

# Insight into entropy

Daniel F. Styer<sup>a)</sup>

Department of Physics, Oberlin College, Oberlin, Ohio 44074

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What is the qualitative character of entropy? Several examples from statistical mechanics (including liquid crystal reentrant phases, two different lattice gas models, and the game of poker) demonstrate facets of this difficult question and point toward an answer. The common answer of “entropy as disorder” is regarded here as inadequate. An alternative but equally problematic analogy is “entropy as freedom.” Neither simile is perfect, but if both are used cautiously and not too literally, then the combination provides considerable insight. © 2000 American Association of Physics Teachers.

Of all the difficult concepts of classical physics—concepts like acceleration, energy, electric field, and time—the most difficult is entropy. Even von Neumann<sup>1</sup> claimed that “nobody really knows what entropy is anyway.” It is concerning entropy that students are most likely to invert their familiar lament and say “I can do the problems, but I just can’t understand the material.”

The qualitative character of entropy has been discussed widely,<sup>2–13</sup> although often only in the restricted context of gases or even in the highly restricted context of noninteracting gases. The metaphoric images invoked for entropy include “disorder,” “randomness,” “smoothness,” “dispersion,” and “homogeneity.” In a posthumous fragment, Gibbs<sup>14</sup> mentioned “entropy as mixed-up-ness.” Images such as these can be useful and important, but if taken too literally they can confuse as well as enlighten, and when misused<sup>15,16</sup> they can result in simple error. Analogies and visualizations *should* be employed, but their limitations as well as their strengths must be kept firmly in mind.

Section I of this paper serves to set the stage and fix the terminology by presenting the formal, mathematical definition of microcanonical entropy in statistical mechanics. (The definition is extended to other ensembles in the Appendix.) Section II (“Cautionary Tales”) gives three examples of the surprises nature provides when this definition is applied to physical systems, and hence illustrates the difficulties involved in seeking qualitative insight into entropy. This survey serves to frame the terms of debate and show why some visualizations of entropy are *not* acceptable. Section III goes to the heart of the matter by examining two versions of a simple model system (the “lattice gas”) in which the relationship between microscopic configurations and macroscopic thermodynamic states is particularly clear. Section IV reinforces the ideas of Sec. III by applying them to the game of poker, and Sec. V draws conclusions. The ideal conclusion for this paper would be to resolve the difficulties raised by producing a concise yet accurate visualization for entropy that appeals to both the gut and the intellect. I am not able to do this. But I am able to use a combination of mathematics and analogy to illuminate the character of entropy.

## I. MATHEMATICAL DEFINITION OF ENTROPY (MICROCANONICAL ENSEMBLE)

In statistical mechanics, many microstates may correspond to a single macrostate. (A macrostate is also called a “thermodynamic state”: for example,  $T$ ,  $V$ , and  $N$  for the canonical ensemble or  $E$ ,  $V$ , and  $N$  for the microcanonical ensemble.) In the microcanonical ensemble the entropy is

found simply by counting: One counts the number  $W$  of microstates that correspond to the given macrostate, and computes the entropy of the macrostate through

$$S = k_B \ln W, \quad (1)$$

where  $k_B$  is Boltzmann’s constant. Clearly,  $S$  is high for a macrostate when many microstates correspond to that macrostate, whereas it is low when few microstates correspond. The entropy of a macrostate measures the number of ways in which a system can be different microscopically and yet still be a member of the same macroscopic state. [The corresponding microstates are often called “accessible” for reasons relating to ergodic theory. Because ergodic theory is rarely discussed at the undergraduate level, I feel it best to avoid that term. Other synonyms for “a microstate corresponding to a macrostate” are “a microstate consistent with (or compatible with) a macrostate” or “a permissible microstate.”]

Note that it requires some skill and interpretation to translate this formal definition into an expression applicable to specific situations. For example, suppose the macrostate of the system is specified by an energy from  $E$  to  $E + \Delta E$ . If the system in question is quantum mechanical with discrete energy levels, then one must count not all quantal states with mean energies in this range, nor all energy eigenstates with energies in this range, but instead the number of elements of an energy eigenbasis with eigenvalues in this range. (In other words, one must properly count degenerate energy states.) If the system is a collection of  $N$  identical classical particles, whether interacting or not, then the macroscopic state may be a gas, liquid, or solid, but in all cases  $W$  is the volume of phase space corresponding to this energy range, divided by  $(N!h_0^{3N})$ . (In classical statistical mechanics,  $h_0$  is an arbitrary constant with the dimensions of action. In quantal statistical mechanics, it takes on the value of Planck’s constant. The so-called delabeling factor,  $N!$ , reflects the fact that  $N!$  different phase space points correspond to the same physical system. These  $N!$  points all represent  $N$  particles at  $N$  given locations and with corresponding given velocities, and differ only in the labels affixed to the various particles. On a more pragmatic vein, if the factor of  $N!$  were absent, then the resulting entropy would not be extensive.<sup>17)</sup>

## II. CAUTIONARY TALES

Before seeking qualitative insight into this formal definition, we examine three situations that demonstrate just how hazardous our search for insight can be.

