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Response to Nagle's Criticism of My Proposed Definition of the Entropy

Robert H. Swendsen[1]

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In a recent paper, Nagle criticized the new definition of entropy that I had proposed in an earlier work. In the examples for which Nagle claims my definition fails, he took a formula that I had derived for one set of experiments and used it to represent my definition for other experiments. However, the formulas obtained from my definition depend on the specific experimental observables. If my definition is correctly applied to Nagle's experiments, no contradictions remain.

KEY WORDS: Entropy; Gibbs' paradox; distinguishability.

1. INTRODUCTION

In an earlier paper,(2) I proposed a new definition of the entropy as "the logarithm of the probability distribution for the experimentally accessible observables in a composite system." Nagle has criticized my definition (Nagle, Submitted) and argued that the Boltzmann definition in terms of a volume in phase space(3,4) is "superior". Space limitations prevent me from addressing Nagle's critique point by point, but I will try to clarify the source of the disagreement. Like Nagle, I will restrict the discussion to the configurational entropy of an ideal gas, which contains the essential aspects of the issues involved.

The main point is that Nagle did not actually use my definition in his critique. Instead, he took a formula that I had derived for one set of experiments (see Eq. (3) in Nagle's paper) and applied it to other experiments for which my definition would lead to different expressions. As I

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[1] Physics Department, Carnegie MellonUniversity, Pittsburgh, PA 15217, USA; e-mail: swendsen@andrew.cmu.edu

will show below, the correct expressions are completely consistent with the expected physical behavior.

Prior to his main discussion, Nagle notes in his Section II that the equations in Section 10 of my paper can be used to used to obtain the factor of $1/N!$ in the Boltzmann definition for identical particles in a more direct way than is normally done. His comment is correct and follows from Eq. (30) in my paper.

2. DISTINGUISHABILITY

A central aspect of our differences concerns the definition of distinguishability. The first definition Nagle gives in his concluding section, that distinguishability means that an exchange of particles results in a different microscopic state, is correct. However, the experiments he describes go beyond this definition to include microscopic measurements of the locations of individual particles.

Nagle's association of the concept of "distinguishable" with that of being "identifiably different" is implicit in his choice of experiments. In his Section V, he makes it explicit with the statement that, "The system of distinguishable particles is merely the conceptual limit in which every particle is a different type." In his appendix, he also states, "that each particle is a different "chemical" species, so that there are N different chemical species present in a system of N distinguishable particles." This point of view seems to have influenced Nagle's choice of experiments, which include microscopic measurements of the locations of individual particles.

Since my original paper only discussed macroscopic measurements, such as the total number of particles in each subsystem, the expression for the entropy that I had derived is not appropriate for Nagle's experiments, as I will show below.

In his concluding section, Nagle suggests that I might have used an unusual definition that particles, "are distinguishable if they are in the classical thermodynamic regime in which the wavefunctions overlap negligibly." Nagle's paper is the first place I have encountered such a definition, and I certainly did not use it myself.

3. THE CONSISTENCY OF MY DEFINITION

In Nagle's Section III, he claims to demonstrate an inconsistency in my definition, but only shows that my definition is not equivalent to Boltzmann's.

Nagle begins by *defining* the partition function through his Eq. (7), which is equivalent to Boltzmann's definition of the entropy. He then uses that equation to derive Boltzmann's entropy and show that it differs from mine. I had demonstrated the difference more directly in my paper. My definition is not equivalent to Boltzmann's, but it is completely self-consistent.

There is one ambiguity in Nagle's discussion. Since he does not explicitly specify the experiments he has in mind in this section, he could have been assuming that the locations of individual particles are measurable. This would be consistent with his discussion of physically different particles in this section, as well as his statements on the meaning of distinguishability quoted above. In that case, the entropy he attributes to my definition is incorrect. As I will show in the next section, my definition gives an expression for such an experiment that does not contain the factor of $1/N!$. Even in this case, no inconsistency arises from my definition.

4. NAGLE'S EXPERIMENTS

In the thought experiments in Nagle's Sections IV and V, he considers microscopic variables that specify which box each particle is in, rather than the macroscopic variables (the total number of particles in each box) that I considered. His comments in these two sections are therefore not directly relevant to the examples of the thermodynamic entropy in my paper.

