

The essential difference between the coherent superposition and the incoherent one regards the *positions* of the field maxima and zeroes. In the coherent case, maxima and zeroes form a *stationary* fringe pattern: in the incoherent case, they form an *instantaneous* pattern that oscillates randomly along the  $y$  axis. On one side, this random motion prevents the fringes from being seen: on the other side, it does not destroy the equality of the phases at A and B, which is responsible for the birth of the fringes in the far field.

<sup>1</sup>As it stands, Eq. (3) is valid for strictly monochromatic radiation; since our laser (see Sec. II B) contains two lines corresponding to a longitudinal mode spacing of 320 MHz, Eq. (3) should contain a beating factor which, however, does not impair fringe visibility.

<sup>2</sup>P. H. van Cittert, "Die wahrscheinliche Schwingungsverteilung in einer von einer Lichtquelle direkt oder mittels einer Linse beleuchteten Ebene," *Physica* **1**, 201–210 (1934).

<sup>3</sup>F. Zernike, "The concept of degree of coherence and its applications to optical problems," *Physica* **5**, 785–795 (1938).

<sup>4</sup>M. Born and F. Wolf, *Principles of Optics* (Pergamon P, New York, 1970), p. 508.

<sup>5</sup>A. T. Forrester, R. A. Gudmundsen, and P. O. Johnson, "Photoelectric Mixing of Incoherent Light," *Phys. Rev.* **99**, 1691–1700 (1955).

<sup>6</sup>G. Magyar and I. Mandel, "Interference fringes produced by superposition of two independent maser light beams," *Nature* **198**, 255–256 (1963).

<sup>7</sup>H. Paul, "Interference between independent photons," *Rev. Mod. Phys.* **58**, 209–231 (1986). This is an excellent review article that may be usefully consulted by a wide spectrum of readers.

## Thermodynamic entropy: The spreading and sharing of energy

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A new approach to thermodynamic entropy is proposed to supplement traditional coverage at the junior–senior level. It entails a model for which: (i) energy spreads throughout macroscopic matter and is shared among microscopic storage modes; (ii) the amount and/or nature of energy spreading and sharing changes in a thermodynamic process; and (iii) the degree of energy spreading and sharing is maximal at thermodynamic equilibrium. A function  $S$  that represents the degree of energy spreading and sharing is defined through a set of reasonable properties. These imply that  $S$  is identical with Clausius' thermodynamic entropy, and the principle of entropy increase is interpreted as nature's tendency toward maximal spreading and sharing of energy. Microscopic considerations help clarify these ideas and, reciprocally, these ideas shed light on statistical entropy. © 1996 American Association of Physics Teachers.

### I. INTRODUCTION

We propose a new approach for teaching and learning about entropy in junior–senior level thermodynamics and statistical physics courses. It is based upon a model in which energy spreads throughout every macroscopic body and is shared among its molecules and their microscopic storage modes. In thermodynamic equilibrium, the degree of this energy spreading and sharing is maximal, and we seek a function  $S$  that represents it. The function  $S$  is assumed to depend on the system's atomic makeup and the amount of energy it stores. A procedure for determining  $S$  is found by requiring it to have a set of reasonable properties. These properties turn out to imply that the function  $S$  that represents the degree of energy spreading and sharing is identical with Clausius' thermodynamic entropy function  $S$ . Therefore the physical picture of maximal energy spreading and sharing in equilibrium provides a metaphor for interpreting and understanding the meaning of entropy.

The proposed approach is intended to supplement traditional coverage of entropy, typically based upon the Clausius and/or Kelvin–Planck statements of the second law of thermodynamics. The development is guided and supported in part by thermodynamic insights obtained from a one-particle gas model.<sup>1</sup> Together with Ref. 1 this article constitutes a

novel two-pronged approach that provides opportunities for enriching traditional methods of teaching thermal physics.

Several caveats are in order. First, we do not attempt to achieve maximum generality, elegance, or mathematical rigor. Clausius' original approach and many common textbook treatments are clearly better in this regard. Our main objective is to provide a useful *physical picture* for understanding entropy. Second, entropy defies simple explanation, and the present approach is not likely to alter this radically. Rather, we hope it can help make entropy less daunting to students and teachers. Third, the construction of a theory based upon a set of required properties is unfamiliar to most students. An important point is that if any of the properties required of the function  $S$  are inconsistent with physical reality, then the results will likely be wrong. In essence, these properties are postulates, and the resulting theory will stand or fall on the basis of their validity. Some students like this challenge.

We outline the motivation for seeking a new approach to thermodynamic entropy in Sec. II. In Sec. III, we elucidate the idea of energy being spread and shared throughout macroscopic matter, and introduce the set of reasonable properties required of a *bona fide*  $S$  function. These properties are used in Sec. IV to show how  $S$  can be determined, and that it is identical with Clausius' thermodynamic entropy. In Sec.

V, we illustrate several ways the concept of energy spreading and sharing can be used to enhance the teaching and learning of thermodynamics. In Sec. VI, we show how a microscopically based realization of  $S$  can be obtained and how the notion of energy spreading and sharing can shed light on statistical entropy. Finally, in Sec. VII we close with brief remarks on Clausius' development of entropy and its relationship with the present approach.

## II. WHY SEEK A NEW APPROACH TO ENTROPY?

In traditional textbook developments of thermodynamics, entropy is "discovered" using the Clausius and/or Kelvin-Planck forms of the second law of thermodynamics in the context of heat engines. This entails clever mathematical manipulations involving the concept of reversibility and the definition of thermodynamic temperature.<sup>2</sup> The *defining* equation for entropy in that approach is the well-known equation,

$$dS = \frac{\delta Q_{\text{rev}}}{T}, \quad (1)$$

where  $dS$  is the entropy change of a system at absolute temperature  $T$  during a reversible heat process for which  $\delta Q_{\text{rev}}$  is the energy added to the system.

It is gross understatement to say that students have difficulty grasping the traditional approach. The arguments leading to it are subtle and sophisticated and the resulting Eq. (1) has no evident physical meaning. Furthermore because entropy changes can occur for irreversible processes even when  $\delta Q = 0$ , Eq. (1) causes considerable student confusion. This is exacerbated when students learn subsequently that entropy is supposed to represent a measure of "disorder," an interpretation that is entirely mysterious within the context of Eq. (1), and is unsatisfactory in some ways.<sup>3</sup>

Various alternatives to the latter traditional approach exist. For example, Landsberg uses the mathematically elegant Carathéodory approach,<sup>4</sup> and Macdonald provides a new, succinct development of the second law.<sup>5</sup> A popular approach by Callen develops thermodynamics using a set of postulates involving internal energy and entropy.<sup>6</sup> Although these approaches are all sound mathematically, none provides a compelling *physical picture* of entropy.

Another way around the subtleties of classical thermodynamics is to use a microscopically based statistical approach to develop thermodynamics.<sup>7-9</sup> Although this provides an excellent physical picture of entropy, and is favored by many teachers, it requires considerable mathematical sophistication (probability theory, ensembles, combinatorics), and the mathematics can distract students from the physics. Studying classical thermodynamics first can focus on the physics fundamentals, illustrate the beauty and generality of the subject, and prepare students well for the subsequent study of statistical mechanics.