## A. The monatomic ideal gas

The entropy of a pure classical monatomic ideal gas, as a function of energy  $E$ , volume  $V$ , and particle number  $N$ , is given by the Sackur–Tetrode formula

$$S(E, V, N) = k_B N \left[ \frac{3}{2} \ln \left( \frac{4 \pi m E V^{2/3}}{3 h_0^2 N^{5/3}} \right) + \frac{5}{2} \right]. \quad (2)$$

Let us examine this result qualitatively to see whether it agrees with our understanding of entropy as proportional to the number of microstates that correspond to a given macrostate. If the volume  $V$  is increased, then the formula states that the entropy  $S$  increases, which certainly seems reasonable: If the volume goes up, then each particle has more places where it can be, so the entropy ought to increase. If the energy  $E$  is increased, then  $S$  increases, which again seems reasonable: If there is more energy around, then there will be more different ways to split it up and share it among the particles, so we expect the entropy to increase. But what if the mass  $m$  of each particle increases? (Experimentally, one could compare the absolute entropy of, say, argon and krypton under identical conditions.<sup>18</sup>) Our formula shows that entropy increases with mass, but is there any way to understand this qualitatively?

In fact, I can produce not just one but two qualitative arguments concerning the dependence of  $S$  on  $m$ . Unfortunately the two arguments give opposite results! The first relies upon the fact that

$$E = \frac{1}{2m} \sum_i p_i^2, \quad (3)$$

so for a given energy  $E$ , any individual particle may have a momentum ranging from 0 to  $\sqrt{2mE}$ . A larger mass implies a wider range of possible momenta, which suggests more microstates and a greater entropy. The second argument relies upon the fact that

$$E = \frac{m}{2} \sum_i v_i^2, \quad (4)$$

so for a given energy  $E$ , any individual particle may have a speed ranging from 0 to  $\sqrt{2E/m}$ . A larger mass implies a narrowed range of possible speeds, which suggests fewer microstates and a smaller entropy. The moral<sup>19</sup> is simple: Qualitative arguments can backfire!

## B. Freezing water

It is common to hear entropy associated with “disorder,” “smoothness,” or “homogeneity.” How do these associations stand up to the simple situation of a bowl of liquid water placed into a freezer? Initially the water is smooth and homogeneous. As its temperature falls, the sample remains homogeneous until the freezing point is reached. At the freezing temperature the sample is an inhomogeneous mixture of ice and liquid water until all the liquid freezes. Then the sample is homogeneous again as the temperature continues to fall. Thus the sample has passed from homogeneous to inhomogeneous to homogeneous, yet all the while its entropy has decreased.

Suppose the ice is then cracked out of its bowl to make slivers, which are placed back into the bowl and allowed to rest at room temperature until they melt.<sup>9</sup> The jumble of irregular ice slivers certainly seems disordered relative to the

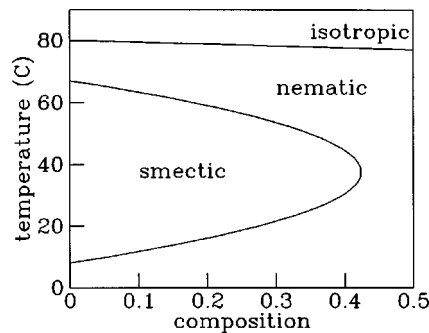


Fig. 1. Phase diagram of a liquid crystal mixture. The variable “composition” refers to the molecular weight ratio of 6OCB to 8OCB. Figure modified from Refs. 21, 22.

homogeneous bowl of meltwater, yet it is the ice slivers that have the lower entropy. The moral here is that the huge number of microscopic degrees of freedom in the meltwater completely overshadow the minute number of macroscopic degrees of freedom in the jumbled ice slivers. But the analogies of entropy to “disorder” or “smoothness” invite us to ignore this moral and concentrate on the system’s gross appearance and nearly irrelevant macroscopic features.

## C. Reentrant phases

When the temperature falls at constant pressure, most pure materials pass from gas to liquid to solid. But the unusual materials called “liquid crystals,” which consist of rodlike molecules, display a larger number of phases.<sup>20</sup> For typical liquid crystals, the high-temperature liquid phase is isotropic, meaning that the positions and the orientations of the molecules are scattered about nearly at random. At lower temperatures, the substance undergoes a transition into the so-called “nematic” phase, in which the molecules tend to orient in the same direction but in which positions are still scattered. At still lower temperatures it passes into the “smectic” phase, in which the molecules orient in the same direction and their positions tend to fall into planes. Finally, at even lower temperatures, the molecules freeze into a conventional solid. The story told so far reinforces the picture of “entropy as disorder,” with lower-temperature (hence lower entropy) phases showing more and more qualitative order.

