Removing the Mystery of Entropy and Thermodynamics – Part V

Harvey S. Leff, Reed College, Portland, OR[a,b]

Part V ends this five-part paper series.[1–4] We discuss the interpretation of entropy as uncertainty and connections between spreading and uncertainty. The too commonly used disorder metaphor for entropy is roundly rejected. Finally, a generalization of the equity concept that was introduced in Part III is presented. The question-answer format is continued and Key Points 5.1–5.3 are enumerated.

Questions and Answers

• *Is entropy a measure of a system's disorder?*

In general the answer is a firm "no." A common definition of disorder is: *a lack of systematic or regular arrangement.* This has a spatial or orientational connotation and is appropriate only when there are clear spatial patterns. For example crystalline solids are typically more ordered spatially than gases. On the other hand, a sufficiently hot solid, or sufficiently large, cold solid, can have a higher entropy than a cool gas; spatial order alone does not guarantee low entropy. A proper metaphor should entail energy, which is a key ingredient in both the Clausius and Boltzmann definitions of entropy.

Introduced by Helmholtz[5] and Boltzmann,[6] the disorder metaphor, unfortunately, has been adopted by many textbook authors and researchers. However, dismissing entropy simply as "a measure of disorder" ignore's entropy's intimate relationship with energy. This is an undesirable oversimplification of a profound physical entity. Of course, one certainly can envisage ordered motion for molecules all moving in a specified direction and relatively "disordered" motion for typical gas molecules. Yet no single definition of disorder describes molecular jiggling, spatial irregularity, orientational randomness, and the expansion of a gas to a larger volume. The energy-spreading metaphor can be applied successfully to *all* of these.

Disorder can be an unhelpful or misleading metaphor. For example, 2 m^3 of copper has twice the entropy of 1 m^3 under the same external conditions. But the 2 m^3 sample is not more disordered in any obvious sense. There are more particles in the larger sample and more uncertainty about them, but uncertainty and disorder are *very different* concepts. The disorder metaphor is unhelpful here.

An example of a misuse of the term *disorder* is a quotation from the *Encyclopedia of Earth*: "The entropy law describes the tendency for all objects to rust, break, fall apart, wear out, and otherwise move to a less ordered state." As observed by Styer,[7] this is misleading because in the reaction for rust, $4Fe + 3O_2 \rightarrow 2Fe_2O_3$, the entropy change is -549.3 J·K^{-1}. This entropy decrease does not support a tendency toward disorder of the iron-oxygen system. Because the concomitant enthalpy change is -1684 kJ·mol^{-1}, the entropy change of the surroundings is 1684 kJ·mol^{-1}/298.15 K = 5650 J·K^{-1}·mol^{-1}; i.e., energy spreads from the system to the environment. But there is no evident increase in "disorder," and the disorder metaphor is misleading. The upshot is that the disorder metaphor is unacceptable as a general interpretive tool, which has given rise to various critiques.[8–15]

Key Point 5.1: *Disorder is generally an unacceptable metaphor for entropy. It gives the misimpression that entropy is governed by spatial or orientational regularity rather than the distribution of energy over the system's volume and spreading over accessible microstates. The disorder metaphor is not consistent with either the Clausius or Boltzmann entropy forms, each of which entails energy.*

• *Is entropy a measure of uncertainty? Missing information?*

Yes, for both. The Boltzmann entropy $S = k \ln W$ can be interpreted as a measure of uncertainty or, more specifically, missing information. Suppose a set of W possible microstates has probabilities $\{P_1, P_2 \ldots \}$, where $0 \leq P_i \leq 1$ is the probability for microstate i, $i = 1, \ldots W$, and the sum of all probabilities equals one. Using methods from information theory, one can obtain a "least-biased" estimate of the individual probabilities.[16]

This is done by finding the set of probabilities that maximizes the Shannon missing information function, $MI \equiv -c[P_1 \ln P_1 + P_2 \ln P_2 + \ldots P_W \ln P_W]$ relative to known constraints, where $c = constant$. If the only constraint is that the sum of the probabilities is unity, the results of this procedure are: $P_i = 1/W$ for all i, and $MI = -cW(1/W) \ln(1/W) = c \ln W$. Further, if the arbitrary constant c is chosen to be k, Boltzmann's constant, the Shannon missing information function MI is identical to the Boltzmann entropy, $S = k \ln W$. Therefore, we interpret S as a measure of missing information—i.e., uncertainty.

Key Point 5.2: *Uncertainty is a good metaphor for entropy. This uncertainty is associated with the missing information about which of the W microstates with energy E (= U) is occupied at any instant. The missing information approach provides a way to justify the principle of equal a priori probabilities, namely, the probability of each state being occupied is the same, $1/W$. This is also related to equity, because no microstate is favored over any other. Energy is central here because the microstates are energy states.*
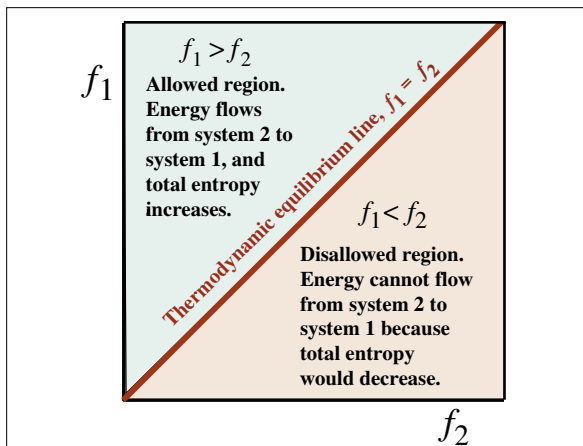
Fig. 1. Graph showing allowed and disallowed regions for an infinitesimal energy transfer from donor system 2 to receiver system 1, as described in the text. Along the 45° line, we say there is "equity," and thermodynamic equilibrium exists.