In 1992 Baierlein<sup>10</sup> solicited ideas for new approaches to thermodynamics, asking: "Why do authors lead students through the labyrinth of Carnot cycles and the attendant 19th-century phenomenology *before* introducing a microscopic notion of entropy...? Why not reverse the order?" He himself subsequently suggested a thoughtful and useful way to do this at the introductory level.<sup>11</sup> Baierlein's request inspired a proposal for a formulation based upon the mixing (i.e., spreading and sharing) of energy within matter,<sup>12</sup> and

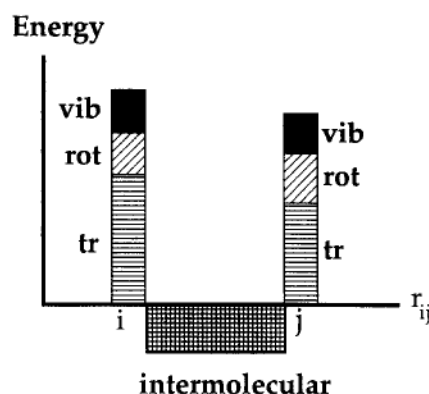


Fig. 1. Stored energies for a pair of gas molecules  $i$  and  $j$ . Each molecule stores translational (tr), rotational (rot), and vibrational (vib) energies. The two atoms store intermolecular potential energy that depends upon their separation,  $r_{ij}$ . Energy is shared within the various shaded regions.

this article brings that proposal to fruition. In a sense the approach here provides a rationale for Callen's otherwise abstract postulates,<sup>6</sup> and extends Rodewald's idea of using the homogeneity concept to help understand entropy.<sup>13</sup>

## III. ENERGY SPREADING AND SHARING

The approach here extends ideas elucidated by Denbigh<sup>14</sup> in 1961: "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 interdiffusion 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."

The present work builds upon these notions using a model in which energy spreads throughout matter and is shared by the atomic constituents of that matter. While Denbigh's remarks were directed at *processes*, we consider the degree of energy spreading and sharing to be a property of *equilibrium states*. An essential postulate is that the degree of energy spreading and sharing is *maximal* when thermodynamic equilibrium exists. This is based upon the view that equilibrium is the result of a process whereby energy seeks out all available storage modes. For example, when hot and cold bodies equilibrate, energy is exchanged between them *as much as possible*. We take this to mean that the exchange occurs until the degree of energy spreading and sharing is maximal. The same is true when a gas fills its available volume, when a solid attains a uniform temperature, and in fact whenever thermodynamic equilibrium exists. To express this mathematically, we postulate the existence of a function  $S$  that represents the degree of energy spreading and sharing.

The energy in a body can be shared by translational, rotational, vibrational, electronic, and intermolecular storage modes. Figure 1 illustrates an example of this energy sharing for a pair of diatomic gas molecules, excluding electronic energy modes. For a monatomic gas, only the translational

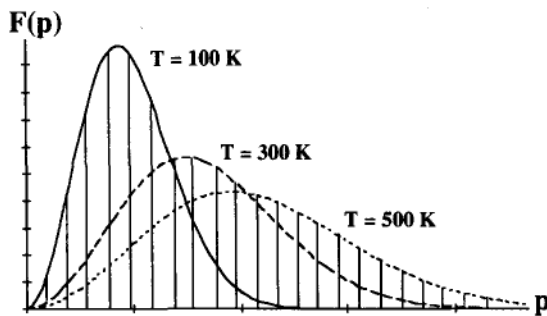


Fig. 2. Maxwell's distribution of momentum magnitudes for three temperatures. The amount of energy spreading and sharing is indicated by the number of momentum cells that contain significant fractions of the particles. The number of these cells increases with temperature.

and intermolecular bond modes are important. While the function  $S$  is expected to increase when rotational and vibrational modes become active, this expectation does not necessarily apply to intermolecular storage modes. The reason is that intermolecular forces can restrict the spatial freedom of molecules, i.e., they can decrease the degree of energy spreading. For example, in a crystalline solid, energy spreading is restricted to specific spatial neighborhoods near lattice sites. In the corresponding vapor phase, where intermolecular forces are relatively weak, such spatial effects are often insignificant.

In what follows, we adopt common postulates on the existence of internal energy, the definition of heat, and the first law of thermodynamics (see the Appendix). We focus attention on homogeneous, single-phase systems for which the internal energy  $U$ , volume  $V$ , and particle number  $N$  uniquely define a thermodynamic state.  $S$  is assumed to be expressible as a function of these variables, i.e.,  $S = S(U, V, N)$ , and the first and second partial derivatives of  $S$  are assumed to exist. Typically it is understood that  $N$  is constant, so we suppress the  $N$  label in partial derivatives, e.g., we write  $(\partial S / \partial U)_{V, N}$  as  $(\partial S / \partial U)_V$ . We require that a *bona fide* function  $S$  have the seven reasonable properties labeled in Eqs. (2a)–(2e), (6), and (15) below. (Note: Postulates are labeled with equation numbers followed by an asterisk—e.g., (2a)\*—to make them easy to locate.)

Suppose a system with fixed  $V$  and  $N$  gains energy. Then more energy is available to spread throughout the system and become shared by the system's energy storage modes. It is reasonable to expect that the degree of energy spreading and sharing increases with added internal energy, and we require that

$$(\partial S / \partial U)_V > 0. \quad (2a)^*$$

An example is a dilute gas that obeys the Maxwellian speed distribution. This distribution can be viewed in terms of momentum magnitudes, as shown in Fig. 2. Three curves, for three different temperatures, show the fraction of molecules in each specified momentum cell. Viewing these cells as "states" the Maxwellian curves explicitly show the fraction of molecules in each state. It is clear from Fig. 2 that energy is shared significantly in more states as the gas temperature and internal energy increase. We interpret this as an increase in the degree of energy spreading and sharing, consistent with Eq. (2a).

For fixed  $U$  and  $N$ , it is reasonable to expect the degree of energy spreading throughout matter to increase with  $V$ , the

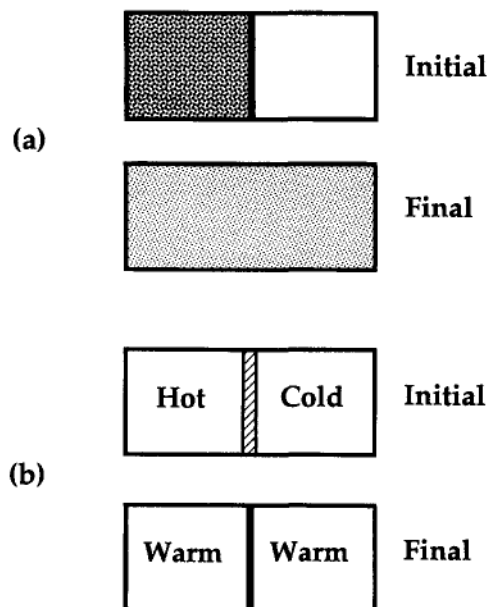


Fig. 3. (a) Free expansion of an ideal gas from the left chamber to the whole container, doubling the volume. The internal energy is unchanged, but becomes more spread spatially, i.e., its degree of energy spreading and sharing increases. (b) Energy transfer from a hot to cold body, decreasing the hot body's degree of energy spreading and sharing and increasing that of the cold body.

volume over which that energy is spread. This is because when more volume is available, the energy  $U$  can spread over more space. Therefore, we require that

$$(\partial S / \partial V)_U > 0. \quad (2b)^*$$

For example, a dilute (ideal) gas that expands freely from volume  $V$  to  $2V$ , as shown in Fig. 3(a), has constant internal energy. Empirically the temperature does not change. However, the degree of energy spreading and sharing increases with  $V$ , consistent with Eq. (2b).

Now consider composite systems, which consist of two or more homogeneous bodies that can exchange energy with one another. A fundamental question is: How are the  $S$  functions for each body related to  $S_{\text{total}}$ , which represents the *total* degree of energy spreading and sharing for the composite system? We adopt the simplest possible relationship, namely, for an  $n$ -body composite system,

$$S_{\text{total}} = S_1 + S_2 + \cdots + S_n, \quad (2c)^*$$

where  $S_i$  refers to body  $i$ . For example in the special case of two identical bodies, labeled 1 and 2, with equal internal energies, the degree of energy spreading and sharing for the composite system is twice that for either of them alone, which seems reasonable. In essence, postulate (2c) means that we require the degree of energy spreading and sharing in the composite system to grow linearly with that in the individual bodies.