But not all liquid crystals behave in exactly this fashion. One material called “hexyloxycyanobiphenyl” or “6OCB” passes from isotropic liquid to nematic to smectic *and then back to nematic again* as the temperature is lowered.<sup>21,22</sup> The first transition suggests that the nematic phase is “less orderly” than the smectic phase, while the second transition suggests the opposite!

One might argue that the lower-temperature nematic phase—the so-called “reentrant nematic”—is somehow qualitatively different in character from the higher-temperature nematic, but the experiments summarized in Fig. 1 demonstrate that this is not the case. These experiments involve a similar liquid crystal material called “octyloxycyanobiphenyl” or “8OCB” which has no smectic phase at all. Adding a bit of 8OCB into a sample of 6OCB reduces the temperature range over which the smectic phase exists. Adding a bit more reduces that range further. Finally, addition of enough 8OCB makes the smectic phase disappear altogether. The implication of Fig. 1 is clear: there is no qualitative difference between the usual nematic and the re-

entrant nematic phases—you can move continuously from one to the other in the temperature–composition phase diagram.

The implication of reentrant phases<sup>23</sup> for entropy is profound: Under some conditions the nematic phase has more entropy than the smectic phase and under other conditions less, while in all cases the nematic is qualitatively less ordered.

Reentrant phases are also encountered in type-II superconductors.<sup>24</sup> For example, when the temperature is lowered at constant magnetic field, some superconductors pass from the “vortex liquid” phase to the “vortex glass” phase and then back to the “vortex liquid” phase. The usual and reentrant instances of the vortex liquid are the same phase, as can be demonstrated by making them merge by changing both the temperature and the magnetic field.

A third example of a reentrant phase appears in the phase diagram of the mixture of water and nicotine.<sup>25</sup> For a wide range of mixing ratios, this mixture is a homogeneous solution at high temperatures, segregates into water-rich and nicotine-rich phases at moderate temperatures, yet becomes homogeneous again at low temperatures. At mixing ratios closer to pure water or pure nicotine, the mixture is homogeneous at all temperatures. Thus the high-temperature and reentrant homogeneous phases are in fact the same phase.

An obvious question at this point is “Why do reentrant phases exist?” The answer is “I don’t know.” I don’t know why water has the phases that it does either. Nature displays an extraordinary variety of phase behaviors,<sup>26</sup> all of which come about through maximizing the entropy of an isolated system, and none of which can (at present) be calculated from first principles. We can only grope at why some phase diagrams are relatively simple and others are mind-numbingly complex. Such gropings are exciting and important, but they do little to illuminate the qualitative character of entropy. That illumination comes instead through examining a simpler—rather than a more complex—model.

### III. ENTROPY AND THE LATTICE GAS

The three examples above should caution us about relying on qualitative arguments concerning entropy. Here is another situation<sup>27</sup> to challenge your intuition: Figures 2 and 3 show two configurations of  $13^2 = 169$  squares tossed down on an area that has  $35 \times 35 = 1225$  empty spaces, each of which could hold a square. This system, called the “lattice gas model,” lacks some familiar features (e.g., energy and temperature), yet it is nevertheless a legitimate and well-studied thermodynamic system.<sup>28</sup> The two configurations shown were produced by two different computer programs (*Toss1* and *Toss2*) that used different rules to position the squares.<sup>29</sup> (The rules will be presented in due course; for the moment I shall reveal only that both rules employ random numbers.) Which configuration do you think has the greater entropy? Be sure to look at the configurations, ponder, and make a guess (no matter how ill-informed) before reading on.

Before analyzing these pictures, I must first confess that my question was very misleading. I asked “Which configuration has the greater entropy?,” but entropy is not defined in terms of a single configuration (a single microstate). Instead, entropy is defined for a macrostate, and is related to the number of microstates that the system can take on and still be classified in that same macrostate. Instead of asking the question I did, I should have pointed out that I had two

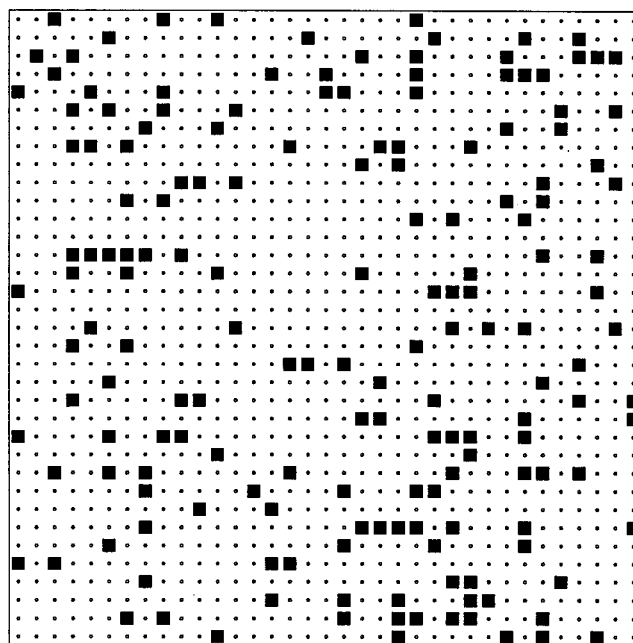


Fig. 2. A lattice gas configuration generated by the program *Toss1*.

classes, two pools, of microstates, and that I used my two computer programs to select one member from each of those two pools. The selection was done at random, so the selected configuration should be considered typical. Thus my question should have been “Which configuration was drawn from the larger pool?,” or “Which configuration is typical of the larger class?.” Given this corrected question, you might want to go back and look at the configurations again.

