Entropy, Its Language, and Interpretation

Harvey S. Leff

Abstract The language of entropy is examined for consistency with its mathematics and physics, and for its efficacy as a guide to what entropy means. Do common descriptors such as *disorder*, *missing information*, and *multiplicity* help or hinder understanding? Can the language of entropy be helpful in cases where entropy is not well defined? We argue in favor of the descriptor *spreading*, which entails space, time, and energy in a fundamental way. This includes *spreading* of energy spatially during processes and *temporal spreading* over accessible microstates states in thermodynamic equilibrium. Various examples illustrate the value of the spreading metaphor. To provide further support for this metaphor's utility, it is shown how a set of reasonable spreading properties can be used to *derive* the entropy function. A main conclusion is that it is appropriate to view entropy's symbol *S* as shorthand for *spreading*.

1 Introduction

Thermodynamics and statistical mechanics were developed to describe macroscopic matter. They differ from mechanics, which describes point particles and rigid bodies, in that they account for internal energy storage modes. Accordingly, a key function of thermodynamics is internal energy, namely, the average *total* energy of a system, including all storage modes. An equally important, but less easily digested, function is entropy. Perhaps because it can be defined in diverse ways, and its behavior in thermodynamic systems can be subtle, entropy's meaning and usefulness have come into question [1]. A commonly used, but inadequate, language surrounding entropy contributes to this. Despite its intimate connection with energy, entropy has been described as a measure of disorder, multiplicity, missing information, freedom, mixed-

H.S. Leff (✉)
Department of Physics, California State Polytechnic University, 3801 W. Temple Ave., Pomona,
CA 91768, USA
e-mail: hsleff@csupomona.edu

up-ness, and the like—none of which involves energy explicitly.[1] The purpose of the present article is to discuss how entropy can be related to energy in a qualitative, interpretive way, offering the possibility of an improved understanding and appreciation of entropy's generality and value.

1.1 The Disorder Metaphor

The most common metaphor for entropy relates it to *disorder*. Usage goes back at least to Boltzmann [2], who wrote, "...one must assume that an enormously complicated mechanical system represents a good picture of the world, and that all or at least most of the parts of it surrounding us are initially in a very ordered—therefore very improbable—state ... whenever two or more small parts of it come into interaction with each other, the system formed by these parts is also initially in an ordered state, and when left to itself it rapidly proceeds to the disordered most probable state."

Unfortunately, the term disorder is deficient. First and foremost, there is no *general* definition of it in the context of thermodynamics. Dictionary definitions typically are: *Lack of order or regular arrangement; confusion; (in medicine) a disturbance of normal functioning.* "Lack of regular arrangement" has a spatial connotation, and one can indeed conceive of *spatial* disorder; i.e., where the positions of particles lack regularity; and *spin* disorder, which refers to the degree of non-regularity of up-down spin orientations. The term *confusion* can be related to the disorder that some associate with higher temperatures, often envisaged in terms of increased *thermal agitation*. The definition of disorder seems to be variable, depending on the situation, which makes the term vague and confusing. Burgers [3] observed that disorder "leads to anthropomorphic forms of reasoning which are often misleading." Yet physicists still tend to gravitate toward use of the disorder metaphor.

Another difficulty is that one can be misled by focusing attention on one obvious type of disorder to the exclusion of important others. For example, this is tempting in the discussion of spontaneous crystal formation in an isolated, metastable supersaturated solution. Here a dissolved solid's concentration exceeds its maximum equilibrium value and a slight perturbation can trigger crystal formation. From a spatial viewpoint, there is more *order* after crystallization, yet the system's entropy (including liquid, solid crystals, and container walls) must increase. The tempting misleading interpretation that entropy decreases, based on increased spatial order is exacerbated by the fact that it is possible that temperature has also decreased. To be sure, the physical phenomena here are not transparent, but the ease of misinterpretation using the disorder metaphor is noteworthy.

The behavior of some binary liquid crystals clearly illustrate weaknesses with the disorder metaphor [4]. At one temperature, such a system can be in a *nematic* phase, where the rod-like molecules tend to align, but positions show no particular spatial order. For lower temperatures, the system can enter the *smectic* phase, where molecules lie in well defined planes, establishing a spatial layering. The increased spatial order

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[1]Some entail energy implicitly. For example, multiplicity refers to the number of accessible *energy* states consistent with specified conditions.

(decreased disorder) does indeed accompany reduced entropy. However, as temperature is lowered further, the system re-enters a *nematic* phase with *increased* spatial disorder, but *lower* entropy. This shows again that the disorder metaphor can easily mislead. Generally, an undue focus on *configurational* entropy (including that associated with the regularity of positions or alignment of rodlike or polarized molecules), without giving proper attention to entropy contributions from linear and angular momentum effects, is a dangerous practice.

Karl Darrow [5] examined examples for which entropy could be associated with disorder, and observed that disorder is not always useful, as indicated by a free expansion of a gas in a constant-temperature environment. Entropy increases, but one cannot unambiguously associate more disorder with the final state. He wrote, "Would anyone spontaneously say that a gas in a two-liter bottle is more disorderly than the same gas at the same temperature in a one-liter bottle?" In another discussion of the free expansion, Bohren and Aldrich [6] write that increased volume only means increased disorder if "we *define* this to be so. But if we do, we have defeated our purpose of supposedly explaining entropy as disorder. That is, we have defined disorder by means of entropy, not the other way around."

Despite Darrow's displeasure with some aspects of the disorder metaphor, he used it subsequently in its variable-definition form and applied it to the zero-temperature limit: "Zero entropy corresponds to perfect order . . . if two or more types of disorder coexist each makes to the total entropy a contribution of its own, which vanishes when it vanishes." This implies that as entropy approaches zero, all possible forms of disorder disappear. Although this circumvents *defining* disorder for the zero-temperature limit, it does not provide much help with finite temperature situations, where definitions of various types of disorder would be needed.

The term disorder has been criticized by a variety of others writers, including Dingle [7], who described the view that entropy is disorder as "a most inessential visualization which has probably done much more harm than good." Wright [8] examined various examples of real phenomena and concluded, ". . . there is no clear correlation between propositions about entropy and anything *intuitively obvious* about disorder." Lambert [9], critically assessed usage of the disorder metaphor in chemistry textbooks, and has successfully convinced authors of 15 textbooks to remove statements relating entropy with *disorder* from new editions of their books.

Upon the death of J. Willard Gibbs, a list of subjects intended for supplementary chapters to Gibbs' *Equilibrium of Heterogeneous Substances* was discovered [10]. One of the topics was "On entropy as mixed-up-ness." Unfortunately, Gibbs did not live to bring this to fruition and it is not known just what Gibbs had in mind. Mixed-up-ness sounds a lot like disorder and Gibbs, who had considerable mathematical skills, might have been able to solidify its meaning. As it stands, even if one places value in the disorder metaphor, its current use does not entail specific reference to energy, the centerpiece of thermodynamics. In this sense, it cannot get to the heart of the physics.

1.2 Missing Information, Multiplicity, Optiony, Freedom, Unavailability

The metaphor of *missing information* for entropy is much preferred over disorder. Edwin T. Jaynes [11], used information theory to develop the full mathematical

framework of equilibrium statistical mechanics. The missing information metaphor is well defined and can be quite useful, especially in understanding that descriptions of macroscopic matter necessarily discard enormous amounts of information about system details, working ultimately with a small number of macroscopic variables such as pressure, volume, and temperature. It does not, however, use space, time, and energy in a qualitatively useful way, and thus cannot replace the spreading metaphor that is proposed herein as an interpretive tool.

Related terms are *multiplicity* [12] or equivalently, *optiony* [13]. These terms refer to the number of microstates that correspond to a given macrostate. With these choices, entropy is defined in terms of Boltzmann's famous $S = k_B \ln(multiplicity) = k_B \ln(optiony)$, where k_B is Boltzmann's constant (the Boltzmann form is discussed further in Sect. 1.3). The Second Law can then be stated: *If an isolated macroscopic system is permitted to change, it will evolve to the macrostate of largest multiplicity (or optiony) and will remain in that macrostate*.

The metaphor *freedom* was proposed by Styer [4], who wrote, "... the advantage of the 'entropy as freedom' analogy is that it focuses attention on the variety of microstates corresponding to a macrostate whereas the 'entropy as disorder' analogy invites focus on a single microstate." Styer also warns of deficiencies in the term *freedom*, and suggests that one use *both* freedom and disorder together to better see the meaning of entropy. The freedom metaphor was proposed independently by Brissaud [14]. Freedom can be related to multiplicity, optiony and missing information, and has some attractive features.