We also require an important extension of postulate (2c). Consider a homogeneous system in a state described by  $(U, V, N)$ . Imagine dividing this system (mentally) into two subvolumes,  $\lambda V$  and  $(1-\lambda)V$ , where  $0 < \lambda < 1$ . Assuming typical short range intermolecular forces, the number of molecules interacting across the boundary separating subvolumes  $\lambda V$  and  $(1-\lambda)V$  is small relative to  $N$ . Therefore the

corresponding interaction energy is negligible. Together with the assumptions of energy additivity and homogeneity, this implies that the two subvolumes have internal energies  $\lambda U$  and  $(1-\lambda)U$ , respectively. Using analogous reasoning, it is reasonable to expect that the degree of energy spreading and sharing in these two subvolumes is  $\lambda S(U, V, N)$  and  $(1-\lambda)S(U, V, N)$ , respectively, and we therefore require that

$$S(\lambda U, \lambda V, \lambda N) = \lambda S(U, V, N) \quad \text{for } \lambda > 0. \quad (2d)^*$$

We removed the restriction  $\lambda < 1$  because if postulate (2d) holds for  $\lambda < 1$ , then writing  $U' = \lambda U$ ,  $V' = \lambda V$ ,  $N' = \lambda N$ , and  $\lambda' = 1/\lambda$ , we have  $S(\lambda' U', \lambda' V', \lambda' N') = \lambda' S(U', V', N')$  with  $\lambda' > 1$ . Postulate (2d) is called *extensivity* and  $S$  is called an *extensive*, or *homogeneous*, thermodynamic variable.

Our assumptions above exclude systems for which long-range interactions such as gravity are dominant,<sup>15</sup> and our functions  $S$  and  $U$  must scale linearly with changes in the energy, size, and amount. In contrast, for example, a common intensive variable is the volume per particle,  $v \equiv V/N$ , with the property  $v(\lambda U, \lambda V, \lambda N) = v(U, V, N)$ , i.e.,  $v$  is invariant when a system is scaled upward or downward in energy, size, and amount of material. Such invariance is the defining property of an intensive variable.

Next, consider a composite system consisting of two bodies which, initially, are constrained from interacting with one another. When the constraint is removed the two bodies exchange energy. How much energy will each of the bodies have when equilibrium is reached? To answer this question, we formalize our main postulate, which was alluded to above. This is the principle that the total degree of energy spreading and sharing becomes as large as possible in equilibrium. To assure that all energy exchanges are accounted for, we restrict this postulate to energetically isolated systems:

*When a constraint is removed in an energetically isolated  $n$ -body system with*

$$U = \sum_{i=1}^n U_i, \quad V = \sum_{i=1}^n V_i, \quad N = \sum_{i=1}^n N_i,$$

*then in equilibrium, the set  $\{U_i, V_i, N_i\}$  is such that*

$$S(U, V, N) = \sum_{i=1}^n S_i(U_i, V_i, N_i)$$

*is maximized relative to the remaining constraints.* (2e)\*

Examination of some simple processes illustrates several of these postulates. Suppose a ball is initially constrained to a fixed position above ground level. Upon removal of the constraint, the ball drops to the ground, bounces, and comes to rest. The kinetic energy,  $K_0$ , of the ball just before its first bounce is transferred to the innards of the ball, earth, and air in ways that are impossible to follow in the realm of mechanics. The additional internal energy is spread and shared within each; i.e.,  $\Delta U_{\text{ball}} > 0$ ,  $\Delta U_{\text{earth}} > 0$ , and  $\Delta U_{\text{air}} > 0$ , and postulate (2a) implies  $\Delta S_{\text{ball}} > 0$ ,  $\Delta S_{\text{earth}} > 0$ , and  $\Delta S_{\text{air}} > 0$ . How much of  $K_0$  becomes final internal energy of the ball, earth, and air, respectively? Postulate (2c) implies  $S_{\text{total}} = S_{\text{ball}} + S_{\text{earth}} + S_{\text{air}}$ , and postulate (2e) requires  $S_{\text{total}}$  to take on its maximum possible value at equilibrium; i.e.,  $\Delta S_{\text{total}} = \Delta S_{\text{ball}} + \Delta S_{\text{earth}} + \Delta S_{\text{air}}$  is maximized. This evidently occurs for a unique set of energy differences,  $\Delta U_{\text{ball}}$ ,  $\Delta U_{\text{earth}}$ , and  $\Delta U_{\text{air}}$ , which answers the question posed above. In classical mechanics, one considers the idealization

of perfectly elastic collisions that enable a ball to bounce endlessly. Indeed, such "pure mechanics" can be viewed as a subset of thermodynamics for which there is zero change in the degree of energy spreading and sharing, and  $S$  is constant.

A very different example is a heat process. Consider two bodies that are identical except that one is hot and the other cold [see Fig. 3(b)]. When an insulating barrier between them is removed, we know from experience that an equilibrium state will be reached for which the bodies have equal temperatures. Furthermore because these bodies are identical, this must occur when they have equal internal energies. During the heat process, the hotter body suffers an energy change,  $\Delta U_h < 0$  and postulate (2a) implies that  $\Delta S_h < 0$ . The degree of energy spreading and sharing decreases as the hotter body loses energy. The cooler body gains energy  $\Delta U_c > 0$  and, from postulate (2a),  $\Delta S_c > 0$ . Postulates (2c) and (2e) require that  $\Delta S_c + \Delta S_h > 0$  or  $\Delta S_c > -\Delta S_h$ . The latter inequality tells us that the increase in the cooler body's degree of energy spreading and sharing exceeds the decrease in the hotter body's. This seems reasonable (though not obvious) because the cooler body has more unoccupied storage modes, and we might expect it to experience a greater change in its degree of energy spreading and sharing. Similar behavior occurred in the one-particle gas in Ref. 1.

It is interesting to ask what would happen if the energy transfer in Fig. 3(b) somehow proceeded *past* the equal temperature point. In such a case, states for which the right side is hotter than the left side would occur, but these are mirror images of states that did *not* emerge as equilibrium states with the left side hotter than the right side. Therefore they are ruled out as equilibrium states. The equilibrium state, with equal temperatures, is special in that it has no mirror image. Postulate (2e) tells us that  $S_{\text{total}}$  is maximum for this special state and is less than maximum whenever the two bodies have different temperatures. A similar property was found for the mechanical model in Ref. 1. For heat processes between *nonidentical* bodies, the postulates are less transparent (because of the lack of symmetry), but provide an equally powerful mathematical criterion for thermodynamic equilibrium.

#### IV. AN ALGORITHM FOR FINDING $S$

Our objective in this section is to obtain an algorithm that enables the determination of  $S$ . We first show that the combination of the additivity property of  $S$  and the principle of maximum energy spreading and sharing imply that  $S$  has a negative second derivative with respect to  $U$ . To see this consider two *identical* bodies, as in Fig. 3(b), each with  $N$  particles and volume  $V$ , but with differing internal energies,  $U_1$  and  $U_2 > U_1$ . From inequality (2a),  $S_2(U_2, V, N) > S_1(U_1, V, N)$ . If the two systems are allowed to share energy, with  $V$  and  $N$  constant in each sample, the final  $U$  and  $S$  must be the same for the two samples because the systems are identical. That is,  $U_1 \rightarrow U_f$ ,  $U_2 \rightarrow U_f$ ,  $S_1(U_1, V, N) \rightarrow S_f(U_f, V, N)$ , and  $S_2(U_2, V, N) \rightarrow S_f(U_f, V, N)$ . Obviously, from postulate (2a),  $S_1$  increases and  $S_2$  decreases. Postulate (2e) implies

$$S_1(U_1, V, N) + S_2(U_2, V, N) \leq 2S_f(U_f, V, N), \quad (3a)$$

where

$$U_f = \frac{1}{2}(U_1 + U_2). \quad (3b)$$

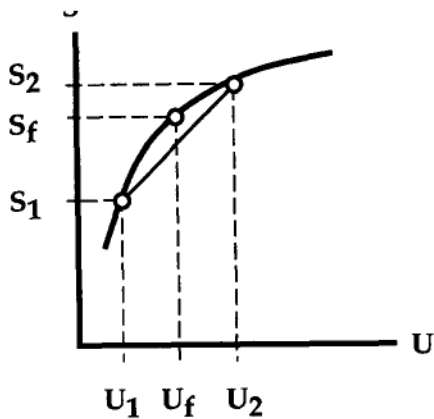


Fig. 4. A typical curve of  $S$  vs  $U$ , with three labeled points,  $(U_1, S_1)$ ,  $(U_2, S_2)$ , and  $(U_f, S_f)$ , where  $U_f$  satisfies Eq. (3b). The inequality (3a) for  $S_f$  assures that  $(U_f, S_f)$  does not lie below the chord that connects  $(U_1, S_1)$  and  $(U_2, S_2)$ . At constant volume,  $S(U)$  must have a concave shape, and  $(\partial^2 S / \partial U^2)_V < 0$ .

