to the age of the universe. Even with such a long observation time, we would still not have an exact result because the average number of particles is generally not an integer. For any reasonable experiment during the lifetime of a physicist, the prediction of thermodynamics is in error by an enormous number of particles and should not be confused with the actual number of particles.

For the same reasons, the energy, the entropy, and the associated free energies are thermodynamic descriptions rather than real properties of a macroscopic system. The entropy is actually defined at a higher level of abstraction than the energy or the number of particles. That is the subject of Sec. VIII.

The distinction between real properties of a system and our knowledge of the system might seem philosophical and a bit pedantic, but it greatly clarifies some issues that might otherwise be rather puzzling.

VIII. ENTROPY

This section considers the controversial question of what "entropy" means and how to define it. Principle 7 is based on the most important of the thermodynamic properties of the

entropy,^{2,12} which leads to both the thermodynamic conditions for equilibrium and the second law of thermodynamics.

Principle 7: The primary property of the entropy is that it is maximized in equilibrium.

Because the macroscopically observable behavior of an isolated system in equilibrium does not change with time, the maximization of the entropy cannot be applied to a simple system. It can be applied to a composite system: simply release a constraint and see what happens. If the definition of the entropy is correct, the location of the maximum of the entropy should predict the observed equilibrium values of extensive macroscopic observables.

Principle 7 also leads directly to the second law of thermodynamics. If the entropy is always maximized in equilibrium for a composite system, then the change in entropy after a constraint is released cannot be negative.

If we compare Principle 7 with the predictions of probability theory, we see that the location of the maximum of the entropy must always coincide with the location of the maximum of the probability distribution.

An immediate consequence of Boltzmann's 1877 definition of the entropy as the logarithm of the probability distribution for macroscopic observables is that the location of the maximum of the entropy *always* coincides with the equilibrium values of those macroscopic observables. If any other definition is used, it requires a separate demonstration to show that it also predicts these values correctly.

The automatic agreement of the predictions of Boltzmann's definition of the entropy with the correct equilibrium values of macroscopic observables makes it the natural choice. It might be possible to define the entropy differently, but the predictions of any alternative definition must be identical to those of Boltzmann's definition in terms of the logarithm of the probability.

Principle 7 completes what I regard as a convincing argument in favor of Boltzmann's 1877 definition of the entropy.

The remainder of the paper takes up issues that are associated with the concept of entropy. Their purpose is both to introduce the remaining principles that have guided my thinking on these issues and to complete the picture presented so far.

IX. ADDITIVITY

Principle 8: Additivity is essential to any consistent definition of the entropy of a system with short-ranged interactions between its particles.

In thermodynamics it is generally assumed that the entropy of a composite system is given by the sum of the entropies of the subsystems. This property is known as "additivity."

For Boltzmann's 1877 definition of the entropy, the validity of the assumption of additivity is based on the short range of molecular interactions, which is much smaller than the dimensions of the system. Only a very small fraction of the particles in one subsystem interact with those in another subsystem, so that the sum of all such interaction energies is still relatively small. If the direct interactions between subsystems can be neglected, the entropy satisfies additivity.

As an aside, using Boltzmann's definition of the entropy suggests the alternative of referring to this property as "separability," because the entropy of a composite system is defined first.

If we were to use a definition of the entropy that did not satisfy additivity and nevertheless wanted to have correct results for composite systems, we could assign an arbitrary function—or simply the value zero—as the entropy of any subsystem. The entropy of a composite system could then be obtained by adding an extra term to recover the Boltzmann expression. It is possible to create such a formalism, but none of the usual expressions for temperature, pressure, or chemical potential in terms of partial derivatives of the entropy would be necessarily valid. Without additivity, we would not have thermodynamics as we know it.

The importance of additivity probably would go without saying if it were not for a suggestion that an otherwise incorrect definition of the entropy might be saved by an extra term for composite systems.⁸ I don't see any virtue to such a procedure, and I stand by Principle 8.

X. THE THERMODYNAMIC LIMIT

The thermodynamic limit is defined as the infinite-size limit of the ratios of extensive quantities—ratios such as the energy per particle U/N or the particle density N/V . The advantage of taking the limit of infinite size is that uncertainties in these ratios go to zero because the relative fluctuations are generally proportional to $1/\sqrt{N}$.

Principle 9: The thermodynamic limit is not required for the validity of thermodynamics.

To judge from some textbooks, this principle might be the most controversial of the ones discussed in this paper.