I have asked these questions of a number of people (both students and professionals) and most of them guess that Fig. 3 is typical of the class with larger entropy. That configuration is smoother, less clumpy. They look at the configuration in Fig. 2 and see patterns, which suggests some orderly pro-

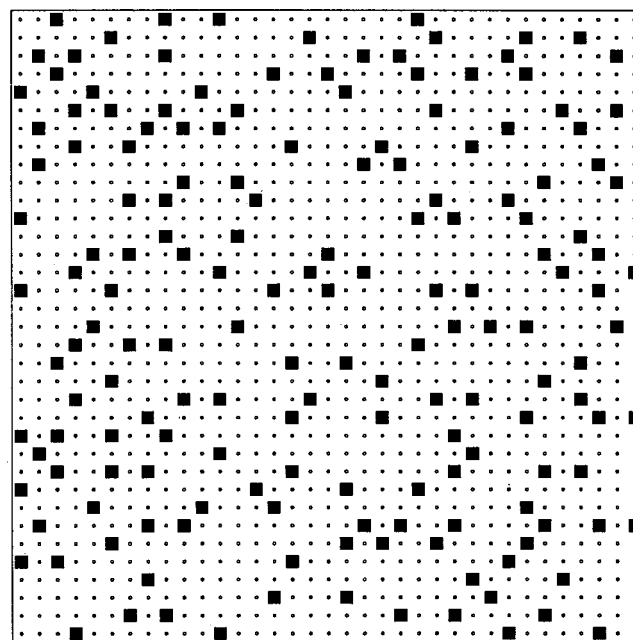


Fig. 3. A lattice gas configuration generated by the program *Toss2*.



cess for producing that configuration, while the smoothness of the lower configuration suggests a random, disorderly construction process.

Having posed the central question, let me end the suspense and tell you how the computer programs produced the two configurations. Figure 2 was produced by tossing 169 =  $(13)^2$  squares down at random onto an area with  $35 \times 35 = 1225$  locations, subject only to the rule that two squares could not fall on the same location. Figure 3 was produced in exactly the same manner except that there was an additional rule, namely that two squares could not fall on adjacent locations either. Thus Fig. 2 was drawn from the pool of *all* patterns with 169 squares, while Fig. 3 was drawn from the much smaller pool of patterns with 169 squares *and with no two squares adjacent*. The configuration of Fig. 2 is typical of the class with more configurations and hence greater entropy.<sup>30</sup>

Look again at Fig. 3. You will notice that there are no squares immediately adjacent to any given square. This “nearest neighbor exclusion” rule acts to spread out the squares, giving rise to the smooth appearance that tricks so many into guessing that the configuration of Fig. 3 is typical of a class with high entropy.

Now look again at Fig. 2. You will notice holes and clumps of squares, the inhomogeneities that lead many to guess that it is typical of a small class. But in fact one should *expect* a random configuration to have holes—only a very exceptional configuration is perfectly smooth.<sup>31</sup> This involves the distinction between a *typical* configuration and an *average* configuration. Typical configurations have holes: some have holes in the upper right, some in the middle left, some in the very center. Because the holes fall in various locations, the average configuration—the one produced by adding all the configurations and dividing by the number of configurations—is smooth. The average configuration is actually atypical. (Analogy: A typical person is not of average height. A typical person is somewhat taller or somewhat shorter than average, and very few people are exactly of average height. Any clothing manufacturer that produced only shirts of average size would quickly go bankrupt.) The presence of holes or clumps, therefore, need not be an indication of a pattern or of a design. However, we humans tend to find patterns wherever we look, even when no design is present. In just this way the ancient Greeks looked into the nighttime sky, with stars sprinkled about at random, and saw the animals, gods, and heroes that became our constellations.

#### IV. ENTROPY AND POKER

An excellent illustration of the nature of entropy is given by the card game poker. There are many possible hands in poker, some valuable and most less so. For example, the hand

A♥, K♥, Q♥, J♥, 10♥

is an example of a royal flush, the most powerful hand in poker. There are only four royal flushes (the royal flush of hearts, of diamonds, of spades, and of clubs) and any poker player who has ever been dealt a royal flush will remember it for the rest of his or her life.