The equality in (3a) holds only if  $U_1 = U_2 = U_f$ .

Equations (3a) and (3b) must hold for arbitrary  $U_1$  and  $U_2$ . They have a simple interpretation: A chord drawn between two points,  $(U_1, S_1)$  and  $(U_2, S_2)$ , lies below the  $S$  curve. Functions satisfying these properties are called concave.<sup>16</sup> This property, with postulate (2a) and the assumption that the second derivatives of  $S$  exist, requires that  $S$  behave as illustrated in Fig. 4. The important mathematical property that emerges is

$$(\partial^2 S / \partial U^2)_V < 0. \quad (3c)$$

Condition (3c) is considered by some to be the essence of thermodynamics, but it is not satisfied by "exotic" systems, e.g., black holes, that have negative heat capacities.<sup>15,17-22</sup> We accept it as an essential property for nonexotic matter. Although we considered two identical bodies in order to arrive at (3c), any two (nonexotic) bodies can be used, and in this respect (3c) is quite general.

From our discussion of Fig. 3(b) in Sec. III,  $S$  must have a relative maximum at equilibrium. Thus, using the constraint,  $U_1 + U_2 = \text{constant}$ , or  $dU_1 = -dU_2$ ,

$$dS = \{(\partial S_1 / \partial U_1)_{V_1} - (\partial S_2 / \partial U_2)_{V_2}\} dU_1 = 0, \quad (4a)$$

and

$$d^2 S = \frac{1}{2} \{(\partial^2 S_1 / \partial U_1^2) - (\partial^2 S_1 / \partial U_2 \partial U_1) - (\partial^2 S_2 / \partial U_2 \partial U_1) + (\partial^2 S_2 / \partial U_2^2)\} dU_1^2 < 0. \quad (4b)$$

In Eq. (4b) we have omitted the subscripts on the partial derivatives for simplicity. The two middle terms in the curly brackets are zero because  $S_1$  is independent of  $U_2$  and  $S_2$  is independent of  $U_1$ . The first and last terms are negative because of Eq.(3c), assuring that the extremum is indeed a maximum.

Condition (4a) implies that at equilibrium,

$$(\partial S_1 / \partial U_1)_{V_1} = (\partial S_2 / \partial U_2)_{V_2}. \quad (5)$$

Referring again to Fig. 3(b), bodies 1 and 2 have initial states with  $U_1$  and  $U_2$ . If the separating partition changes from insulating to conducting, the final state  $f$  is attained and Eq. (5) holds. Based upon experience, we interpret this to reflect

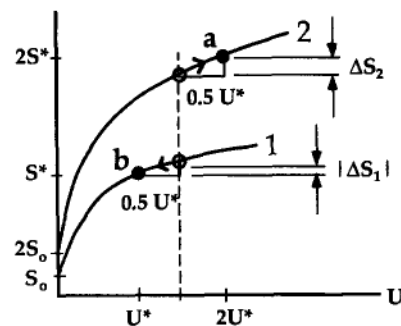


Fig. 5.  $S$  functions for body 1 with  $(V, N)$  and body 2 with  $(2V, 2N)$ . The initial energy  $= 1.5 U^*$  for each body (open circles). In the final states,  $a$  and  $b$  (solid circles), the two curves have equal slopes.

temperature equality. Notice that Eq. (3c) implies that  $(\partial S / \partial U)_V$  is a decreasing, function of internal energy, which suggests that it is inversely related to temperature  $T$ . The simplest such relationship is

$$(\partial S / \partial U)_V \equiv 1/T > 0 \quad \text{or equivalently, } T \equiv (\partial U / \partial S)_V > 0. \quad (6^*)$$

The requirement that  $S$  must satisfy Eq. (6) constitutes our sixth postulate.

We adopt postulate (6) subject to validation after we determine the algorithm for  $S$ . Notice that it implies that  $S$  has units  $\text{JK}^{-1}$ . Equation (6) has the desirable property that  $T$  is an intensive variable, because the derivative of an extensive variable with respect to an extensive variable is intensive. To see this, consider two bodies that are identical except that one is twice the size of the other, with twice the energy, and twice the particle number. The existence and additivity of  $S$  imply that  $S(2U, 2V, 2N) = 2S(U, V, N)$ . Therefore if  $T_1 = 1/(\partial S(U, V, N) / \partial U)_V$  is the temperature of the smaller system, then

$$T_2 = [\partial S(2U, 2V, 2N) / \partial (2U)]^{-1} = [\partial S(U, V, N) / \partial U]^{-1} = T_1, \quad (7)$$

where the derivatives are taken with  $V$  and  $N$  fixed. This can be generalized to show that  $T(U, V, N) = T(\lambda U, \lambda V, \lambda N)$ .

To appreciate the importance of Eqs. (5)–(7), it is helpful to discuss the following example for which two bodies are made of the same material. Body 1 has volume  $V$  and  $N$  molecules, and body 2 has volume  $2V$  and  $2N$  molecules, but both bodies have the same, initial energy, say  $1.5U^*$ . If we allow the bodies to exchange energy, then initially body 1 has more than its fair share of energy, based upon proportional scaling, and body 2 has less than its fair share. We expect that energy spreading and sharing will lead to an equilibrium situation whereby body 1 has half the energy of body 2. Furthermore because body 1 has excess energy initially, we expect it to have a higher initial temperature than body 2. When the bodies are placed in thermal contact, we expect energy to flow from body 1 to body 2 until temperature equality exists, i.e., the internal energy of body 2 increases from  $1.5U^*$  to  $2U^*$  and that for body 1 decreases from  $1.5U^*$  to  $U^*$ .

We now show that our postulates imply behavior that is consistent with these expectations. Figure 5 shows that initially, the slope of the  $S$  curve is smaller for body 1 than for body 2, which corresponds to  $T_1 > T_2$ , as expected. During

body 2's energy gain of  $0.5U^*$ , the shape of  $S$  vs  $U$  assures that its increased degree of energy spreading and sharing,  $\Delta S_2$ , exceeds the magnitude,  $|\Delta S_1|$ , of body 1's decreased degree of energy spreading and sharing. Bodies 2 and 1 attain the equilibrium states **a** and **b**, respectively. Equations (5)–(7) show that when body 1 has energy  $U^*$  and body 2 has energy  $2U^*$ , the two curves in Fig. 5 have equal slopes, i.e.,  $T_1 = T_2$  as expected. This completes this example.

For the constant volume heat processes we have been discussing, zero work is done *on* the system. For an infinitesimal energy transfer, the first law of thermodynamics is  $dU = \delta Q$  and the relationship  $(\partial S/\partial U)_V = 1/T$  implies  $dS = dU/T$  or

$$dS = \delta Q/T \text{ along a constant-volume path.} \quad (8)$$

$\delta Q$  is the infinitesimal heat to the body, whose temperature is  $T$ , altering its degree of energy spreading and sharing by  $dS$ . The notation  $\delta Q$  rather than  $dQ$  is a reminder that heat is *not* a state function but rather a path-dependent energy transfer.