However, the thermodynamic limit is misnamed. It is not essential to the foundations of thermodynamics. It cannot be essential if we are to apply thermodynamics to real systems, which are necessarily finite. We never do experiments on infinite systems. If thermodynamics worked only for infinite systems, it might still be interesting as mathematics, but it would be irrelevant as science.

The thermodynamic limit is mathematically convenient for certain problems. Phase transitions, for example, only exhibit nonanalytic behavior in the thermodynamic limit, which makes for a much cleaner mathematical description. Nevertheless, the thermodynamic limit should not play any essential role in the foundations of statistical mechanics and thermodynamics.

XI. DISTINGUISHABILITY AND INDISTINGUISHABILITY

Principle 10: "Indistinguishability" is a property of microscopic states. It does not depend on experimental resolution.

In my opinion, this principle should be an obvious consequence of the definitions found in any textbook on quantum mechanics. However, I have had enough arguments about it to know that it is far from obvious.

The definitions of distinguishability and indistinguishability are simple: (1) If the exchange of two particles in a system results in a different microscopic state, the particles are distinguishable. (2) If the exchange of two particles in a system results in the original microscopic state, the particles are indistinguishable. (For fermions, two states are usually regarded as identical if they differ only by an overall minus sign.)

The definition of indistinguishability does not have anything to do with the interactions between particles. It is possible in either quantum or classical physics for two distinct

states to have the same energy. Nevertheless, if the microscopic state is different after the exchange of two particles, those particles are distinguishable.

Unfortunately, “distinguishable” is sometimes confused with what might be called “observably different.” Two particles are observably different if exchanging them alters the properties of the system in a way that is observable. Clearly, if particles are observably different, they must be distinguishable. In contrast, particles can be distinguishable without their exchange producing any observable differences.

A simple example of this distinction is provided by a mixture of ^3He and ^4He . It would not be possible for a macroscopic measurement to detect the difference in the microscopic states that would result from exchanging a single ^3He atom with a single ^4He atom. Nevertheless, there would be a difference in the microscopic states, and the two isotopes of helium are *not* mutually indistinguishable.

The term “identical particles” is often used as a synonym for indistinguishable particles. This use has the unfortunate consequence that a model of classical distinguishable particles with identical properties might be mistaken for a model of indistinguishable particles.

The concept of indistinguishability is foreign to classical mechanics. Consider the trajectory of an isolated classical system in phase space (the $6N$ -dimensional space defined by the positions and momenta of all particles in the system) in which the microscopic state is described by a point. If two particles are exchanged at a given time, the trajectory becomes discontinuous. The exchange of particles has resulted in a different microscopic state, regardless of whether the Hamiltonian gives the same energy for the two microstates.

In quantum mechanics N -particle states of indistinguishable particles are characterized by a wave function that has been symmetrized (or antisymmetrized) by summing over all permutations of the particles, with a change in sign for each permutation for fermions, or without a change in sign for bosons.

A classical system of indistinguishable particles can be described by the same procedure. The microscopic state of a classical system of indistinguishable particles would be described by the $N!$ points in phase space found from the set of all permutations of the particles. The trajectory (or trajectories) of the set of $N!$ points is clearly unaffected by the exchange of any two particles at any point in time.

The idea of representing a classical state by $N!$ points in phase space is a bit odd, but that is because indistinguishability is not a classical concept. However, if indistinguishability is to be imposed on a classical system, this representation seems to be the most reasonable way of doing it.

Many textbooks claim that classical systems with distinguishable and indistinguishable particles are described by different expressions for the entropy. However, it is straightforward to demonstrate that the macroscopic properties of a classical system are exactly the same whether the particles are distinguishable or indistinguishable.² Since the macroscopic behaviors of classical systems with distinguishable and indistinguishable particles are the same, it seems natural that their entropies should also be the same, which leads to my next principle.

Principle 11: Systems with identical macroscopic properties should be described by the same entropy.

Boltzmann’s 1877 definition of the entropy gives the same expression for the entropy for classical systems with either

distinguishable or indistinguishable particles.² The traditional definition in terms of a volume in phase space, which is often erroneously attributed to Boltzmann,⁵ gives different expressions, at least one of which must clearly be incorrect. The worst failings of the traditional definition of the entropy for a system of distinguishable particles are that it violates the second law of thermodynamics and makes incorrect predictions for equilibrium with respect to the exchange of particles between subsystems.²

The error in the traditional definition of the entropy of a classical system of distinguishable particles also has the consequence that it predicts that the entropy of an ideal gas is not extensive. This problem is not really fundamental, but it has bothered people. And it leads to the next principle.