By contrast, no one can remember whether he or she has been dealt the hand

4♦, 3♦, J♥, 2♠, 7♦

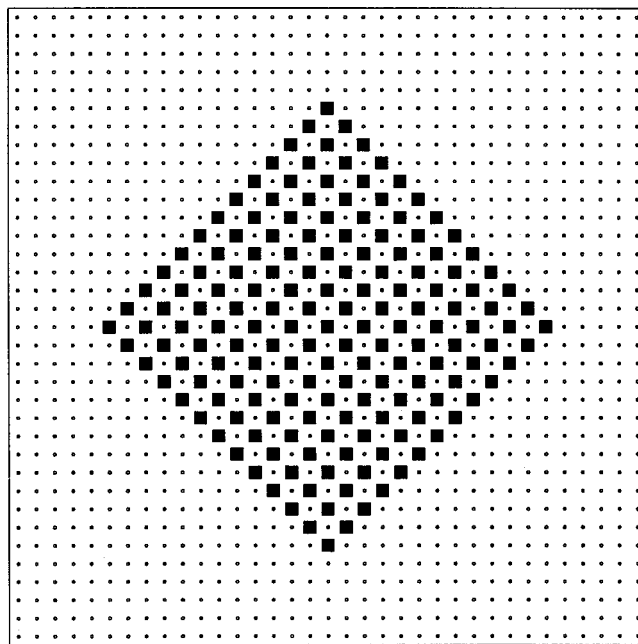


Fig. 4. An orderly lattice gas configuration that is a member of both the large class and the small class of configurations.

because this hand is a member of an enormous class of not-particularly-valuable poker hands. But the probability of being dealt this hand is *exactly* the same as the probability of being dealt the royal flush of hearts. The reason that one hand is memorable and the other is not has nothing to do with the rarity of that particular hand; it has everything to do with the size of the class of which that hand is a member.

This powerful and graphic illustration of the importance of class rather than of individual configuration may be called “the poker paradox.”

#### V. CONCLUSION

It is often said that entropy measures the disorder of a system. This qualitative concept has at least three failings: First, it is vague. There is no precise definition of disorder. Some find the abstract paintings of Jackson Pollock to be disorderly; others find them pregnant with structure. Second, it uses an emotionally charged word. Most of us have feelings about disorder (either for it or against it), and the analogy encourages us to transfer that like or dislike from disorder, where our feelings are appropriate, to entropy, where they are not. The most important failing, however, is that the analogy between entropy and disorder invites us to think about a single configuration rather than a class of configurations. In the lattice gas model there are many “orderly” configurations (such as the checkerboard pattern of Fig. 4) that are members of both classes. There are many other “orderly” configurations (such as the solid block pattern of Fig. 5) that are members only of the larger (higher entropy!) class.<sup>32,33</sup> The poker hand

2♣, 4♦, 6♥, 8♠, 10♣

is very orderly, but a member of a very large class of nearly worthless poker hands.

Given the clear need for an intuition concerning entropy, and the appealing but unsatisfactory character of the simile “entropy as disorder,” what is to be done? I suggest an

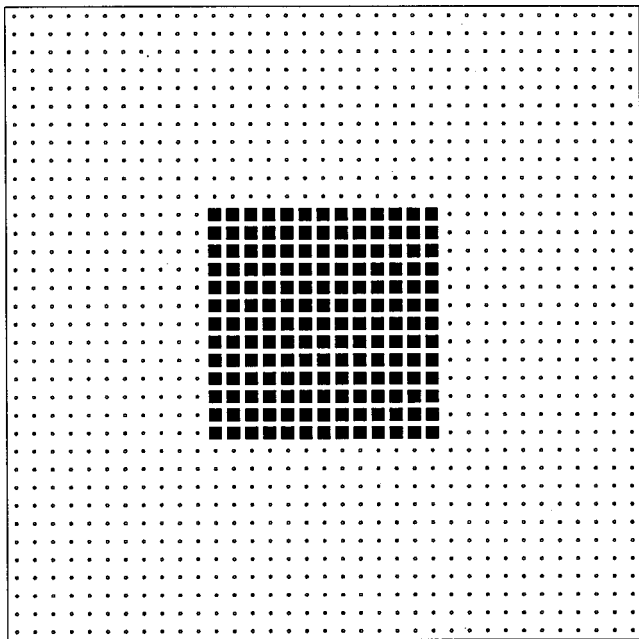


Fig. 5. An orderly lattice gas configuration that is a member of only the large (high entropy!) class of configurations.

additional simile, namely “entropy as freedom,” which is to be used not by itself but only in conjunction with “entropy as disorder.”

“Freedom” means a range of possible actions, while “entropy” means a range of possible microstates. If only one microstate corresponds to a certain macrostate, then the system has no freedom to choose its microstate—and it has zero entropy. If you are free to manage your own bedroom, then you may keep it either neat or messy, just as high entropy macrostates encompass both orderly and disorderly microstates. The entropy gives the number of ways that the constituents of a system can be arranged and still be a member of the club (or class). If the class entropy is high, then there are a number of different ways to satisfy the class membership criteria. If the class entropy is low, then that class is very demanding—very restrictive—about which microstates it will admit as members. In short, 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.