There is a subtlety associated with Eq. (8), which holds along finite, constant-volume paths. These paths must consist *solely* of equilibrium states, as illustrated in Figs. 4 and 5 because only then is the temperature in Eqs. (6) and (8) a well-defined property. Physically, a path of equilibrium states requires an infinitely slow process which, in principle, requires an infinite sequence of energy reservoirs, each with a temperature slightly different from the last. Such processes can be reversed using the sequence of reservoirs in the reverse order and thus (8) can be rewritten

$$dS = \delta Q_{\text{rev}}/T \text{ along a reversible constant-volume path.} \quad (9)$$

Although real heat processes can pass through nonequilibrium states, Eq. (9) enables the calculation of  $\Delta S$  between initial and final equilibrium states for such processes.

Our next task is to consider how  $S$  varies with the volume  $V$ . Using the first law of thermodynamics for infinitesimal variations at constant particle number  $N$ ,

$$dU = \delta Q + \delta W. \quad (10)$$

As usual, the terms on the right side are both path dependent, while their sum, and thus the left side, is path independent. We assume  $S = S(U, V)$  and that work is done *only* via volume changes. Inverting  $S(U, V)$  to get  $U = U(S, V)$ , it follows that

$$\begin{aligned} dU &= (\partial U/\partial S)_V dS + (\partial U/\partial V)_S dV \\ &= TdS + (\partial U/\partial V)_S dV. \end{aligned} \quad (11)$$

The first term in the last line follows from Eq. (6). Applying Eqs. (10) and (11) to the *same* process, we can eliminate  $dU$ , to obtain

$$dS = \delta Q/T + [\delta W - (\partial U/\partial V)_S dV]/T. \quad (12)$$

We now examine four important special cases of Eq. (12).

*Case 1. Constant-volume pure heat process.* Here,  $\delta W = 0$  and  $dV = 0$ , giving Eq. (9). The caveat preceding Eq. (9) applies.

*Case 2. Slow adiabatic volume change.* Here,  $\delta Q = 0$ . For a compression, two opposing effects occur: (i) positive external work on the system increases its energy, tending to increase  $S$ , but (ii) the volume reduction decreases the available space over which energy can spread, tending to decrease

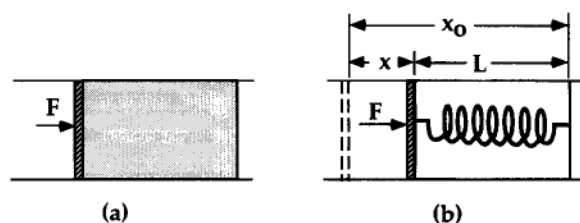


Fig. 6. (a) Cylinder with a movable piston. The interior can contain a gas or a compressed spring. (b) Cylinder containing a coiled spring, compressed to length  $L = x_0 - x$  where  $x_0$  is its equilibrium length.

$S$ . For an expansion, similar opposing effects occur. The question is: Which of these effects dominates?

For an infinitely slow volume change, the external pressure  $p_{\text{ext}}$  on the system and the internal pressure  $p$  within the system differ by an arbitrarily small amount and the external work done *on* the system is

$$\delta W = -p_{\text{ext}} dV = -p dV. \quad (13)$$

The first law reduces to  $dU = \delta W_{\text{rev}} = -p dV$ , and Eq. (12) becomes

$$dS = -[p + (\partial U/\partial V)_S] dV. \quad (14)$$

Equations (13) and (14) show how  $S$  varies with  $V$  for a slow, adiabatic volume change. To pin down  $S$  further, we must specify more about  $(\partial U/\partial V)_S$ .

Consider the process in Fig. 6(a), which depicts a cylinder with a movable piston. An external force  $F$  is needed to keep the piston in equilibrium and the corresponding pressure is  $p = F/A$ , where  $A$  is the piston area. Suppose the cylinder contains a coiled spring, as shown in Fig. 6(b). For this system, a slow compression is a pure-mechanics process, for which the system energy can be written  $U(S, V) = k_s [x_0 - (V/A)]^2/2$ , where  $k_s$  is the spring constant, and  $V/A$  is the cylinder length. The quantity in square brackets is the deviation from the spring's equilibrium length,  $x_0$ . This shows that  $U$  is independent of  $S$  and

$$-(\partial U/\partial V)_S = k_s [x_0 - (V/A)]/A = F/A = p.$$

For this process, Eq. (14) reduces to  $dS = 0$ , which is consistent with the view that in pure mechanics, the degree of energy spreading and sharing does not vary.

This is also consistent with the result in Ref. 1 that an infinitely slow volume change induces *exactly compensating effects* on the classical action (which is closely related to  $S$ ) from the energy increase and volume decrease that leave the action function unchanged. The invariance was linked to the symmetry of reversibility associated with slow volume changes. We generalize this, requiring that *the total degree of energy spreading and sharing is conserved under slow, reversible, adiabatic volume changes*, i.e.,

$$dS = 0 \text{ for a slow, adiabatic volume change.} \quad (15)^*$$

Equation (14) and postulate (15) imply

$$p = -(\partial U/\partial V)_S. \quad (16)$$

Postulate (15) means that if an adiabatic expansion is sufficiently slow, the increased energy spreading and sharing associated with the volume change is *exactly* offset by the decreased energy spreading and sharing from the concomitant

lowered gas energy. A similar statement can be made for slow adiabatic compressions.

The combination of Eqs. (6) and (16) leads to the important relationship,

$$(\partial S/\partial V)_U = p/T, \quad (17)$$

which can be verified using the cyclic identity of partial differentiation; i.e.,

$$\begin{aligned} (\partial U/\partial S)_V(\partial S/\partial V)_U(\partial V/\partial U)_S \\ = (\partial U/\partial S)_V(\partial S/\partial V)_U/(\partial U/\partial V)_S = -1. \end{aligned}$$

*Case 3. Constant-volume work processes.* Combining Eqs. (12) and (16), we find

$$dS = \delta Q/T + [\delta W + pdV]/T. \quad (18)$$

Positive, constant-volume work on a system can be induced, for example, by mechanical stirring of a gaseous system or by electrical work on a wire system, inducing an electric current in it (assuming negligible volume change). Recall that we have in mind homogeneous, constant- $N$  systems whose states can be specified in terms of  $T$  and  $V$ . It is impossible to do negative constant-volume work on these systems; i.e., to get positive work out of them. For example, we cannot get electric work out of such a system because it is homogeneous, which precludes it from containing a battery. The point is that if  $dV=0$ , then  $\delta W \geq 0$ . Therefore, Eq. (18) becomes

$$dS \geq \delta Q/T \text{ for constant volume work processes.} \quad (19)$$

The equality holds if and only if the constant-volume work is identically zero.

*Case 4. Rapid volume change.* For a sufficiently rapid work process, we expect the effect of increased energy to dominate over the volume effect, resulting in an overall increase in  $S$ . For example, a rapid infinitesimal compression of a gas that changes its volume by  $dV < 0$ , entails work  $\delta W = -p_{\text{ext}}dV$ , where  $p_{\text{ext}}$  is the external pressure. Obviously,  $p_{\text{ext}} > p$ , the equilibrium gas pressure, or the process cannot be "fast." Thus  $\delta W > -pdV$ , i.e., extra work, above and beyond  $-pdV$ , is done on the gas. Similar behavior was seen also in the simple mechanical model of Ref. 1. The latter inequality also can be argued on other grounds.<sup>23</sup> Using it in Eq. (18), we find

$$dS \geq \delta Q/T \text{ during a volume change.} \quad (20)$$

The equality holds if and only if  $\delta W = -pdV = \delta W_{\text{rev}}$ , namely, for an infinitely slow, reversible volume change. This concludes case 4.

Our discussion of cases 1–4 shows that for an infinitesimal change of thermodynamic variables in a system, the first law of thermodynamics, Eq. (10), holds and the corresponding change  $dS$  in the degree of energy spreading and sharing satisfies

$$dS = \delta Q_{\text{rev}}/T \text{ for reversible processes,} \quad (21a)$$

and

$$dS > \delta Q/T \text{ for irreversible processes.} \quad (21b)$$

Equation (21a) is identical with the traditional *defining* equation for entropy in classical thermodynamics. Evidently, the degree of energy spreading and sharing,  $S$ , is identical to the entropy function (within an additive constant). Together, Eqs. (21a) and (21b) constitute a statement of the second law of thermodynamics.