Finally, there exists a common metaphor that entropy is a measure of the *unavailability* of energy that can be converted to work in some processes. Because the energy alluded to is macroscopic energy in this engineering-oriented definition, it cannot help us understand why, for example, 2 kg of copper has twice the entropy of 1 kg of copper.

Although the above terms can all be helpful, they do not convey the notions that thermodynamic processes entail energy spreading and that thermodynamic equilibrium is a dynamic equilibrium at a microscopic level.

1.3 The 'Spreading' Metaphor

The metaphor of *spreading* is based explicitly upon space, time, and energy. Space is intimately involved because energy tends to *spread* spatially to the extent possible. For example when hot and cold objects are put in thermal contact, energy spreads *equitably* (discussed in Sect. 3) between them. And when an object is in thermal equilibrium at constant temperature, its quantum state varies temporally as the system's state point *spreads* over accessible quantum states that are consistent with the thermodynamic state. Spatial spreading is a helpful interpretive tool for *processes* and *equilibrium states*, and temporal spreading is particularly useful for interpreting entropy in a particular thermodynamic state.

Clausius came close to using the concept of spreading even before he published his path-breaking 1865 paper that introduced entropy. In 1862 he proposed a function that he called *disgregation* [15]. Clausius pictured molecules as being in constant motion

and viewed this *heat*[2] as tending to "loosen the connection between the molecules, and so to increase their mean distances from one another." Clausius went further in his 1865 introduction of entropy, writing

$$S - S_o = \int \frac{dQ}{T} = \int \frac{dH}{T} + \int dZ. \qquad (1)$$

This represents entropy relative to its value (S_o) in a reference state as the sum of two terms. In the first, dH is the change in what Clausius called *heat content*, which we now call the average kinetic energy as calculated in the canonical ensemble of classical statistical mechanics. In the second term, dZ is the change in disgregation, which we now understand [16] comes from the position integrals of the canonical partition function in classical statistical mechanics. This is consistent with disgregation being related to what is referred to herein as *spatial spreading*.

Denbigh [17] used the spreading idea to describe irreversibility, citing three forms that display *divergence toward the future*: (i) a branching towards a greater number of distinct kinds of entities; (ii) a divergence from each other of particle trajectories, or of sections of wave fronts; (iii) a spreading over an increased number of states of the same entities. These statements entail space and time and although they do not refer specifically to *energy*, they can easily be interpreted in terms of it. Earlier, Denbigh wrote [18], "As soon as it is accepted that matter consists of small particles which are in motion it becomes evident that every large-scale natural process is essentially a process of mixing, if this term is given a rather wide meaning. In many instances the spontaneous mixing tendency is simply the intermingling of the constituent particles, as in inter-diffusion of gases, liquids and solids.... Similarly, the irreversible expansion of a gas may be regarded as a process in which the molecules become more completely mixed over the available space.... In other instances it is not so much a question of a mixing of the particles in space as of a mixing or sharing of their total energy." To this it should be added that when particles move and mix, they carry with them their translational kinetic and stored (e.g., rotational or vibrational) energies; i.e., they spread their energies and exchange energy with other particles.

While multiplicity, missing information, and the like entail the number of *possible* states, the spreading metaphor entails a picture of *dynamic* equilibrium in terms of continual shifts from one microstate to another. The difference can be viewed as use of a noun (multiplicity, information, ...) *vs.* use of a verb (spreading). The spreading route envisages an *active* system, where macroscopically invisible energy exchanges take place—even in equilibrium—while the alternative noun descriptors picture what is possible, rather than what happens spatially and temporally. The mathematics is the same for both, but the interpretations differ significantly.

There seems to be a tendency for some people to link uncertainty with disorder. For example, after a free expansion, the average volume per particle is larger, and we are less certain about where a particle is at any instant. In this sense, missing information has increased. Each molecule carries its translational and internally stored energies to a larger spatial region, but if the gas temperature is unchanged, or has

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[2]This language is obsolete. The term *heat* is now reserved for energy transfers induced by temperature gradients.

decreased, in what sense has the gas become more disordered? Evidently some relate their own uncertainties about a particles' whereabouts with the degree of disorder in the gas itself. The poorly defined term *disorder* has anthropomorphic underpinnings that seem to make it acceptable for some to bend its meaning with its use.

The spreading metaphor is powerful, and offers a physically motivated, transparent alternative to the metaphors discussed above. Styer [4] observed that the most important failing of "...the analogy of entropy and disorder invites us to think about a single configuration rather than a class of configurations." The spreading metaphor addresses this deficiency by focusing on temporal shifts between configurations. In 1996, the spreading metaphor was used to introduce and motivate the development of thermodynamics pedagogically [19]. In 2002, Lambert [9, 20] argued in favor of energy-based language to replace the inadequate metaphor of disorder in chemistry textbooks. The present paper is intended to extend the discussion of the spreading metaphor for a wider audience of research scientists.

2 Spreading in Equilibrium Thermodynamic States

2.1 Following Boltzmann's Lead

Microscopic connections between entropy and spreading can be seen best via the Boltzmann entropy expression

$$S = k_B \ln W(E, V, N), \tag{2}$$

where k_B is Boltzmann's constant and $W(E, V, N)$ is the number of microstates that are consistent with total system energy E, volume V, and particle number N. Classically, $W(E, V, N)$ is an integral over the $6N$-dimensional phase space [21],

$$W(E, V, N) = \frac{1}{N!} \int \left(\frac{d^3q \, d^3p}{h^3} \right)^N \delta(E - H_N), \tag{3}$$

where H_N is the system's Hamiltonian. The delta function $\delta(E - H_N)$ restricts nonzero contributions to the integrals to a $6N - 1$ dimensional constant-energy surface. These equations are the basis of the microcanonical ensemble formalism of statistical mechanics, from which the more widely used canonical, and grand canonical ensemble formalisms are derived. It is natural to use the fundamentally important (2) and (3) to introduce the concept of *spreading*.

The space and momentum integrals run over all possible spatial positions and momenta for each particle. By varying initial conditions, *any* point in the phase space volume $W(E, V, N)$ is accessible.[3] The functions $W(E, V, N)$ and $S(E, V, N)$ therefore increase with E and V, holding the remaining two variables fixed, because an increase in either of these variables increases the accessible phase space volume.[4]

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[3]It is implicitly assumed that accessible phase space regions with equal phase space volumes are equally likely and that equal times are spent in them.

[4]Changes with N at fixed E and V are more subtle, and we *cannot* conclude that $S(E, V, N)$ always increases with N.

A single system's phase point traverses the phase space in time as particles move and exchange energy. This traversal provides a graphic image of a system's particles spreading and exchanging energy through space, as time progresses. Energy, space, and time are all explicitly involved. In this sense, entropy can be thought of as a *spreading* function.

In real systems, the total energy is never exactly constant and energy exchanges with the environment, even if weak, cause continual changes in the system's microstate. To address this case, the function $W(E, V, N)$ in (2) can be replaced by $W(E, \Delta E, V, N)$, the phase space volume of the set of points $\{q, p\}$ such that $E - \frac{1}{2}\Delta E <$ system energy $< E + \frac{1}{2}\Delta E$. This is the phase space volume of points in an energy shell rather than on an energy surface. Here energy exchanges with the environment cause continual changes in the system's phase point, in addition to the constant energy flow envisaged originally.

For a quantum system, $W(E, V, N)$ is the number of quantum states with total energy E; i.e., the degeneracy of E. In principle, the system can be in any of these states, or more generally a superposition of them. For an ensemble, if each system's state could be measured, one would find many of the possible states. This can be interpreted as a kind of spreading over the members of the ensemble. For a real system that interacts with its environment, as in the classical case, the number of states, $W(E, \Delta E, V, N)$, in the energy interval $(E - \frac{1}{2}\Delta E, E + \frac{1}{2}\Delta E)$ can be used. The interactions induce continual jumps from one quantum state to another, a veritable 'dance' over accessible states. This is *temporal spreading*, and this view provides an interpretation for a number of familiar properties of entropy.