While “entropy as freedom” has these benefits, it also has two of the drawbacks of “entropy as disorder.” First, the term “freedom” is laden with even more emotional baggage than the term “disorder.” Second, it is even more vague; political movements from the far right through the center to the extreme left all characterize themselves as “freedom fighters.” Is there any way to reap the benefits of this analogy without sinking into the mire of drawbacks?

For maximum pedagogical advantage, I suggest using *both* of these analogies. The emotions and vaguenesses attached to “freedom” are very different from those attached to “disorder,” so using them together tends to cancel out the emotion. A simple sentence like “For macrostates of high entropy, the system has the freedom to choose one of a large number of microstates, and the bulk of such microstates are

microscopically disordered” directs attention *away* from glib emotional baggage and *toward* the perspective of “more entropy means more microstates.”

“The unexamined life is not worth living,” claims Socrates. Similarly, the unexamined analogy is as likely to mislead as to edify. Using two different analogies, which superficially appear in opposition, can help insure that both analogies are used critically and thoughtfully.

## ACKNOWLEDGMENTS

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## APPENDIX: GENERAL MATHEMATICAL DEFINITION OF ENTROPY

The formal statistical-mechanical definition of entropy, valid for any equilibrium ensemble, is

$$S = -k_B \sum_m p_m \ln p_m, \quad (\text{A1})$$

where  $k_B$  is Boltzmann’s constant, the sum runs over all the microstates  $m$  of the system, and  $p_m$  is the probability that microstate  $m$  is occupied in the given ensemble.<sup>34</sup> The entropy is a function of the system’s macrostate (also called its “thermodynamic state”: for example,  $T$ ,  $V$ , and  $N$  for the canonical ensemble or  $E$ ,  $V$ , and  $N$  for the microcanonical ensemble). The microstate probabilities  $p_m$  are of course also functions of that macrostate.

Note that the function  $-\ln x$  is monotonically decreasing and that

$$S = -k_B \langle \ln p_m \rangle \quad \text{where} \quad \sum_m p_m = 1. \quad (\text{A2})$$

These three facts together give us a good picture of the relation between the occupation probabilities  $p_m$  and the entropy. The largest value of  $p_m$  corresponds to the smallest value of  $-\ln p_m$ , and because  $p_m$  is large this small value is weighed heavily when forming the average  $-\langle \ln p_m \rangle$ . Clearly, a small entropy comes from having a few microstates with high occupation probabilities while all the rest have small occupation probabilities. (Indeed, the minimum value  $S=0$  comes whenever one microstate has  $p_m=1$  and all the rest have  $p_m=0$ .) Just as clearly, a large entropy comes when the occupation probability is nearly equally shared among the several possible microstates. (Indeed, using Lagrange multipliers it is a trivial matter to show that the maximum value of  $S$  comes when all the occupation probabilities are equal.) In short, the entropy of a given macrostate measures the extent to which the occupation probabilities  $p_m$  are “spread around” among the various microstates corresponding to the macrostate.

The significance of the “spread around” quality is most clearly seen in the microcanonical ensemble, as described in Sec. I. (In an undergraduate course, I feel that the general argument of this Appendix should *not* be used, and only the microcanonical-specific argument of Sec. I presented.) In this ensemble, microstates are either “in” ( $p_m = \text{a constant}$ ) if they correspond to the given macrostate or else they’re

“out” ( $p_m=0$ ) if they do not. If the number of corresponding microstates is  $W$ , then the nonvanishing probabilities are  $p_m=1/W$ , and the general entropy definition Eq. (A1) becomes

$$S = k_B \ln W, \quad (\text{A3})$$

which is Eq. (1) of Sec. I.

<sup>a)</sup>Electronic mail: Dan.Styer@oberlin.edu

<sup>1</sup>Oral remark by John von Neumann to Claude Shannon, recalled by Shannon. See page 354 of Myron Tribus, “Information theory and thermodynamics,” in *Heat Transfer, Thermodynamics, and Education: Boelter Anniversary Volume*, edited by Harold A. Johnson (McGraw-Hill, New York, 1964), pp. 348–368.

<sup>2</sup>Karl K. Darrow, “The concept of entropy,” *Am. J. Phys.* **12**, 183–196 (1944).

<sup>3</sup>P. G. Wright, “Entropy and disorder,” *Contemp. Phys.* **11**, 581–588 (1970).

<sup>4</sup>P. W. Atkins, *The Second Law* (Scientific American Books, New York, 1984).

<sup>5</sup>Bernd Rodewald, “Entropy and homogeneity,” *Am. J. Phys.* **58**, 164–168 (1990).

<sup>6</sup>Harvey S. Leff and Andrew F. Rex, Eds., *Maxwell’s Demon: Entropy, Information, Computing* (Princeton University Press, Princeton, NJ, 1990).

<sup>7</sup>Ralph Baierlein, “Entropy and the second law: A pedagogical alternative,” *Am. J. Phys.* **62**, 15–26 (1994).