Although Eq. (21a), by itself, gives little indication that  $S$  has any physical significance, the development that led to it is replete with physical underpinnings. The contrast between the physical picture of  $S$  as a measure of the degree of internal energy spreading and sharing and the obscure nature of Eq. (21a) is striking. Equation (21a) is best viewed as a valuable *algorithm* that enables us to determine  $S(U, V)$  relative to its value in some chosen reference state,  $(U_i, V_i)$ , using a fictitious reversible path. Just as the complex chemical reactions that occur during the baking of a cake are not evident from its recipe, the physical meaning of energy spreading and sharing is well hidden by its algorithm.

We now confirm the validity of our temperature definition in Eq. (6). Consider a reversible Carnot cycle, which consists of two isothermal (constant- $T$ ) segments at temperatures  $T_h$  and  $T_c < T_h$ , alternated with two adiabatic segments. The net change in  $S$  for the working fluid is zero for a complete cycle, and Eq. (21a) implies that  $Q_h/T_h = Q_c/T_c$ , where  $Q_i$  is the *magnitude* of the heat to the system at temperature  $T_i$  for  $i = c, h$ . We choose  $T_h$  or  $T_c$  to be a reference temperature, say,  $T_{\text{tr}} = 273.16$  K at the triple point of  $\text{H}_2\text{O}$ , and the other temperature can be expressed in terms of  $Q_c$  and  $Q_h$ . The prescription in this paragraph actually *defines* the Kelvin temperature scale. Therefore, Eq. (6) plus our chosen reference temperature gives a temperature scale that is identical with the Kelvin scale.

## V. ENHANCING THE TEACHING AND LEARNING OF THERMODYNAMICS

In this section, we suggest several ways that the present approach might be helpful to teachers and students of thermodynamics. First, the approach suggests an unconventional definition: Thermodynamics is the science dealing with energy spreading and sharing in macroscopic bodies, and with changes in the degree and/or nature of that energy spreading and sharing induced by work and/or heat processes. This can be compared with a definition from a respected, modern dictionary:<sup>24</sup> "thermodynamics (is the) science concerned with the relations between heat and mechanical energy or work, and the conversion of one into the other; modern thermodynamics deals with the properties of systems for the description of which temperature is a necessary coordinate." This common definition is inadequate in two ways: (i) it omits a fundamental aspect of thermodynamics, namely, that energy is stored within matter; and (ii) it seems to exclude the free expansion of a gas (and perhaps any *adiabatic* process) as a *bona fide* thermodynamic process. Classroom discussions comparing these definitions can stimulate critical thought about the essence of thermodynamics.

The first and second laws can be summarized in terms of energy spreading and sharing as follows: Macroscopic systems store energy that spreads over accessible space and is shared by available microscopic energy storage modes. Like energy, the degree of energy spreading and sharing is a quantifiable, additive function of state. Changes in the way energy is spread and shared conserve energy, and the total degree of energy spreading and sharing is maximized at equilibrium. Additionally, the third law of thermodynamics can be framed as follows: At ultra-low temperatures, the degree of energy spreading and sharing approaches an absolute minimum, which is independent of externally variable parameters, and can be defined to be zero. With the latter definition, we associate the limit  $S \rightarrow 0$  with limit  $T \rightarrow 0$ ; i.e., for  $T \rightarrow 0$ , the

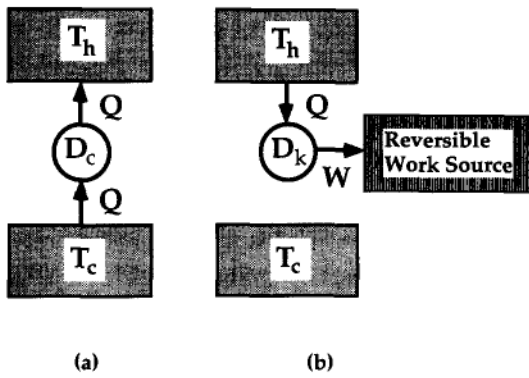


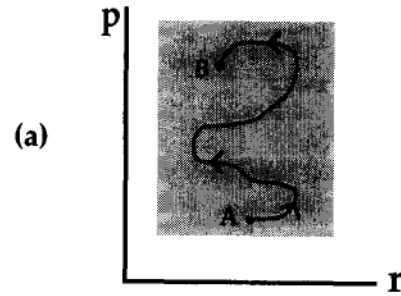
Fig. 7. (a) Device  $D_c$  that violates the Clausius statement of the second law. (b) Device  $D_k$  that violates the Kelvin–Planck statement of the second law. Each device would decrease the total degree of energy spreading and sharing in the universe, which is impossible.

degree of energy spreading and sharing approaches a minimum because the amount of energy available to be spread and shared decreases to a minimum. In effect the third law of thermodynamics adds one more postulate to those in Secs. III and IV.

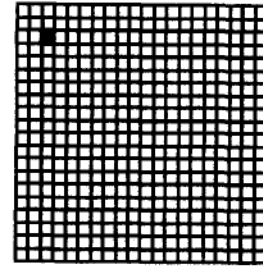
The concept of energy spreading and sharing can help clarify conventional statements of the second law of thermodynamics and the idea of a maximum heat engine efficiency. Consider first the Clausius statement of the second law: It is impossible for any device  $D_c$  to operate such that its sole effect is energy transfer from a constant-temperature reservoir at  $T_c$  to another reservoir at  $T_h > T_c$ . The term “sole effect” implies a cyclic process for the engine itself. It is helpful to consider the two reservoirs as massive bodies that are identical to one another in all respects except that the one with temperature  $T_c$  stores less energy than the one with temperature  $T_h$ . In a violation of the Clausius statement [see Fig. 7(a)], the degree of energy spreading and sharing in the low-temperature reservoir would decrease more than that in the high-temperature reservoir would increase (as implied by the shape of the  $S$  vs  $U$  curve in Figs. 4 and 5). This amounts to a spontaneous diminution of the total degree of energy spreading and sharing, moving the reservoirs further away from equilibrium, in violation of postulate (2e).

The Kelvin–Planck statement of the second law is: It is impossible for any device  $D_k$  to operate such that its sole effect is energy transfer  $Q$  from a constant-temperature reservoir at  $T_h$  and energy delivery in the form of work  $W = Q$ , delivered to a reversible-work source. A violation of this statement is illustrated in Fig. 7(b). Were this possible, the degree of energy spreading and sharing in the high-temperature reservoir would decrease, with no compensation in the (uninvolved) low-temperature reservoir. This violates postulate (2e).

Next consider a heat engine with heat processes at temperatures  $T_h$  and  $T_c < T_h$  and generation of work  $W = Q_h - Q_c$  on an external agent. For a given  $Q_h$ , the engine is more efficient the smaller  $Q_c$  is. The Kelvin–Planck statement rules out the extreme case, for which  $Q_c = 0$ . For nonzero  $Q_c$  if  $Q_c$  is “too small” then the decrease in the  $T_h$  reservoir’s degree of energy spreading and sharing exceeds the increase in that for the  $T_c$  reservoir, violating postulate (2e). This limitation gives rise to the maximum efficiency,  $\eta_{\max}$  in Carnot’s theorem:  $\eta \leq \eta_{\max} = 1 - T_c/T_h$ . The point is



(a)



(b)

Fig. 8. (a) Phase space trajectory from state  $A$  to  $B$ . The shaded rectangle represents the total available phase space volume  $\Omega$ . (b) The volume per atom,  $v$ , is divided into  $M = v/\lambda^3$  cells, each the size of a wave packet. An atom’s wave packet (dark square) can spread to any of these cells. If temperature increases, the cell size decreases and  $M$  increases; a temperature decrease increases the cell size and  $M$  decreases.

that this theorem has a simple interpretation: The total degree of energy spreading and sharing in the two reservoirs cannot decrease.