For example, under given temperature and pressure conditions, the entropy per particle of monatomic ideal gases tend to increase with atomic mass [19, 22]. This can be understood because the energy levels of an ideal gas are inversely proportional to atomic mass and thus are closer together for higher mass atoms. Thus, in any energy interval ΔE, there will be more states for gases with higher atomic mass, and more states over which the dance over accessible states can occur. This increased *temporal* spreading over states corresponds to higher entropy.

Another example is a comparison of the entropy per particle $S(T, p, N)$ of N-particle monatomic and polyatomic gases at temperature T and pressure p. It is found that $S_{\text{mono}}(T, p, N) \leq S_{\text{poly}}(T, p, N)$. This a consequence of there being more states in an energy interval ΔE in the neighborhood of the average system energy because of the existence of rotations and vibrations in polyatomic molecules. Furthermore, substances comprised of polyatomic molecules with more atoms/molecule tend to have higher entropy values [22] for the same basic reason. More degrees of freedom lead to more states in a given energy interval. This implies a greater degree of temporal spreading over microstates and higher entropy.

2.2 Maxwell Momentum Distribution

Spreading can be viewed in various ways, one of which is through the Maxwell momentum distribution $F(p)$, as illustrated in Fig. 1. Here momenta are separated into bins, in the spirit of the energy cells used by Boltzmann to enable combinatoric counting arguments. The momentum distribution is shown rather than the more

Fig. 1 Probability density of gas particles as a function of momentum for three temperatures
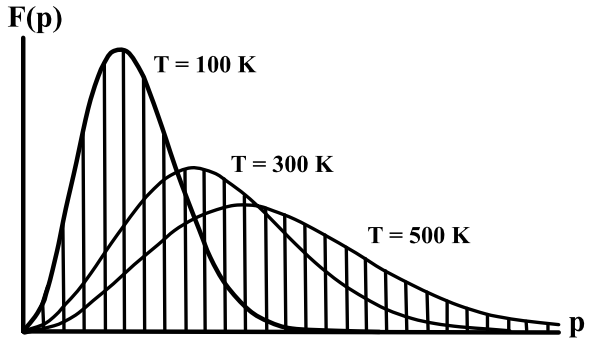
familiar speed distribution because momentum is a more informative variable, containing both speed and mass information—and furthermore, it is the variable used, along with position, in the phase space. Examination of the curves shows that, as expected, more higher-momentum bins become significantly occupied as temperature increases. As gas molecules exchange energy with one another and with container walls, they shift from bin to bin. This reflects a temporal spreading similar to that described above in terms of the phase space trajectory for classical systems and for a dance over discrete energy states for quantum systems. More temporal spreading over bins at higher temperatures means higher entropy.

2.3 Effects of Interparticle Forces

The existence of interparticle forces can inhibit spreading and lower the value of $W(E, V, N)$ and thus the corresponding entropy. This effect can be appreciated by examining a one-dimensional classical harmonic oscillator with energy $E = p^2/2m + kx^2/2$. For fixed energy E, the momentum is bounded by $|p| \leq (2mE)^{1/2}$ and the position is bounded by $|x| \leq (2E/k)^{1/2}$. The system's phase space trajectory is an ellipse and its phase space *volume* is the ellipse's circumference. The semi-axes have lengths $(2mE)^{1/2}$ and $(2E/k)^{1/2}$. Although an exact closed form expression for the circumference does not exist, it is clear that in the limit of zero force constant k, the circumference approaches infinite length and as k becomes large the circumference approaches a minimum for fixed E. Here $W(E, V, N)$ is independent of V, and $N = 1$, so the simple argument here along with (2) imply that S is a decreasing function of k for arbitrarily high and low values. Of course the functions W and S are of questionable value here, but this example does illustrate how a force can inhibit spreading.

In classical statistical mechanics, a gas with temperature T, volume V, and particle number N, has maximum entropy when there are zero interparticle forces; i.e., $S_{\text{ideal}}(T, V, N) \geq S_{\text{nonideal}}(T, V, N)$. To see how this comes about, suppose the system has Hamiltonian $H = K + \Phi$, where K and Φ are the kinetic and potential energies. In the canonical ensemble, the entropy for a system with Hamiltonian H is $S_H = k_B \ln Q_H + \langle H \rangle/T$. Here $Q_H = Tr[\exp(-H/(k_B T))]$, and for classical systems, the trace is taken to be the integral operator $(h^3 N!)^{-1} \int (d^3q \, d^3p)^N$. For an ideal gas at the same temperature and volume, the entropy is $S_K = k_B \ln Q_K + \langle K \rangle/T$.

The Gibbs–Bogoliubov inequality [23], which compares two systems with Hamiltonians A and B, is $-k_B T \ln Q_B \leq k_B T \ln Q_A + Q_A^{-1} Tr[(B - A) \exp(-A/(k_B T))]$. Choosing $A \equiv H$ and $B \equiv K$, the inequality implies $S_K - S_H \geq T^{-1}[\langle K \rangle_K - \langle K \rangle_H]$. In classical statistical mechanics, it is easy to see that $\langle K \rangle_K = \langle K \rangle_H$, showing that $S_K \geq S_H$, and thus, as stated above,

$$S_{\text{ideal}}(T, V, N) \geq S_{\text{nonideal}}(T, V, N). \tag{4}$$

Equation (4), derived by Baierlein [24] and generalized by Leff [25], reflects the fact that position-dependent forces reduce the degree of spatial spreading and the degree of temporal spreading as particles exchange energy. This occurs in the sense that correlations exist between the positions of interacting molecules, and these molecules are not as free to spread their energy as they are in an ideal gas. Equation (4) holds for charged particles in a magnetic field and for lattices of discrete and continuous spins [25].

Despite the fact that one can give a plausible argument for (4) to hold in the quantum domain,[5] it does *not* do so in general [26]. A counterexample has been exhibited for a two-dimensional model of low-density helium monolayers and for ideal quantum gases at sufficiently low temperatures. An interpretation is that this reflects the existence of *effective forces* associated with Bose–Einstein and Fermi–Dirac statistics that can offset the effects of *electromagnetic* intermolecular forces—and thus the degree of energy spreading. The delicacy of the competition between quantum mechanical and electromagnetic forces is evident from the result that (4) is violated in helium monolayers for low temperatures sufficient for quantum effects to exist, but is actually satisfied for *even lower* temperatures.

Additionally, writing $E = K + \phi$, the well known constant-volume heat capacity relation, $k_B T^2 C_v = \langle (E - \langle E \rangle)^2 \rangle$ implies

$$k_B T^2 C_v = [\langle K^2 \rangle - \langle K \rangle^2] + [\langle \Phi^2 \rangle - \langle \Phi \rangle^2] + 2[\langle K\Phi \rangle - \langle K \rangle \langle \Phi \rangle]. \tag{5}$$

For position dependent potential energies Φ, in classical statistical mechanics the last bracket vanishes. The first bracket is $k_B T^2 C_{v,\text{ideal}}$, and the middle bracket is non-negative. Thus we find the pleasing inequality

$$C_{v,\text{nonideal}} \geq C_{v,\text{ideal}}. \tag{6}$$

In essence, the existence of potential energy, in addition to kinetic energy, provides a second mode for energy storage, increasing the heat capacity. Using (6), constant-volume integration between specified initial and final temperatures, provides the constant-volume entropy inequality,

$$(\Delta S_{\text{nonideal}})_v \geq (\Delta S_{\text{ideal}})_v. \tag{7}$$

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[5]When the ideal gas energy states are highly degenerate, one expects the addition of interparticle forces to split this degeneracy, and thereby *lower* the system entropy [24]; i.e., there will be fewer states and thus less spreading in a given energy interval. Perhaps high enough degeneracy is guaranteed only for sufficiently high energy states, which dominate only in the classical domain.

Here is an interpretation of (7) for heating. At higher temperatures, forces become less effective and spatial spreading in the nonideal gas entropy approaches that for the ideal gas. Given the initially reduced spatial spreading in the nonideal gas, this accounts for (7).