<sup>8</sup>Harvey S. Leff, “Thermodynamic entropy: The spreading and sharing of energy,” *Am. J. Phys.* **64**, 1261–1271 (1996).

<sup>9</sup>Thomas A. Moore and Daniel V. Schroeder, “A different approach to introducing statistical mechanics,” *Am. J. Phys.* **65**, 26–36 (1997).

<sup>10</sup>Vinay Ambegaokar and Aashish A. Clerk, “Entropy and time,” *Am. J. Phys.* **67**, 1068–1073 (1999).

<sup>11</sup>J. Machta, “Entropy, information, and computation,” *Am. J. Phys.* **67**, 1074–1077 (1999).

<sup>12</sup>Roger Balian, “Incomplete descriptions and relevant entropies,” *Am. J. Phys.* **67**, 1078–1090 (1999).

<sup>13</sup>Harvey S. Leff, “What if entropy were dimensionless?” *Am. J. Phys.* **67**, 1114–1122 (1999).

<sup>14</sup>J. Willard Gibbs, *Collected Works* (Yale University Press, New Haven, CT, 1928), Vol. 1, p. 418.

<sup>15</sup>John W. Patterson, “Thermodynamics and evolution,” in *Scientists Confront Creationism*, edited by Laurie R. Godfrey (Norton, New York, 1983), pp. 99–116.

<sup>16</sup>Duane T. Gish, *Creation Scientists Answer their Critics* [sic] (Institute for Creation Research, El Cajon, California, 1993). An Appendix contribution by D. R. Boylan seeks to split entropy into the usual entropy which is “due to random effects” and a different sort of entropy related to the “order or information in the system” (p. 429). An even greater error appears in Chap. 6 (on pp. 164 and 175) where Gish claims that scientists must show not that evolution is *consistent* with the second law of thermodynamics, but that evolution is *necessary* according to the second law of thermodynamics. The moon provides a counterexample.

<sup>17</sup>Detailed discussion of this  $N!$  factor and the related “Gibbs paradox” can be found in David Hestenes, “Entropy and indistinguishability,” *Am. J. Phys.* **38**, 840–845 (1970); Barry M. Casper and Susan Freier, “‘Gibbs paradox’ paradox,” *ibid.* **41**, 509–511 (1973); and Peter D. Pešić, “The principle of identity and the foundations of quantum theory. I. The Gibbs paradox,” *ibid.* **59**, 971–974 (1991).

<sup>18</sup>The Sackur-Tetrode formula (2) predicts that  $S_{K_r} - S_{A_r} = (3/2)k_B N \ln(m_{K_r}/m_{A_r})$ . The data in Ihsan Barin, *Thermochemical Data of Pure Substances*, 3rd ed. (VCH Publishers, New York, 1995), pp. 76 and 924, verify this prediction to 1.4% at 300 K, and to 90 parts per million at 2000 K.

<sup>19</sup>The *moral* of the paradox is given in the body of this paper. The *resolution* of the paradox is both deeper and more subtle: It hinges on the fact that the proper home of statistical mechanics is phase space, not configuration space, because Liouville’s theorem implies conservation of volume in phase space, not in configuration space. See Ludwig Boltzmann, *Vorlesungen über Gastheorie* (J. A. Barth, Leipzig, 1896–98), Part II, Chaps. III and VII [translated into English by Stephen G. Brush: *Lectures on Gas Theory* (University of California Press, Berkeley, 1964)]; J. Willard Gibbs, *Elementary Principles in Statistical Mechanics* (C. Scribner’s Sons, New York, 1902), p. 3; and Richard C. Tolman, *The Principles of Statistical*

*Mechanics* (Oxford University Press, Oxford, U.K., 1938), pp. 45, 51–52.

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<sup>21</sup>J. David Lister and Robert J. Birgeneau, “Liquid crystal phases and phase transitions,” *Phys. Today* **35**, 26–33 (May 1982).

<sup>22</sup>D. Guillon, P. E. Cladis, and J. Stamatoff, “X-ray study and microscopic study of the reentrant nematic phase,” *Phys. Rev. Lett.* **41**, 1598–1601 (1978).

<sup>23</sup>The phenomenon of reentrance in general, and particularly in liquid crystals, is reviewed in section 6 of Shri Singh, “Phase transitions in liquid crystals,” *Phys. Rep.* **324**, 107–269 (2000).

<sup>24</sup>Y. Yeshurun, A. P. Malozemoff, and A. Shaulov, “Magnetic relaxation in high-temperature superconductors,” *Rev. Mod. Phys.* **68**, 911–949 (1996). See page 916 and Fig. 4b on page 915.

<sup>25</sup>G. W. Castellan, *Physical Chemistry*, 2nd ed. (Addison-Wesley, Reading, MA, 1971), p. 330.