XII. EXTENSIVITY

Principle 12: Extensivity is not essential to thermodynamics.

Extensivity is the property that the macroscopic observables of a system are all directly proportional to its size. This property implies that ratios, such as U/N , V/N , and S/N , are all independent of the size of the system. In many textbooks, extensivity is taken to be a fundamental postulate of thermodynamics.¹² It is certainly convenient mathematically, because it leads directly to the Euler and Gibbs–Duhem equations. It is an appropriate assumption when the physical properties of a material are being investigated, and the surface or interface contributions can be neglected.

However, real systems have surfaces and interfaces, which are important topics of research. Because the surface-to-volume ratio changes with the size of the system, real systems are not extensive, and the deviations from extensivity can be very important. For example, a real gas in a real container will usually be adsorbed to some extent on the inner walls of the container. At low temperatures, the fraction of adsorbed molecules can be quite large, which is exploited in the construction of cryopumps.

To describe the thermodynamics of a surface, we must be able to describe the thermodynamics of a nonextensive system and extract the parts of the free energy, etc. that are not directly proportional to the size. Therefore, statistical mechanics and thermodynamics must be applicable to nonextensive systems.

Recognizing that extensivity is not an essential property of thermodynamic systems is important in deciding on an appropriate definition of entropy. Some colleagues claim that a definition of entropy that gives a demonstrably incorrect expression can be made acceptable by imposing extensivity with an additional term of the form $-k_B \ln(N!)$. However, because thermodynamics should also correctly describe nonextensive systems, that is, systems with entropies that cannot be made extensive by a term that depends only on N , such a correction is not feasible.

There is also another difficulty in trying to impose extensivity on the fundamental definition of the entropy. If the system under consideration contains more than one kind of particle, the criterion of extensivity is ambiguous. For example, suppose we have a gas mixture of distinguishable particles, with N_A particles of type A and N_B particles of type B . The common textbook definition of the entropy as the logarithm of a volume in phase space gives an answer that is not extensive (and incorrect for other reasons²). We might try to impose extensivity with the addition of either

$-k_B \ln(N_A!N_B!)$ or $-k_B \ln[(N_A+N_B)!]$. The first choice is the one we want, of course, but the criterion of extensivity does not eliminate the second. If this path were to be taken, at least one more principle would have to be invoked to obtain an unambiguous definition.

Although extensivity is a useful assumption when analyzing the properties of a material, rather than a system with surfaces, it is not essential to either thermodynamics or statistical mechanics, and should not be included as part of the definition of entropy.

XIII. CONSEQUENCES OF THE 12 PRINCIPLES

The principles I have given have led me to the conclusion that Boltzmann's 1877 definition of the entropy as the logarithm of the probability of macroscopic states for composite systems is superior to any other proposed definition. In particular, it is superior to a definition in terms of a volume in phase space that is often found in textbooks for classical statistical mechanics.

If the principles I have presented in this paper are correct, any other valid definition of entropy must turn out to be equivalent to defining entropy in terms of probability.

XIV. GIBBS' PARADOX

Alternatives to Boltzmann's 1877 definition of the entropy have led to problems that have been debated for over a hundred years. The debate has centered on Gibbs' paradox, which refers to a set of old problems in statistical mechanics.¹³ The two main problems concern the properties of the entropy of systems of distinguishable particles. In my opinion, they are both easy to resolve on the basis of the principles I have given.

A. Extensivity

The first version of Gibbs' paradox concerns the properties of the entropy as defined in terms of the logarithm of a volume in phase space. Boltzmann's 1877 definition in terms of the logarithm of the probability of a composite system does not have this problem.

If U is the energy, V is the volume, and N is the number of particles, the volume in phase space (often denoted by Ω) consists of all points for which N particles are in a container of volume V with a total energy less than or equal to U . For an ideal gas, this volume is given by

$$\Omega = V^N \frac{\pi^{3N/2}}{\Gamma(3N/2 + 1)} U^{3N/2}. \quad (1)$$

If the entropy is defined in terms of the logarithm of this volume in phase space,

$$S_\Omega = k \ln \Omega, \quad (2)$$

Stirling's approximation gives an expression for the entropy of the form

$$S_\Omega(U, V, N) = Nk_B \left[\frac{3}{2} \ln \left(\frac{U}{N} \right) + \ln V + \ln X \right], \quad (3)$$

where X is a constant that can be calculated from Eq. (1).

This expression for the entropy, Eq. (3), is not extensive. As explained in Sec. XII, I do not regard the lack of exten-

sivity as a problem in itself. However, Eq. (3) leads to a violation of the second law of thermodynamics.⁶ That is a problem!