2.4 Photon Gas

The photon gas in an otherwise empty container whose walls are at constant temperature T is an interesting system [27]. If the container is a cylinder and one of the cylinder's end walls is a movable piston, one can envisage (in principle) starting out with zero photons, with the piston making contact with the opposite (fixed) end. If the piston is slowly moved away from the fixed end, photons pour into the container from the walls, establishing average photon number $N(T, V) = rVT^3$, with $r = 2.03 \times 10^7 \ \mathrm{m}^{-3} \, \mathrm{K}^{-3}$, at volume V. The photon gas has literally been formed by movement of the piston, providing space for the photons. The corresponding internal energy is $U(T, V) = bVT^4$, where $b = 7.56 \times 10^{-16} \ \mathrm{J} \, \mathrm{K}^{-4} \, \mathrm{m}^{-3}$. The pressure of the photon gas at volume V is $p = \frac{1}{3}bT^4$ and the work done by the gas in the volume change from zero to V is $W = \frac{1}{3}bVT^4$. The first law of thermodynamics then implies isothermal heat transfer $Q = \frac{4}{3}bVT^4$, and thus the final photon gas entropy is

$$S(T, V) = Q/T = \frac{4}{3}bVT^3. \tag{8}$$

Note that $S(T, V) \propto N(T, V)$.

In the process of building the gas, photons and their energies *spread* throughout the container, clearly increasing the spatial spreading of energy. Once established, the dance over accessible states can be understood in terms of the continual absorption and emission of photons over time. If T is increased, the average number N of photons increases, which increases the amount of temporal energy spreading associated with absorption and emission of photons. Additionally, Fig. 2 shows that the entropy density—namely, the entropy per unit volume, per unit frequency of the photon gas—changes with temperature in a manner reminiscent of the Maxwell momentum distribution discussed in Sect. 2.2. An increasing number of bins hold significant numbers

Fig. 2 Entropy per unit volume, per unit frequency of a photon gas for three temperatures

Entropy per unit volume, per unit frequency

T = 300 K

T = 600 K

T = 900 K

Frequency
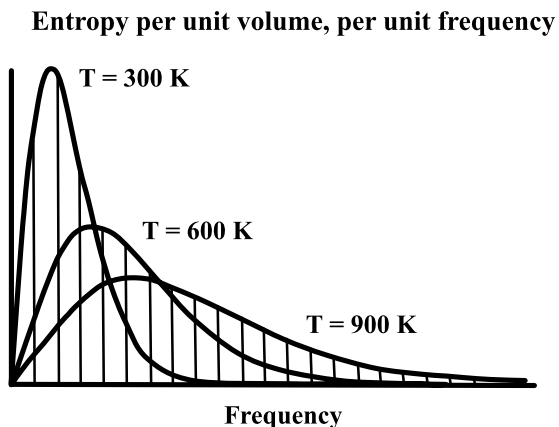
of photons at higher temperatures. This implies a greater degree of temporal spreading because of continual absorption and emission of photons and fluctuating numbers of photons and energy within more bins.

2.5 Thermal Wavelength and Spreading

When (2) is evaluated for a classical ideal gas, and the thermodynamics equation $(\partial S/\partial E)_V = 1/T$ is invoked, the result obtained in the large N limit is

$$S(T, V, N) = Nk_B[\ln(v/\lambda^3) + \text{constant}], \tag{9}$$

with $v \equiv V/N$, $\lambda = h/(2\pi mk_B T)^{1/2}$, the thermal wavelength.

The thermal wavelength can be viewed as the quantum extent of each particle and λ^3 as its quantum volume; i.e., an estimate of the volume of its wave packet. For $v > \lambda^3$, v/λ^3 is an indicator of the fraction of the container that is "occupied." Strictly speaking (9) holds only for $v \gg \lambda^3$; i.e., in the classical limit. Equation (9) predicts that S decreases as T is decreased with v fixed.

Commonly, the effects of temperature change are viewed in terms of momentum, but (9) suggests a very different view of the situation [19]. Suppose the total spatial volume V is divided into $M = V/\lambda^3$ cells, each the size of a wave packet. An atom can spread its energy to any of the M cells. The particles behave as independent entities, with negligible quantum interference if $M \gg N$; i.e., $\lambda^3 \ll v$. As T is lowered, M decreases and the number of accessible cells becomes smaller, reducing the degree of energy spreading in the sense that it becomes more likely, and eventually, necessary that some cells contain more than one particle. Increasing the temperature leads to the opposite conclusion, namely, the amount of energy spreading increases. All of this is consistent with the expected inequality, $(\partial S(T, V, N)/\partial T)_V > 0$.

Although (9) and the cell picture above hold for non-interfering particles only— i.e., for $\lambda^3 \ll v$, the thermal wavelength concept is valid for all temperatures. As T is lowered and λ increases, it becomes more likely that two or more particles will have overlapping wave packets; i.e., for $M < N$, some cells *must* be occupied by more than one particle. Let T_o denote the temperature at which $\lambda^3 = v$. At this temperature there are as many wave packet-sized cells as particles. As T is lowered below T_o, quantum interference builds, as illustrated symbolically in Fig. 3, and extreme quantum effects become possible. Such effects are expected for

$$T < T_o = \frac{h^2}{2\pi mk_B v^{2/3}}. \tag{10}$$

Bose–Einstein condensation is an extreme low-temperature behavior that has been verified experimentally [28]. Einstein's treatment of the ideal B-E gas shows a phase transition for *any* specific volume v at the critical temperature $T_{c,BE}$ such that $\lambda_c^3/v = 2.612$ [29]. This condition is consistent with expectations; i.e., $T_c < T_o$. Specifically,

$$T_{c,BE} = \frac{h^2}{2\pi mk_B(2.612)^{2/3}v^{2/3}} = 0.53T_o. \tag{11}$$

Higher temperature   Lower temperature
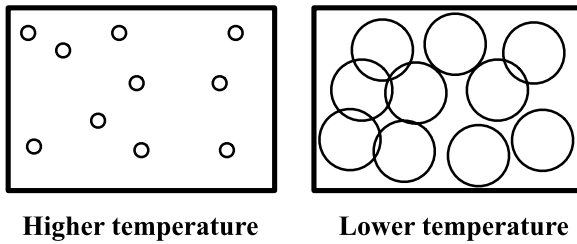
Fig. 3 Symbolic representation of particle wave packets for higher temperatures, where $\lambda^3 \ll v$ and lower temperatures, where $\lambda^3 \approx v$. The rectangular boundaries represent spatial regions within the fluid (*not the full container volume*). The thermal wavelength λ does not become of macroscopic size until T is well below temperatures that have been reached in any laboratory

The main point here is that the growth of the thermal wavelength at low temperatures restricts spreading, albeit with some quantum subtleties.[6,7] The reduced spatial spreading signals reduced entropy and as T decreases toward absolute zero spatial spreading and entropy approach zero.

Although $\lambda \to \infty$ as $T \to 0$, in actual experiments λ does not become of macroscopic size until T is lower than temperatures that have been reached in any laboratory. For example, in the neighborhood of helium's lambda point, 2.7 K, where extreme quantum behavior is observed, $\lambda^3/v \approx 3$ (remarkably close to the condition for B-E condensation in an ideal gas) and $\lambda \approx 5 \times 10^{-10}$ m.

Nothing in our discussion of thermal wavelength restricts it to systems satisfying B-E statistics, and it should apply equally well to Fermi–Dirac statistics. In particular, (10) should still hold. For an ideal gas with spin 1/2 particles, which satisfies F-D statistics, the Fermi temperature is [29]

$$T_F = \frac{h^2}{2\pi m k_B v^{2/3}} \left(\frac{3\pi^{1/2}}{8} \right)^{2/3} = 0.76 T_o. \tag{12}$$

Thus the Fermi temperature, below which extreme quantum effects occur, does indeed lie in the region where such effects are expected, based upon thermal wavelength considerations—and inspired by the spreading metaphor.

In summary, the view of inhibited spatial spreading as temperature is lowered and thermal wavelength increases is consistent with known behavior of entropy decreasing toward zero with decreasing temperature.

2.6 Free and Non-Free Expansions

The free expansion, which was alluded to earlier, is conceptually simple, but it illustrates profound truths about entropy. In its most basic form, it entails a container with

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[6]One subtlety is that λ^3 does not represent a rigid volume; it is only an indicator of the range over which quantum interference becomes strong.

[7]S. Chu argued that B-E condensation can be viewed in terms of increased particles wavelength; American Institute of Physics Symposium: Diverse Frontiers of Science, May 3, 2006, Washington, DC. This provided the impetus for addressing low temperature ideal gases in this section.

insulating walls and total volume $2V$. A partition separates the container into left and right chambers, each with volume V. There is a gas in the left chamber and the right chamber is devoid of matter. The insulation is breached briefly while the gas temperature T is measured. The thermometer is removed and the insulation is replaced. The partition is then removed quickly enough that few collisions with gas molecules occur during the process; i.e., removal does not disturb the gas measurably and the internal energy change of the gas is zero: $\Delta E = 0$. According to the discussion in Sect. 2, the phase space volume has increased and thus the entropy has increased, because gas energy has become spread over a larger spatial volume.