<sup>26</sup>See, for example, Max Hansen and Kurt Anderko, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958); David A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991); Robert J. Birgeneau, “Novel magnetic phenomena and high-temperature superconductivity in lamellar copper oxides,” *Am. J. Phys.* **58**, 28–40 (1990) (Fig. 4); C. Lobban, J. L. Finney, and W. F. Kuhs, “The structure of a new phase of ice,” *Nature* (London) **391**, 268–270 (1998); and I-Ming Chou, J. G. Blank, A. F. Gohcharov, H.-k. Mao, and R. J. Hemley, “*In situ* observations of a high-pressure phase of H<sub>2</sub>O ice,” *Science* **281**, 809–812 (1998).

<sup>27</sup>The argument of this section was invented by Edward M. Purcell and is summarized in Stephen Jay Gould, *Bully for Brontosaurus* (W. W. Norton, New York, 1991), pp. 265–268, 260–261.

<sup>28</sup>See, for example, H. Eugene Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971); D. C. Radulescu and D. F. Styer, “The Dobrushin-Shlosman phase uniqueness criterion and applications to hard squares,” *J. Stat. Phys.* **49**, 281–295 (1987); and Ref. 2.

<sup>29</sup>These computer programs, which work under MS-DOS, are available for free downloading through <http://www.oberlin.edu/physics/dstyer/>.

<sup>30</sup>The model of Fig. 2 is called the “ideal lattice gas,” while the nearest-neighbor-excluding model of Fig. 3 is called the “hard-square lattice gas.” (These are just two of the infinite number of varieties of the lattice gas model.) Although the entropy of the hard-square lattice gas is clearly less than that of the corresponding ideal lattice gas, it is difficult to calculate the exact entropy for either model. Such values can be found (to high accuracy) by extrapolating power series expansions in the activity  $z$ : details and results are given in D. S. Gaunt and M. E. Fisher, “Hard-sphere lattice gases. I. Plane-square lattice,” *J. Chem. Phys.* **43**, 2840–2863 (1965) and R. J. Baxter, I. G. Enting, and S. K. Tsang, “Hard-square lattice gas,” *J. Stat. Phys.* **22**, 465–489 (1980).

<sup>31</sup>Reference 4 promotes the idea that entropy is a measure of homogeneity. (This despite the everyday observation of two-phase coexistence.) To buttress this argument, the book presents six illustrations (on pp. 54, 72, 74, 75, and 77) of “equilibrium lattice gas configurations.” Each configuration has 100 occupied sites on a 40×40 grid. If the occupied sites had been selected at random, then the probability of any site being occupied would be 100/1600, and the probability of any given pair of sites both being occupied would be  $1/(16)^2$ . The array contains  $2 \times 39 \times 39$  adjacent site pairs, so the expected number of occupied adjacent pairs would be  $2(39/16)^2 = 11.88$ . The actual numbers of occupied nearest-neighbor pairs in the six illustrations are 0, 7, 3, 7, 4, and 3. A similar calculation shows that the expected number of empty rows or columns in a randomly occupied array is  $(15/16)^{10} \times 2 \times 40 = 41.96$ . The actual numbers for the six illustrations are 28, 5, 5, 4, 4, and 0. I am confident that the sites in these illustrations were not occupied at random, but rather to give the impression of uniformity.

<sup>32</sup>Someone might raise the objection: “Yes, but how many configurations would you have to draw from the pool, on average, before you obtained exactly the special configuration of Fig. 5?” The answer is, “Precisely the same number that you would need to draw, on average, before you obtained exactly the special configuration of Fig. 2.” These two configurations are equally special and equally rare.

<sup>33</sup>In this connection it is worth observing that in the canonical ensemble (where all microstates are “accessible”) the microstate most likely to be occupied is the ground state, and that this is true *at any positive temperature, no matter how high*. The ground state energy is not the most probable energy, nor is the ground state typical, yet the ground state is the most

probable microstate. In specific, even at a temperature of 1 000 000 K, a sample of helium is more likely to be in a particular crystalline microstate than in any particular plasma microstate. However, there are so many more plasma than crystalline microstates that (in the thermodynamic limit) the sample occupies a plasma macrostate with probability 1.

<sup>34</sup>The definition of entropy in Eq. (1) is the best starting place for teaching

about entropy, but it holds only for the microcanonical ensemble. The definition Eq. (A1) is harder to understand but is also more general, applying to any ensemble. The two definitions are logically equivalent. See, for example, Richard E. Wilde and Surjit Singh, *Statistical Mechanics: Fundamentals and Modern Applications* (Wiley, New York, 1998), Sec. 1.6.1.

### COMPUTERS IN THE CLASSROOM

I've paid my dues in physics and astronomy, and in those basic sciences, computers have nothing to do with learning.

No computer can help someone understand the meaning of a wave function, angular momentum, or the relativistic-twins paradox. Software can simulate these on a glass screen, but these simplifications depend on someone else's understanding, which may be quite limited.

Up and down the line, computer programs feed us someone else's logic, instead of encouraging us to develop our own. When confronted by a quandary, we're fed someone else's rubric rather than creating our own assaults on the problem.

Clifford Stoll, *Silicon Snake Oil* (Doubleday, New York, 1995), p. 121.