## VI. MICROSCOPIC CONNECTIONS

Our search for a suitable measure of energy spreading and sharing has helped us construct a thermodynamics theory that is equivalent mathematically to the conventional one, but is based *a priori* on a physical picture of what the state function  $S$  represents. It is unnecessary to search *retrospectively* for an interpretation of what entropy “means.” Although it is outside the domain of classical thermodynamics, further understanding can be obtained using a microscopic approach similar to that in statistical physics. It is simplest (though not essential) to frame our discussion in terms of a classical, monatomic, ideal gas with  $N$  atoms, each of mass  $m$ , in volume  $V$ , and with total energy  $U$ . Denoting the vector momentum of atom  $i$  by  $\mathbf{p}_i$ , the internal energy of the gas can be written as  $U = p_1^2/2m + p_2^2/2m + \dots + p_N^2/2m$ . At time  $t$  the mechanical state of the gas is known from the displacement and momentum of each of the  $N$  atoms; i.e.  $(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \dots, \mathbf{r}_N, \mathbf{p}_N)$ . This represents a single point,  $P_t$ , in the  $6N$ -dimensional phase space consisting of three displacement and momentum components of each atom.

As time advances,  $P_t$  follows a trajectory in the phase space because atoms move, collide with one another, and bounce off the walls. In principle,  $P_t$  can reach any part of the phase space that is consistent with the atoms all being in the volume  $V$ , with total energy  $U$ , as indicated symbolically in Fig. 8(a). This phase space trajectory represents both the spatial spreading of atoms and their energies, and energy sharing between atoms. The total available phase space volume is



$\Omega(U, V, N)$

$$= \int_V d^3\mathbf{r}_1 d^3\mathbf{r}_2 \cdots d^3\mathbf{r}_N \int_{\sum_i p_i^2 = 2mU} d^3\mathbf{p}_1 d^3\mathbf{p}_2 \cdots d^3\mathbf{p}_N$$

$$= V^N [2\pi^{3N/2} (2mU)^{(3N-1)/2} / \Gamma(3N/2)], \quad (22)$$

where  $\Gamma(3N/2)$  is a gamma function. The factor  $V^N$  comes from the configurational integrals and the quantity in square brackets is the surface area of a  $3N$ -dimensional sphere of radius  $\sqrt{2mU}$ , which comes from the momentum integrals.<sup>25</sup>

The important point is that the multiple integrals in Eq. (22) account for all possible spatial configurations (i.e., energy spreading) and momentum combinations (i.e., energy sharing), and therefore  $\Omega$  is a measure of the maximal degree of energy spreading and sharing. Although the second derivative of  $\Omega$  with respect to  $U$  is *not* negative,  $\ln \Omega$  has a negative second derivative and also obeys the additivity requirement. For reasons related to the so-called Gibbs paradox,  $\ln \Omega$  is not properly extensive but  $\ln(\Omega/N!)$  is. A *general* form (not restricted to the ideal gas) that is consistent with all required properties of  $S$  is

$$S(U, V, N) = k \ln[\Omega(U, V, N)/(N!\Omega_0)], \quad (23)$$

where  $\Omega_0$  is an arbitrary reference phase space volume that makes the argument of the logarithm dimensionless, and  $k$  is an arbitrary constant.  $\Omega_0$  may be taken to be  $1.00 (Js)^{3N}$  for simplicity. A more common choice,  $\Omega_0 = h^{3N}$ , where  $h$  is Planck's constant, is motivated by quantum considerations.

As mentioned, Eq. (23) transcends the ideal gas, and is applicable to any  $N$ -particle classical system. It is a *bona fide* measure of the degree of maximal energy spreading and sharing because it accounts for all allowed displacements and momenta. In fact, Eq. (23) is the standard entropy function of classical statistical mechanics in the microcanonical ensemble formalism, with  $k$  equal to Boltzmann's constant. The argument here supports the notion that the degree of spreading and sharing is quantifiable. Reciprocally, the idea of energy spreading and sharing enriches our understanding of entropy in statistical physics. Typically Eq. (23) is encountered in the context of an ensemble of systems whose energies lie in a relatively small interval about  $U$ , but without a compelling physical picture.

Returning to the ideal gas, there is another microscopic argument that helps show that  $S$  is a measure of the degree of energy spreading and sharing. First, we use Eq. (22) in Eq. (23), replace  $(3N-1)/2$  by  $3N/2$  for large  $N$ , and apply Eqs. (6) and (17). This leads to the well-known equations  $U = 3NkT/2$  and  $p = NkT/V$ . Then  $S$  can be simplified using Stirling's approximation,  $\ln \Gamma(n+1) \approx n \ln(n) - n$ , for large  $n$  where, for integral  $n$ ,  $\Gamma(n+1) = n!$ . It is helpful to use the shorthand notation  $v \equiv V/N$  and

$$\lambda = h/(2\pi mkT)^{1/2}. \quad (24)$$

$v$  is the specific volume (per atom) and  $m$  is the atomic mass.  $\lambda$  is called the thermal wavelength, which is the same order of magnitude as the quantum mechanical deBroglie wavelength.  $\lambda$  represents the spatial extent of an atom's wave packet, and  $\lambda^3$  is the corresponding wave packet's volume. The entropy function can be written as

$$S(T, V, N) = Nk[\ln(v/\lambda^3) + \text{constant}]. \quad (25)$$

This equation can be obtained directly using classical thermodynamics, by integrating the equations  $(\partial S/\partial U)_V = 3Nk/2U$  and  $(\partial S/\partial V)_U = Nk/V$ , and requiring that  $S$  be

extensive. The specific volume can be envisaged as follows. Mentally divide  $V$  into  $N$  nonoverlapping subvolumes, each with volume  $v$ . On average, each subvolume contains one atom. If one atom leaves a particular subvolume and another one enters it, the situation is unchanged because atoms are considered to be indistinguishable from one another. In this sense, the volume  $v$ , per atom, is a meaningful quantity.

Equation (25) has an interesting interpretation.  $S$  is a function of  $v/\lambda^3$ , the ratio of the specific volume to the quantum volume of the particle. Because each wave packet occupies volume  $\lambda^3$ , the remaining volume available to it is  $(v-\lambda^3)$ . In the classical domain,  $v \gg \lambda^3$ , and an atom's wave packet is a tiny blob of volume  $\lambda^3$  that spreads throughout the much larger volume  $v-\lambda^3$ . If the blob has volume  $\lambda_0^3$  at a given temperature  $T_0$ , then at temperature  $T > T_0$ , the blob's volume is  $\lambda^3 < \lambda_0^3$ . The blob has a bit *more* space over which to spread because it occupies less volume itself, and thus  $S$  is higher. For temperature  $T < T_0$ , the reverse is true. A refinement of this view is that  $v$  can be divided (mentally) into a grid of  $M \equiv v/\lambda^3$  cells, each the size of a wave packet, as depicted in Fig. 8(b). The atom can spread its energy to any of these  $M$  cells. Increasing the temperature decreases  $\lambda$  and increases  $M$ ; thus, energy can spread over more cells. This increases  $S$ . Decreasing the temperature has the opposite effect.

Therefore an energy gain at fixed volume causes (i) each gas atom to share more energy, and (ii) each atomic blob to spread its energy over more space because  $\lambda^3$  decreases. Similarly, an energy loss will decrease both energy sharing and spreading. In this view, energy spreading and sharing are intertwined, and energy spreading depends on  $T$  as well as  $V$ . This is a quantum mechanical nuance in a system that is describable largely by classical physics. Of course, if  $T$  is lowered sufficiently,  $\lambda^3$  becomes comparable with  $v$  and the atoms' wave packets interfere with one another. Then Eq. (25) breaks down and a proper quantum mechanical expression for  $S$  must be used.

A similar argument using Eqs. (24) and (25) brings another interesting result. The deBroglie wavelength,  $\lambda$ , changes with atomic mass at fixed temperature. This means that, for example, a dilute  $N$ -atom gas of neon at temperature  $T$  is expected to have a lower entropy than a similar gas of radon, whose atoms are about ten times more massive. Entropy data<sup>26</sup> in Fig. 9(a) for monatomic gases confirm this tendency, but also show deviations caused by other contributions, e.g., from electronic states. We did not address these and the oscillatory behavior in Fig. 9(a) suggests that they are not negligible. Figure 9(b) shows similar data for monatomic solids. Again  $S$  tends to increase, but deviations from this tendency can come from variations in crystal structure and atomic properties.