If the gas is ideal and is in the classical region of temperature and density, its temperature does not change. If interparticle forces exist, the temperature can either decrease or increase, depending on its initial temperature [30]. There exists an inversion temperature T_I that is similar to the more well known inversion temperature for Joule throttling processes. For temperatures above T_I, the gas temperature *increases* in a free expansion. At temperatures below T_I, the gas temperature *decreases*. Typically, T_I is higher than is encountered under most experimental conditions and free expansions normally lead to cooling. Helium has $T_I \approx 200$ K, so for a free expansion beginning at room temperature, helium's temperature rises, giving a further contribution to gas entropy's increase. The crux of the matter is this: If the gas particles have sufficiently high kinetic energies, they can get close enough to other particles that the average force is repulsive. In this case, expansion to a larger volume diminishes this effect and reduces the average potential energy, which demands a concomitant average kinetic energy increase to assure that $\Delta E = 0$.

In terms of spreading, when the average force between molecules is repulsive, spatial spreading is *enhanced* and this adds to the effect of the volume increase. Thus larger entropy changes are expected, consistent with an increased volume *plus* a higher temperature. In the more common situation, when the average force between molecules is attractive, spreading is constrained and this reduces the net amount of spatial spreading. This is consistent with the effect of increased volume being partially offset by a temperature decrease. Because temperature changes experienced in free expansions are relatively small, all free expansions lead to a *net* increase in spatial spreading and thus entropy.

To close this section, consider an isothermal expansion of a classical fluid, for which [31, 32],

$$(\Delta S_{\text{nonideal}})_T \geq (\Delta S_{\text{ideal}})_T. \tag{13}$$

A spreading interpretation is that interparticle forces in the nonideal system constrain spreading and depress entropy. In an expansion, the average interparticle distance between gas particles lessens, spreading is less constrained, and ultimately—for large enough volume—approaches the degree of spreading of an ideal gas. The left side of (13) exceeds the right side because of the initial depressed degree of spreading at smaller volume, where interparticle forces are strongest on average.

2.7 Mixing of Gases

Consider two gases, each with N molecules, initially in separate but equal volumes V separated by a central partition, as shown in Fig. 4(a). The entire system has tem-

Fig. 4 (**a**)–(**b**) Process I:
Mixing of two ideal gases (black
and empty circles) under
classical conditions, each
initially in volume V and finally
sharing volume $2V$. (**b**)–(**c**)
Process II: Isothermal
compression to volume V

(a)

(b)

II

(c)
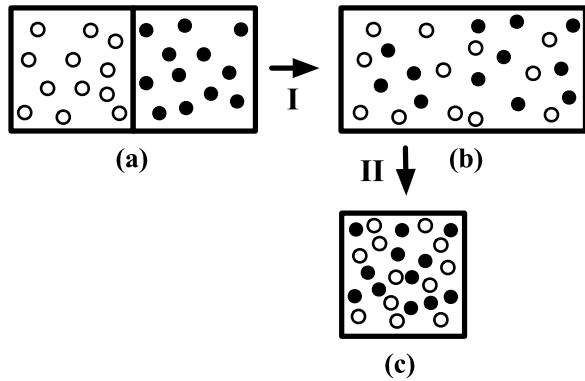
perature T. If the partition is removed, the gases spontaneously mix together, there is
no temperature change, and the entropy change is

$$\Delta S = \begin{cases} 2Nk_B \ln 2 & \text{for distinguishable gases,} \\ 0 & \text{for identical gases.} \end{cases} \tag{14}$$

For *distinguishable* molecules, process I yields the standard "entropy of mix-
ing", (15). Despite its name, this entropy change actually comes from the expan-
sion of each species; i.e., $\Delta S_I = Nk_B \ln 2 + Nk_B \ln 2 = 2Nk_B \ln 2$. Process II,
Fig. 4(b), (c), is an isothermal compression of the container in (b), so $\Delta S_{II} =
-2Nk_B \ln 2$. In the latter process, energy spreading is *negative* for the gas, with pos-
itive energy spreading occurring in the constant-temperature environment, which re-
ceives energy. Thus

$$\Delta S_{\text{total}} = \Delta S_I + \Delta S_{II} = 0 \quad \text{for } \textit{distinguishable} \text{ particles.} \tag{15}$$

Here is an energy spreading interpretation. For *distinguishable* gases, energy
spreads from volume V to $2V$ by *each* species in process I, accounting for $\Delta S_I =
2Nk_B \ln 2$. Note that upon removal of the partition, the energy spectrum of each
species becomes compressed because of the volume increase and, most important,
spreads through the entire container. That is, energy states of "black" particles exist in
the right side as well as the left, with a corresponding statement for "white" particles.
In process II, each species gets compressed from $2V$ to V, so $\Delta S_{II} = -2Nk_B \ln 2$.
In configuration (c), each species spreads energy over volume V, just as in (a), con-
sistent with the overall result $\Delta S_{\text{total}} = 0$.

For *indistinguishable* molecules (black circles become white) in process I there is
no change in energy spreading because the lone species energy was already spreading
energy in both chambers, and $\Delta S_I = 0$.[8] In process II, the lone species is compressed
from $2V$ to V, so

$$\Delta S_{\text{total}} = \Delta S_{II} = -2Nk_B \ln 2 \quad \text{for } \textit{indistinguishable} \text{ particles.} \tag{16}$$

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[8]In Fig. 4(a), the N particles on the left and N particles on the right have identical energy spectra. In
Fig. 4(b), the $2N$ particles have a single, compressed spectrum because of the volume increase. In this
view, the result in (15) is not apparent.

In (c), $2N$ molecules of the lone species spread energy over volume V, while in (a), N molecules of the species spread energy over volume V and another N molecules spread energy over a *different* volume V. Thus, there is more spreading of the given species and higher entropy in (a), consistent with $\Delta S_{\text{total}} = \Delta S_I + \Delta S_{II} = -2Nk_B \ln 2$.

2.8 Metastability, Frozen-in States, and Maxwell's Demon

It has been assumed throughout that internal energy spreading proceeds unimpeded in macroscopic systems, consistent with existing *external* constraints. However, in some cases there exists *internal* metastability, which inhibits full spreading of energy over space and energy modes. This occurs in the cooling of some materials toward 0 K. For example, glycerin can be cooled to low temperatures without it becoming a solid. A consequence is that near absolute zero *supercooled* glycerin's entropy exceeds the value of solid glycerin at the same temperature. For the supercooled "glassy liquid," full energy spreading to the cold surroundings has not occurred and the substance is in an internal metastable state, which could be destroyed—with a concomitant energy transfer to the surroundings—by a small perturbation. This situation is commonly described in terms of the glassy liquid being "more disordered" than the corresponding solid. The latter description hides the important point that energy interactions within the glycerin are too weak to achieve full spreading—i.e., thermal equilibrium—on the time scale of the experiments. Put differently, the lowest possible energy state has not been reached.

An interesting situation exists where states are "frozen in," and in this case, it is used to good advantage. A digital memory maintains a state (e.g., magnetization "upward") because of the existence of strong internal forces. In the simplest possible case, one can envisage a single particle in a double potential well, say with occupation of the left well denoting a "one" and occupation of the right well denoting a "zero." Once a particle is in one of the wells, a central potential barrier prevents passage to the other well under normal temperatures. To erase such a memory one must either lower the central barrier or raise the particle temperature so that the particle has no left-right preference.

Rolf Landauer addressed the issue of memory erasure in 1961 [33] and concluded that erasure of *one bit* at temperature T requires dissipation of at least energy $k_B T \ln 2$ to the environment, with entropy change $\Delta(S_{\text{system}} + S_{\text{surroundings}}) \geq k_B \ln 2$. This result, commonly called *Landauer's Theorem*, has been used to argue that memory erasure "saves" the second law of thermodynamics from the mischief of a Maxwell's demon. The simplest way to understand this is through an ingenious model proposed by Szilard [34–37]. He envisaged the hypothetical one-particle heat engine illustrated in Fig. 5.