Consider an ideal gas of N particles in a volume V , and assume that the entropy before inserting the partition is given by Eq. (3). Now insert a partition that divides the system into two equal volumes. The total entropy after inserting the partition is given by twice the entropy of a system half the size of the original one,

$$\begin{aligned} 2S_\Omega(U/2, V/2, N/2) \\ = 2 \frac{N}{2} k_B \left[\frac{3}{2} \ln \left(\frac{U/2}{N/2} \right) + \ln \left(\frac{V}{2} \right) + \ln X \right]. \end{aligned} \quad (4)$$

The change in S_Ω is

$$\Delta S_\Omega = 2S_\Omega(U/2, V/2, N/2) - S_\Omega(U, V, N) = -Nk_B \ln 2. \quad (5)$$

The decrease in entropy predicted by the entropy in Eq. (3) violates the second law of thermodynamics as expressed in the Clausius inequality,¹⁴

$$\Delta S \geq \int_i^f \frac{dQ}{T}, \quad (6)$$

where i and f refer to the initial and final macroscopic states, before and after inserting the partition. Because $dQ=0$ while the partition is being inserted, the Clausius inequality is violated by Eq. (5). This violation eliminates a definition of the entropy in terms of the logarithm of a volume in phase space from consideration as the entropy of a classical gas.⁶

Boltzmann's definition of entropy in terms of the logarithm of the probability gives exactly the same result for classical particles whether they are distinguishable or not,²

$$S_B(U, V, N) = Nk_B \left[\frac{3}{2} \ln \left(\frac{U}{N} \right) + \ln \left(\frac{V}{N} \right) + \ln X \right]. \quad (7)$$

Because Eq. (7) for the entropy does not violate the second law of thermodynamics, there is no paradox and no problem.

B. Continuity

Another problem, which is also known as Gibbs' paradox, concerns the desire for continuity as the interactions between particles in a system go continuously from being measurably different to being the same for all particles.

For example, consider a classical ideal gas with N_A particles of type A and N_B particles of type B . All particles of a given type have the same properties, but these properties are different for type A and type B particles. The entropy of this system differs from the entropy of an ideal gas of $N=N_A+N_B$ particles of a single kind by the amount

$$\Delta S = -k_B \left[N_A \ln \left(\frac{N_A}{N} \right) + N_B \ln \left(\frac{N_B}{N} \right) \right] > 0. \quad (8)$$

Equation (8) is the well-known entropy of mixing.

The concern is that as the differences in the properties of the two types of particles vanish, the entropy of the system changes discontinuously by the entropy of mixing given in Eq. (8).

First of all, it is quite possible for the interactions between particles to be essentially identical, but to still be able to separate them in some way—using differences in diffusion

rates for different isotopes, for example. In that case, the entropy would not change discontinuously as the differences in the interactions vanish.

However, suppose all differences in interactions, masses, etc. could be made to go continuously to zero. At some point, the differences would become smaller than the resolution of our experiments. Nevertheless, at any level of difference in the interactions, we either would or would not be able to measure the difference.

If the entropy were a property of the system (reality)—instead of a description of the system (representation of our knowledge), as argued in Sec. VII—a discontinuity of the entropy would be strange. However, the entropy is given by the probability, which is, in turn, related to our knowledge of the system. There is no problem with our description (or knowledge) of a system changing discontinuously when our information changes discontinuously. If we cannot determine experimentally that there are two different types of particles, then a description that lumps them together will still be correct. Common practice lumps the various isotopes of an element together for most thermodynamic applications. Although different isotopes are clearly distinguishable, the macroscopic predictions are not affected.

The problem of continuity is often expressed in terms of a continuous change from distinguishable to indistinguishable particles. However, such a change is intrinsically discontinuous and does not occur simply because the interactions between the particles become identical.

XV. SUMMARY

I have put forward 12 principles that have led me to conclude that Boltzmann's 1877 definition of the entropy in terms of the logarithm of the probability of macroscopic states of composite systems is superior to all other options.

It would be too much to hope that my arguments will find universal agreement. However, I hope that further discussions will be clarified by an improved understanding of one point of view. Those who might have different points of view have the opportunity to express which of the principles they object to and present their own alternatives.

The issues I have discussed have been the subject of disagreements for well over a century. It might be that, in the

end, the conclusions of the scientific community deviate from the principles I have listed here. However, the purpose of this paper will be fulfilled if it paves the way to a final consensus.

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