The latter mass dependence can be understood also in terms of the fact that the quantized energy spectrum becomes more dense with increasing mass. To appreciate this effect, we introduce a quantum-based interpretation of energy spreading and sharing. A system can reside in any of a (typically large) number of many-particle states that are consistent with existing conditions, such as fixed temperature. Suppose a list of these available states is printed on paper, with a bullet ( $\bullet$ ) placed alongside the state that is occupied at time  $t$ . For later times there can be transitions to other states and the bullet shifts from one state on the list to another. The bullet's trajectory is analogous to the phase space trajectory we examined earlier in this section. Here the degree of en-

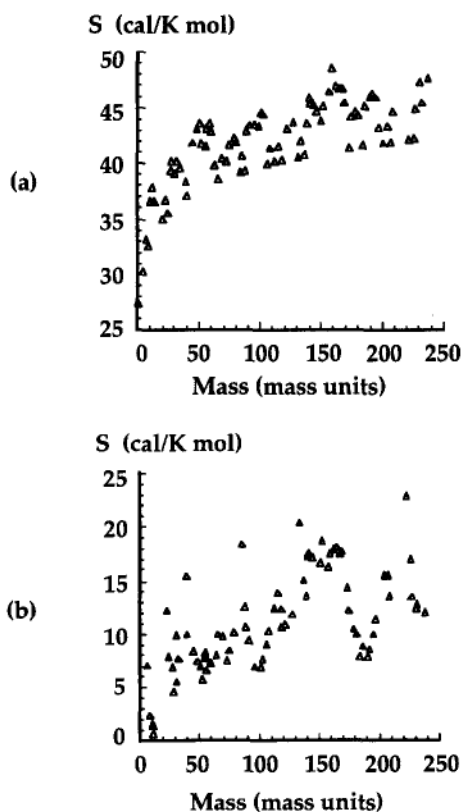


Fig. 9. (a) Entropy vs molar mass for monatomic gases. (b) Entropy vs molar mass for monatomic solids. All data are for  $T=298.15$  K and  $p=1.01325 \times 10^5$  Pa. Source: Ref. 26.

ergy spreading and sharing depends on the density of the system's quantum states, which is known to increase with particle mass for various model systems, such as ideal gases and Debye solids. Thus we expect  $S$  to increase with atomic mass, subject to the kinds of deviations evident in Figs. 9(a) and 9(b).

## VII. CONNECTIONS WITH CLAUSIUS

We close with a brief discussion of Clausius' two original approaches to entropy, and their relationship with the present approach. The more general of these rested on three fundamental principles: the equivalence of work and heat (i.e., the first law of thermodynamics), Clausius' statement of the second law (discussed in Sec. V), and the law of the equivalence of transformations. The latter entailed the idea that in cyclic processes, certain transformations (e.g., heat to work) are equivalent to other ones (e.g., heat conduction) in a well-defined sense. Clausius postulated the existence of numerical equivalence values for such transformations and used his "law of the equivalence of transformations" to ultimately arrive at what is now called the Clausius inequality and the entropy function.<sup>27-29</sup> Clausius' analysis was brilliant, but the equivalence value idea is difficult to grasp, and is not even mentioned in most thermodynamics textbooks. The main points to be emphasized here are: (i) Clausius' development required postulates, as *all* developments of thermodynamics do; and (ii) although his approach based on equivalence of transformations is rigorous and general, it provides little indication of what the state function entropy represents.

Clausius' other approach to entropy had microscopic underpinnings through the concept of disgregation.<sup>30</sup> He justified this less general approach on the grounds that the first approach "retains an abstract form, which is embraced with difficulty by the mind, and we feel compelled to look for the precise physical cause, of which (the Clausius inequality) is a consequence." Disgregation was defined as "the degree of dispersion of the body," where dispersion refers to the spatial arrangement of molecules. As examples, Clausius cited that disgregation increases in going from the solid to liquid to vapor phases. He postulated that disgregation is a state function, which he denoted by  $Z$ . Through a set of postulates, he related  $Z$  to the entropy  $S$  via the expression

$$dS = dH/T + dZ. \quad (26)$$

In Eq. (26)  $H$  is the "heat in a body" (a remnant of caloric theory) which was assumed to be solely a function of temperature. Equation (26) shows that entropy changes can be attributed to changes in molecular kinetic energy plus changes in the degree of spatial dispersion. In terms of the present analysis, energy sharing is involved in both terms of Eq. (26), while energy spreading seems to be confined to the volume-dependent second term.

Despite the fact that Clausius' development in terms of disgregation gives a more clear picture of the physical significance of entropy than his more general, but abstract, development, the disgregation concept has largely died, and does not appear in most thermodynamics books. This is evidently because Clausius' disgregation-based theory led him to an incorrect result on specific heats, and he therefore deleted disgregation from the second edition of his book on the mechanical theory of heat.<sup>31</sup> Clausius planned to return to disgregation in a third volume, but did not live to do so.

Subsequently, the development of the canonical ensemble formalism of classical statistical mechanics by Boltzmann and Gibbs showed that entropy can be decomposed into two terms that correspond precisely to those on the right side of Eq. (26). The first comes from momentum integrals involving the kinetic energy, and is the same for all monatomic systems. The second term comes from the configurational integrals involving the intermolecular potential energy, and can vary for different systems. Unfortunately Clausius did not foresee this corroboration of his insight.

The concept of disgregation seems akin to that of energy spreading and sharing, especially that of spreading. However, disgregation is a more limited concept than energy spreading and sharing, which is central in *both* terms on the right side of Eq. (26), while disgregation is confined to the second term. The main link between the present approach to entropy and Clausius' disgregation approach is that both provide physical pictures of entropy that can be used to shed light on more rigorous, but abstract, developments of the subject.

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suggestions that led me to adopt the terminology “energy spreading and sharing” in place of the less precise “mixing,” which I had chosen originally.<sup>12</sup>

## APPENDIX: ACCEPTED COMMON POSTULATES

We adopt the following three common postulates. The first one addresses the existence of equilibrium states and internal energy. The formal statement is: For a thermodynamic system with  $N$  particles (atoms and/or molecules), equilibrium states exist. An equilibrium state  $\mathbf{a}$  has the internal energy,  $U_a$ . Specification of a unique, *reproducible* state  $\mathbf{a}$  requires at least two variables, e.g., temperature and volume, for fixed  $N$ .

The second postulate is that heat is definable in terms of work. This is essential to bridge the gap between mechanics and thermodynamics. The formal postulate is: Any two states can be connected adiabatically.<sup>6,32</sup> This enables a determination of  $\Delta U = W$ , where  $W$  is the work done on the system. An example is raising the temperature of water by a pure-work process using a blender’s rotating blades to agitate the water molecules. Once  $\Delta U \equiv U_b - U_a$  is known, then for a pure heat process (with zero work on the system) taking the system from state  $\mathbf{a}$  to state  $\mathbf{b}$ ,  $Q \equiv \Delta U = U_b - U_a$ , where  $Q$  is the energy transferred to the system.

The third postulate is the first law of thermodynamics, which entails three major ideas: (i) energy exchanges can be in the form of heat or work; (ii) the state function,  $U$ , exists; and (iii) energy is conserved. The formal statement is: For a process  $\mathbf{a} \rightarrow \mathbf{b}$  that involves work  $W$  (on the system) and heat  $Q$  (energy transfer to the system),  $\Delta U = U_b - U_a = Q + W$ . Evaluation of  $\Delta U$  with a pure-work (adiabatic) process, as discussed above, enables the definition of  $Q$ . The heat  $Q$  depends upon the specific path along which work  $W$  is done, and both  $W$  and  $Q$  are path-dependent quantities, while  $\Delta U$  is path independent.

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