Insertion of a partition leaves the particle either on the left or right. With information on which side it resides, one would know how to configure a pulley system and external weight pan to enable the "gas" to do work lifting the weight pan. Once this is done the partition is unlocked, becoming a frictionless, movable piston, and the gas can do external work $W = k_B \ln 2$ as the gas volume is doubled, lifting the weight pan. Strictly speaking, to keep the process slow and reversible, grains of sand

Fig. 5 Szilard one-particle gas
engine, as described in the text
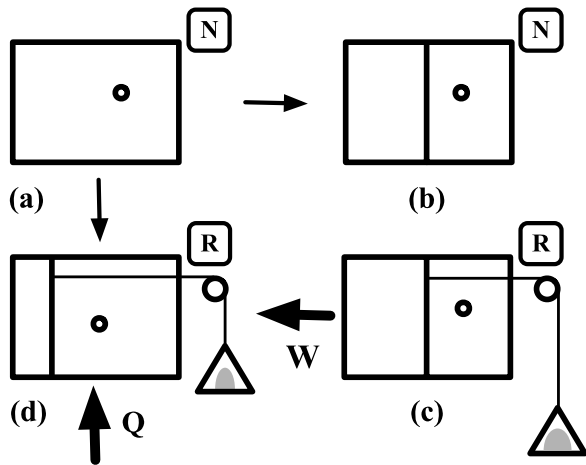
can be removed from the weight pan and deposited on shelves (not shown) as the gas
pressure decreases. Replenishment heat energy $Q_{in} = k_B T \ln 2$ would come in from
the surroundings, through the container walls and to the particle itself. Measurement
of the particle's location after partition insertion could be done in principle by a tiny
intelligent being, namely, one with great microscopic observation skills, speed, and a
memory. This constitutes what has come to be called a Maxwell demon [37].

After this work is done, the pulley system and partition are removed and the gas
is in its initial state. A weight has been lifted and the environment has lost some
energy because of the energy transfer to the container, and the particle. In essence,
heat has been converted to work and, ignoring the demon's memory, it appears that
the second law of thermodynamics has been violated, albeit on a microscopic scale.
But, as pointed out first by Penrose [38] and independently by Bennett [39], the state
of the demon's memory cannot be ignored.

In Fig. 5(a)–(d), the state of the demon's memory (RAM) is shown in the small
upper right box. It is initially neutral (N, which can be either R or L), but after mea-
surement, it is R (for right side in this example). After the cycle is run, the memory
must be brought back to its initial, neutral state; i.e., its memory must be erased and
the initial memory state restored, in order to do complete entropy bookkeeping. Ac-
cording to Landauer's theorem, erasure will send at least energy $Q_{erasure} \geq k_B T \ln 2$
to the surroundings. The latter energy (at least) replenishes the surroundings, and the
work needed to effect memory erasure "pays" for the lifted weight's gravitational po-
tential energy increase. Assuming thermodynamics ideas can be sensibly applied at
this microscopic level, and that Landauer's theorem holds, the second law is saved.

In terms of the spreading metaphor, without accounting for the demon, the sur-
roundings would have suffered negative energy spreading because of its loss of en-
ergy. Because there is no energy spreading associated with ideal frictionless macro-
scopic work, this signals a net entropy drop for the isolated system of Szilard engine
plus surroundings. But after erasure of the memory the situation is very different:

There is a non-negative net change in energy spreading and no violation of the second law.

The most interesting aspect of this problem is the situation *just before* memory erasure. The environment still has less entropy than it had initially, the weight has been lifted, and the memory state is either R or L. The question is: at this point in time, is the second law intact? For this to be so, an entropy of (at least) $k_B \ln 2$ must be attributable to the memory. Because the memory's bit state is "frozen in," there is zero spreading over the R and L states; the memory is either in one or the other.[9] From a spreading viewpoint, the second law is violated just prior to erasure, but is saved by the erasure process.

In contrast, a missing information view leads to assignment of entropy $k_B \ln 2$ based upon the absence of information about the bit state of the memory. Similarly, an algorithmic information view leads to the same entropy for the memory, based upon the number of bits of information needed to specify its state [40]. The dichotomy between the spreading and information theory approaches is notable. Related difficulties have generated criticisms of arguments that the second law can be saved by memory erasure for the Maxwell's demon conundrum [41, 42].

Finally, it is observed that the validity of Landauer's theorem, and indeed the second law itself, has come in question for small or mesoscopic systems under extreme quantum conditions [1, 43–47]. These are beyond the scope of this article.

3 Seeking a Spreading Function

We have argued that entropy is a function that represents a measure of spatial spreading of energy and a temporal spreading over energy states. In this section, we indicate how one can arrive at entropy by seeking a function that is a measure of spreading. The value of this exercise is that it demonstrates the richness and depth of the spreading metaphor. Typically, existing constraints restrict the spreading of energy spatially. Examples of such constraints are an insulating wall, immovable partition, non-porous wall, open electrical switch, and electric or magnetic shielding.

Processes that increase energy spreading are driven by gradients—e.g., of temperature, pressure, or chemical potential. Removal of such a constraint will lead to increased energy spreading that proceeds so as to decrease the gradient(s). It has been said [48] that "nature abhors a gradient," and indeed, all *changes* in the degree of spreading are driven by gradients. Examples are replacing an insulating wall with a conducting one (in the presence of a temperature gradient), making an immovable wall movable (in the presence of a pressure gradient), and removal of a non-porous partition (when there is a chemical potential gradient).

Consider an energy exchange between two *identical* macroscopic bodies that are initially at different temperatures. The higher temperature body has larger internal energy, and the energy exchange allows the energy to become distributed *equitably*. Symmetry dictates that the final internal energies be equal. Evidently, energy spreads

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[9]It is assumed that the thermodynamic entropy, and concomitant spreading, associated with the memory's other degrees of freedom, have not changed throughout the engine's operation.

over space maximally. If it spreads *less* than maximally, the lower temperature body would end with a temperature below the other body, and if it spread 'too much,' the initially lower temperature body would become the higher temperature one—and such configurations are equivalent to the less than maximal ones that were discussed already.

Does a spreading function exist for this two body system? That is, can energy spreading be quantified? We require that a *bona fide* spreading function, which we call $\mathcal{J}$, have the following properties. In essence, these are postulates that are deemed reasonable for such a function.

1. *For a homogeneous body, $\mathcal{J}$ is a function of the system's energy E, volume V, and particle number N.* Rationale: These are common thermodynamic variables, for one-component systems.
2. *At uniform temperature, $\mathcal{J}$ is an increasing function of energy E.* Rationale: More energy means there is more energy to spread and thus more spreading.
3. *For a body made of the same material, but with twice the volume and energy, the value $\mathcal{J}$ is double that of the original body; i.e., $\mathcal{J}(2E, 2V, 2N) = 2\mathcal{J}(E, V, N)$. This requires the degree of spreading to double when twice the energy spreads over twice the number of particles occupying twice the volume. A generalization is that for any real $\beta \geq 0$, $\mathcal{J}(\beta E, \beta V, \beta N) = \beta \mathcal{J}(E, V, N)$, which is the property called extensivity.*[10] Rationale: Clearly there should be *more* spreading for $\beta > 1$, and it is reasonable that, for example, doubling E, V, N also doubles $\mathcal{J}(E, V, N)$. Halving E, V, N would give half as much spreading, and so forth.
4. *For two systems, labeled a and b, $\mathcal{J}_{a+b} = \mathcal{J}_a(E_a, V_a, N_a) + \mathcal{J}_b(E_b, V_b, N_b)$.* Rationale: We require that the spreading function be additive, as are internal energy, volume, and particle number themselves. This is based on the belief that spreading effects on boundaries of systems a and b are negligible, being overwhelmed by the spreading over volumes. It is assumed that particles interact via short-range interatomic and intermolecular forces.
5. *$\mathcal{J}_{a+b}$ is maximal at equilibrium.*[11] Rationale: Spreading continues until equilibrium is reached and cannot become larger. This will become more clear in the following example.

Using a symmetry argument, the assumed existence of maximum spatial spreading at equilibrium for *identical* systems demands that if the initial body energies are E_a and $E_b > E_a$, then the final energy of each is

$$E_f = \frac{1}{2}(E_a + E_b). \tag{17}$$

According to postulate 4, after equilibration,

$$\mathcal{J}_{a+b} = \mathcal{J}_a(E_f) + \mathcal{J}_b(E_f) = 2\mathcal{J}(E_f), \tag{18}$$

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[10]Systems with long-range forces—e.g., gravitational and electric—do *not* satisfy the extensivity condition and the framework here does not apply to such systems.