• How can the meaning of equitable energy distribution be understood generally?

Here, we illustrate definitions of *equity* that are suggested using the Boltzmann entropy form. Suppose two subsystems of an isolated composite system exchange an amount of energy via a heat and/or work process. System 1 gains a small amount of energy and system 2 loses an equal amount of energy. Because entropy increases with increasing energy, the number of accessible microstates for the receiving system increases and that for the donor system 2 decreases. Because the number of accessible states increases with energy, $dW_1 > 0$ and $dW_2 < 0$. And because $S_i = k \ln W_i$ for $i = 1, 2$, and the total number of states for the composite system is $W_{\text{tot}} = W_1 W_2$ and $S_{\text{tot}} = k \ln W_{\text{tot}}$, it follows that $S_{\text{tot}} = S_1 + S_2$. The second law of thermodynamics requires that

$$dS_{\text{tot}} = k \left[\left| \frac{dW_1}{W_1} \right| - \left| \frac{dW_2}{W_2} \right| \right] = k[f_1 - f_2] \geq 0. \qquad (1)$$

Here, $f_i \geq 0$ is the fractional change of the number of states in system i, for $i = 1, 2$. Equation (1) shows that to satisfy the second law of thermodynamics, system 1 cannot gain a smaller fraction of states than system 2 loses. This assures that the total number of microstates of the composite system, and thus the total entropy, increase.

Under a small energy exchange that increases the energy of system 1, energy proceeds to flow in that direction provided $f_1 > f_2$, and continues until $f_1 = f_2$, when thermal equilibrium exists. If an energy fluctuation leads to $f_1 < f_2$, the fluctuation corrects itself—i.e., there is no finite energy flow increasing the energy of system 1 because the total number of states over which the composite system can spread would decrease. This would lower the entropy and violate the second law of thermodynamics. If $f_1 = f_2$, thermodynamic equilibrium exists, and the receiving system increases its number of states by the same fraction that the donor system loses.

If a finite energy exchange were to reverse the inequality

in Eq. (1), this would violate the principle of entropy increase. Measurable energy transfers in this "wrong" direction, though possible in principle, have such low probabilities that they are not observed. A graphic view of "equity" is given in Fig. 1.

Key Point 5.3: *For an isolated composite system with two subsystems, an equitable energy distribution exists when any infinitesimal energy exchange brings equal and opposite fractional changes in the numbers of accessible states of the subsystems. This signals equity in three ways: (i) the receiving and donor systems are on par with one another, with neither experiencing a greater fractional change in its number of accessible states; (ii) the number of accessible states over which the composite system can spread is maximized; away from thermodynamic equilibrium, there is less equity in that fewer states are accessible—i.e., more are excluded; (iii) the principle of equal a priori probability implies that no accessible microstate is favored over another.*

Notice that if the composite system consists of two *identical* systems, the total number of states $W_{tot} = W(E_1)W(E_2)$. It is straightforward to show that W_{tot} is maximized for $E_1 + E_2 = E = constant$ for $E_1 = E_2 = E/2$. This agrees with our earlier findings regarding equity.[2-3]

Discussion

Relating entropy to spreading is not new. Clausius hinted at it with his introduction of *disgregation*, which was mentioned in Part II,[2] and others have mentioned the relevance of spreading—though typically of particles rather than energy per se. Traditionally entropy has been described qualitatively in ways that do not entail energy explicitly—e.g., using the disorder metaphor, which is rejected here. This is surprising given the Clausius algorithm, $dS = đQ_{rev}/T$, which explicitly relates energy and entropy and the Boltzmann form $S = k \ln W$, in which W is a function of the system energy.

I examined connections between energy and entropy in three prior articles[17-19] and independently, Lambert[8-11] proposed a similar idea. He prefers the term "energy dispersal" rather than "spreading," but the basic idea is the same. Authors of dozens of general and physical chemistry textbooks have adopted this concept and purged their books of references to disorder. Far better than disorder are the metaphors of entropy as spreading (or dispersal) and missing information or, equivalently, uncertainty. Together, these metaphors can help illuminate entropy.

Although no metaphor is perfect and oversimplifications can mislead,[13] both the spreading and missing information metaphors highlight the fact that entropy is related to *choice*. Spreading a given amount of energy over a larger volume of material or adding more energy to a fixed volume results in more accessible microstates—i.e., higher multiplicity.[20] This results in more choice, namely, the system can spread over more states, and there is greater uncertainty—more missing information—about which microstate is occupied. Spreading and missing information provide complementary, useful views of entropy.[21]

A strength of the spreading metaphor is that it explicitly entails energy, which lies at the very heart of physics generally and thermodynamics in particular. This is explicit in both the Clausius and Boltzmann entropy equations. Additionally, spatial energy spreading can be related qualitatively to heat and work processes, which is aesthetically pleasing. This inspires an apt closing poem:

> "*S stands for spreading; it's easy as can be. This mnemonic sheds light on entropy.*"

References

a. hsleff@csupomona.edu
b. Visiting Scholar, Reed College; Emeritus Professor, California State Polytechnic University, Pomona. Mailing address: 12705 SE River Rd., Apt. 501S, Portland, OR 97222.
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