[11]The development here is for equilibrium states only. It is not known if a generalization of the spreading picture to nonequilibrium states is possible.
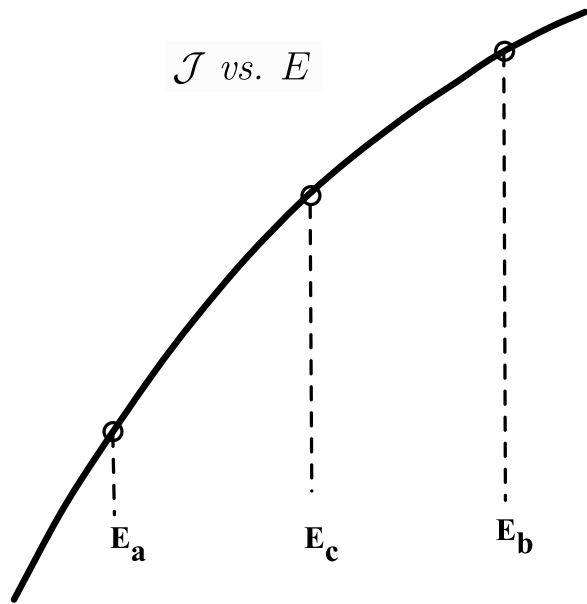
and postulate 5 demands that

$$\mathcal{J}_{a+b}(E_f) = 2\mathcal{J}(E_f) \geq \mathcal{J}(E_a) + \mathcal{J}(E_b) \quad \text{with } E_a \leq E_f \leq E_b. \qquad (19)$$

Expression (19) defines a concave function, and the temperature equilibration process looks as shown in Fig. 6. In the final state, the value of $\mathcal{J}$ is the same for each body and, of course, all derivatives are the same. Figure 6 shows that although systems a and b each experience the same magnitude energy change, concavity assures that system a has a greater increase in its spreading function than system b.

Now consider two bodies of the same material, one (system a) of which has twice the volume and particle number of the other (system b), with total energy $E_a + E_b = E$. Suppose the two bodies each have equal initial energies: $E_{a,i} = E_{b,i} = E/2$. We expect system a's initial temperature to be lower than system b's, given that is has the same energy as the smaller system b. When the two systems are put in thermal contact with one another, energy will spread until it is shared *equitably* by the two subsystems, namely, with final energies $E_a = 2E/3$ and $E_b = E/3$. A bit of mathematics shows that this is consistent with $\mathcal{J}_{a+b}$ being maximized; i.e., *equitable* energy sharing occurs when the total spreading function is maximized relative to the existing constraint $E_a + E_b = E$. Specifically,

$$(\partial \mathcal{J}_a / \partial E_a)|_{E_a = 2E/3} = (\partial \mathcal{J}_b / \partial E_b)|_{E_b = E/3}. \qquad (20)$$

This analysis can easily be extended to system a being β times larger than the otherwise identical system b. After equilibration, the final energies will be $E_{a,f} = \beta E/(\beta + 1)$ and $E_{b,f} = E/(\beta + 1)$, with $(\partial \mathcal{J}_a / \partial E_a)|_{E_{a,f} = \beta E/(\beta+1)} = (\partial \mathcal{J}_b / \partial E_b)|_{E_{b,f} = E/(\beta+1)}$. Again, this maximizes J_{a+b}. More generally, for *any* two
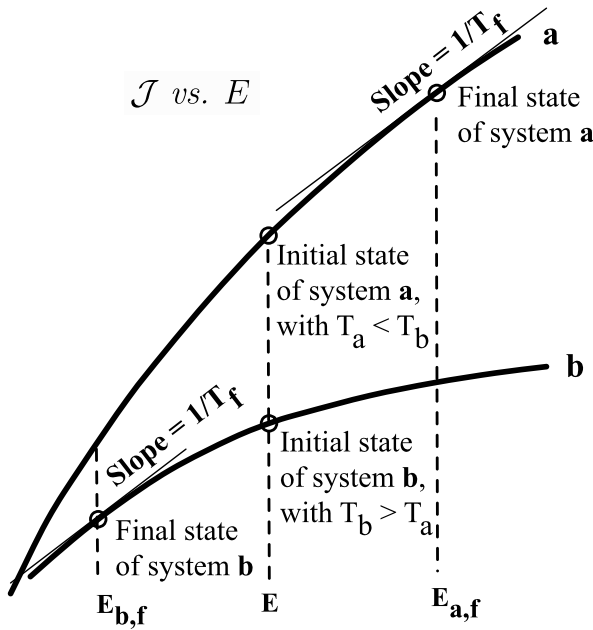
Fig. 7 Spreading functions $\mathcal{J}(E, V, N)$ *vs.* E for two different materials. Initially, the systems have the same energy E, and $(\partial \mathcal{J}_a/\partial E_a)|_{E_a=E} > (\partial \mathcal{J}_b/\partial E_b)|_{E_b=E}$. Concavity guarantees that the *only* energies for which an infinitesimal variation of E_a and E_b with $E_a + E_b$ fixed gives $d\mathcal{J} = 0$ are $E_{a,f}$ and $E_{b,f}$, at which $(\partial \mathcal{J}_a/\partial E_a)|_{E_a=E_{a,f}} = (\partial \mathcal{J}_b/\partial E)|_{E_b=E_{b,f}}$

different systems, of different types and/or sizes, maximization of spreading leads to the following generalization of (20),

$$(\partial \mathcal{J}_a/\partial E_a)|_{E_a=E_{a,f}} = (\partial \mathcal{J}_b/\partial E_b)|_{E_b=E_{b,f}} \tag{21}$$

which determines $E_{a,f}$ and $E_{b,f} = E - E_{a,f}$. Here, we assume, based on the pattern seen above, that *equitable* energy sharing occurs when spreading is maximized.

Figure 7 shows how the spreading functions and the equilibration process might look for two different-sized and/or different type systems that begin with equal energies and then share energy until thermal equilibrium exists. Given the above discussion and the observation, using Fig. 7, that $(\partial \mathcal{J}_a/\partial E_a)|_{E_a=E} > (\partial \mathcal{J}_b/\partial E_b)|_{E_b=E}$ it is suggestive that $\partial \mathcal{J}/\partial E$ is inversely related to temperature. The simplest such relationship is

$$(\partial \mathcal{J}/\partial E)_{V,N} = 1/T. \tag{22}$$

With this definition, $\partial \mathcal{J}/\partial E$ decreases and T increases as energy increases for each system. Furthermore, $\mathcal{J}_a$ increases more than $\mathcal{J}_b$ decreases, consistent with the total spreading function $\mathcal{J} = \mathcal{J}_a + \mathcal{J}_b$ increasing to a maximum at equilibrium.

For a constant-volume heating process that proceeds along a given $\mathcal{J}$ curve, $dE = \delta Q$, where δQ is the (inexact) heat differential. Equation (22) implies that $d\mathcal{J} = dE/T \equiv \delta Q/T$, in analogy with the Clausius entropy form $dS = \delta Q/T$.

Thus, with the temperature definition (22), the spreading function $\mathcal{J}$ shares the important mathematical property $d\mathcal{J} = \delta Q / T$ with entropy S. More connections between $\mathcal{J}(E, V, N)$ and $S(E, V, N)$ can be made, and the interested reader is directed to Ref. [19] for further details. The main conclusion is

$$\mathcal{J} \longleftrightarrow S. \tag{23}$$

Entropy has properties of a spreading function and, in turn, one can use expected properties of a spreading function to obtain the entropy function.

4 Concluding Remarks and Questions

Although entropy is intimately related to the second law of thermodynamics, it is also true that the well known statements of the second law by Clausius and by Kelvin and Planck neither use nor require the entropy concept. Čápek and Sheehan [1] have pointed out that most current challenges to the second law entail heat and work, rather than entropy. Further, they wrote, "Entropy remains enigmatic. The more closely one studies it, the less clear it becomes. Like a pointillism painting whose meaning dissolves into a collection of meaningless points when observed too closely, so too entropy begins to lose meaning when one contemplates it at a microscopic level."

The scope of this article is highly limited, being directed primarily at developing the spreading metaphor as an *interpretive* tool. It is by no means clear whether the spreading concept can developed more fully mathematically, for example, for systems not in thermodynamic equilibrium. Were that possible, one might hope for a way to address non-equilibrium entropy. Similarly it is not clear if the spreading concept can be usefully extended to non-extensive systems characterized by long-range gravitational and/or electric forces.

Questions abound. Can improved language help to clarify the meaning and improve the utility of entropy and, if so, can the spreading metaphor help in this regard? Can the spreading metaphor be helpful when S is not well defined? Can this metaphor shed light on situations where the second law of thermodynamics is suspected of being, or is shown to be, violated? Can the spreading concept be used in combination with one or more other metaphors—e.g., multiplicity and/or missing information—to provide a more complete qualitative description of entropy? It is hoped that time will bring answers to these questions.

References

1. Čápek, V., Sheehan, D.P.: Challenges to the Second Law of Thermodynamics—Theory and Experiment. Springer, Dordrecht (2005)
2. Boltzmann, L.: Lectures on Gas Theory—Part I, pp. 441–443. Barth, Leipzig (1896), reprinted by University of California Press, Berkeley (1964)
3. Burgers, J.M.: Entropy and disorder. Br. J. Philos. Sci. **5**, 70–71 (1954)

 4. Styer, D.F.: Insight into entropy. Am. J. Phys. **68**, 1090–1096 (2000)
 5. Darrow, K.K.: The concept of entropy. Am. J. Phys. **12**, 183–196 (1944)
 6. Bohren, C.F., Albrecht, B.A.: Atmospheric Thermodynamics, pp. 150–152. Oxford University Press, Oxford (1998)
 7. Dingle, H.: Bull. Inst. Phys. **10**, 218 (1959)
 8. Wright, P.G.: Entropy and disorder. Contemp. Phys. **11**, 581–588 (1970)
 9. Lambert, F.L.: Disorder—a cracked crutch for supporting entropy discussions. J. Chem. Ed. **79**, 187–192 (2002), revised web version: http://www.entropysite.com/cracked_crutch.html. See also Lambert's website, http://www.entropysite.com for related discussions
10. Gibbs, J.W.: The Scientific Papers of J. Willard Gibbs, vol. 1, p. 418. Constable, London (1906), reprinted by Dover, New York (1961)
11. Jaynes, E.T.: Information theory and statistical mechanics. Phys. Rev. **106**, 620–630 (1957)
12. Baierlein, R.: Teaching the approach to thermodynamic equilibrium: some pictures that help. Am. J. Phys. **46**, 1042–1045 (1978)
13. Swanson, R.M.: Entropy measures amount of choice. J. Chem. Ed. **67**, 206–208 (1990)
14. Brissaud, J.B.: The meanings of entropy. Entropy **7**, 68–96 (2005)
15. Clausius, R.: On the application of the theorem of the equivalence of transformations to the internal work of a mass of matter. Philos. Mag. **24**, 81–97 (1862), Reprinted in Kestin, J. (ed.) The Second Law of Thermodynamics. Dowden, Hutchinson & Ross, Stroudsberg (1976)
16. Klein, M.J.: Gibbs on Clausius. Hist. Stud. Phys. Sci. **1**, 127–149 (1969)
17. Denbigh, K.G.: The many faces of irreversibility. Br. J. Philos. Sci. **40**, 501–518 (1989)
18. Denbigh, K.G.: The Principles of Chemical Equilibrium. Cambridge University Press, Cambridge (1961), Sect. 1.7
19. Leff, H.S.: Thermodynamic entropy: the spreading and sharing of energy. Am. J. Phys. **64**, 1261–1271 (1996)
20. Lambert, F.L.: Entropy is simple, qualitatively. J. Chem. Ed. **79**, 1241–1246 (2002), revised web version: http://www.entropysite.com/entropy_is_simple/index.html
21. Gross, D.H.E.: Microcanonical Thermodynamics: Phase Transitions in 'Small' Systems. World Scientific, Singapore (2001)
22. Leff, H.S.: What if entropy were dimensionless? Am. J. Phys. **67**, 1114–1122 (1999)
23. Falk, H.: Physica **29**, 1114 (1963)
24. Baierlein, R.: Forces, uncertainty, and the Gibbs entropy. Am. J. Phys. **36**, 625–629 (1968)
25. Leff, H.S.: Entropy differences between ideal and nonideal systems. Am. J. Phys. **37**, 548–553 (1969)
26. Bruch, L.W., Schick, M., Siddon, R.L.: Limitation on the quantum-mechanical extension of Baierlein's entropy theorem. Am. J. Phys. **44**, 1007–1008 (1976)
27. Leff, H.S.: Teaching the photon gas in introductory physics. Am. J. Phys. **70**, 792–797 (2002)
28. Anderson, M.H., Ensher, J.R., Matthews, M.R., Wieman, C.E., Cornell, E.A.: Observation of Bose–Einstein condensation in a dilute atomic vapor. Science **269**, 198–201 (1995)
29. Pathria, R.K.: Statistical Mechanics, 2nd edn. Butterworth–Heinemann, Oxford (1996), Chaps. 7, 8
30. Goussard, J., Roulet, B.: Free expansion for real gases. Am. J. Phys. **61**, 845–848 (1993)
31. Lesk, A.M.: Entropy changes in isothermal expansions of real gases. Am. J. Phys. **42**, 1030–1033 (1974)
32. Leff, H.S.: Entropy changes in real gases and liquids. Am. J. Phys. **43**, 1098–1100 (1975)
33. Landauer, R.: Irreversibility and heat generation in the computing process. IBM J. Res. Dev. **5**, 183–191 (1961)
34. Szilard, L.: On the decrease of entropy in a thermodynamic system by the intervention of intelligent beings. Z. Phys. **53**, 840–856 (1929)
35. Feld, B.T., Weiss Szilard, G.: The Collected Works of Leo Szilard: Scientific Papers. pp. 103–129. MIT Press, Cambridge (1972), English translation is by A. Rapoport and M. Knoller
36. Wheeler, J.A., Zurek, W.H.: Quantum Theory and Measurement, pp. 539–548. Princeton University Press, Princeton (1983)
37. Leff, H.S., Rex, A.F. (eds.): Maxwell's Demon 2: Entropy, Classical and Quantum Information, Computing. Institute of Physics, Bristol (2003), now distributed by Taylor & Francis
38. Penrose, O.: Foundations of Statistical Mechanics, pp. 221–238. Pergamon, Oxford (1970)
39. Bennett, C.H.: The thermodynamics of computation—a review. Int. J. Theor. Phys. **21**, 905–940 (1982), reprinted in Ref. [37]
40. Zurek, W.H.: Algorithmic randomness and physical entropy. Phys. Rev. **40**, 4731–4751 (1989)
41. Earman, J., Norton, J.D.: Exorcist XIV: the wrath of Maxwell's demon, part I: from Maxwell to Szilard. Studies Hist. Philos. Mod. Phys. **29**, 435–471 (1998)

42. Earman, J., Norton, J.D.: Exorcist XIV: the wrath of Maxwell's demon, part II: from Szilard to Landauer and beyond. Studies Hist. Philos. Mod. Phys. **30**, 1–40 (1999)
43. Allahverdyan, A.E., Nieuwenhuizen, T.M.: Breakdown of the Landauer bound for information erasure in the quantum regime. Phys. Rev. E **64**, 0561171–0561179 (2001)
44. Allahverdyan, A.E., Nieuwenhuizen, T.M.: Testing the violation of the Clausius inequality in nanoscale electric circuits. Phys. Rev. B **66**, 1153091–1153095 (2002)
45. Allahverdyan, A.E., Balian, R., Nieuwenhuizen, T.M.: Thomson's formulation of the second law: an exact theorem and limits of its validity. In: Sheehan, D.P. (ed.) Quantum Limits to the Second Law. AIP Conference Proceedings, vol. 643. American Institute of Physics, New York (2002)
46. Allahverdyan, A.E., Nieuwenhuizen, T.M.: Unmasking Maxwell's demon. In: Sheehan, D.P. (ed.) Quantum Limits to the Second Law. AIP Conference Proceedings, vol. 643. American Institute of Physics, New York (2002)
47. Nieuwenhuizen, T.M., Allahverdyan, A.E.: Quantum Brownian motion and its conflict with the second law. In: Sheehan, D.P. (ed.) Quantum Limits to the Second Law. AIP Conference Proceedings, vol. 643. American Institute of Physics, New York (2002)
48. Schneider, E.D., Sagan, D.: Into the Cool: Energy Flow, Thermodynamics, and Life. University of Chicago Press, Chicago (2005)