The formula that Nagle claims to obtain from my definition for his experiments is incorrect. To apply my definition of the entropy to Nagle's experiments, the "experimentally accessible observables" must be specified. In his Section IV, Nagle considers the measurement of N microscopic variables that give which subsystem each particle is in. We can denote them as $\{N_{1j}, N_{2j} | j = 1, \ldots, N\}$, with the values 0 and 1, and $N_{1j} + N_{2j} = 1$. Assuming that each of these variables is independent, their probability distribution is

$$W\left(\{N_{1j}, N_{2j} | j = 1, \ldots, N\}\right) = \prod_{j=1}^{N} \left[\left(\frac{V_1}{V}\right)^{N_{1j}} \left(\frac{V_2}{V}\right)^{N_{2j}} \right] \tag{1}$$

My definition of the entropy of the combined system uses the logarithm of this expression and gives

$$\begin{aligned} S_{SC,N(4)}\left(\{N_{1j}, N_{2j} | j = 1, \ldots, N\}\right) &= k \sum_{j=1}^{N} \left[N_{1j} \ln(V_1) + N_{2j} \ln(V_2) \right] \\ &\quad - kN \ln(V) \end{aligned} \tag{2}$$

If we introduce the short-hand notation, $N_1 = \sum_{j=1}^{N} N_{1j}$ and $N_2 = \sum_{j=1}^{N} N_{2j}$, the entropy of subsystem i is just $kN_i \ln(V_i)$, which looks the same as the Boltzmann expression. However, it is really a function of N microscopic variables.

Although Eq. 2 is just $-k$ times the Shannon information, I would not say that it is a *thermodynamic* entropy because it does not satisfy the thermodynamic postulates. It contains microscopic observables that do not have a narrow distribution, and Eq. (2) does not take on its maximum value in equilibrium.

In his Section V, Nagle considers a different set of experiments. Again, the equation he quotes does not follow from my definition. A correct analysis requires labeling the different types of particles with an index α. My expression for the entropy of the composite system in an experiment with M types of particles and N_α particles of each type is

$$\begin{aligned} S_{SC,N(5)}\left(\{N_{1\alpha}, N_{2\alpha} | \alpha = 1, \ldots, M\}\right) \\ = k \sum_{\alpha=1}^{M} \left[\ln\left(\frac{V_1^{N_{1\alpha}}}{N_{1\alpha}!}\right) + \ln\left(\frac{V_2^{N_{2\alpha}}}{N_{2\alpha}}\right) - \ln\left(\frac{V^{N_\alpha}}{N_\alpha!}\right) \right] \end{aligned} \tag{3}$$

where $N_{1\alpha} + N_{2\alpha} = N_\alpha$.

As long as there are enough particles of each type for the width of the probability distribution to be less than the experimental error, Eq. (3) satisfies the thermodynamic postulates. However, in Nagle's limit of one particle of each type, the variables become microscopic. In that case, $M = N$, $\{N_{i\alpha} \in \{0, 1\} | i = 1, 2; \alpha = 1, \ldots, N\}$, $N_{i\alpha}! = 1$, and the entropy of a subsystem is given by the Boltzmann expression $kN_i \ln(V_i)$, where $N_i = \sum_\alpha N_{i\alpha}$. The entropy of the composite system is additive, but because the observables are microscopic, this expression for the entropy of the composite system will no longer take on its maximum value in equilibrium.

In every thermodynamic case Nagle discusses in his Section V, a positive entropy change is obtained from my definition, contradicting his claims to the contrary.

5. NAGLE'S "IRREVERSIBLE PROCESS"

Nagle's first experiment in his Section IV begins with two boxes, each of which has the same density of particles. A partition between them is opened. After some period of time, it is closed and each box is found to have the same number of particles as before. Nagle claims that this process demonstrates irreversibility.

If only the number of particles is measured, as I had discussed in my paper, no change is observed, irreversible or otherwise, and $\Delta S = 0$. This is correctly reflected in my definition and the expression for the entropy that I had derived in my paper for such an experiment.

For Nagle's microscopic measurement of the location of each particle, the situation is different. The entropy that follows from my definition is given in Eq. (2), and has the same form as the Boltzmann expression.

To understand this result, consider the case of identical volumes, so that each measurement of a particle position corresponds to flipping a coin. If we observe whether a coin lying on the table is heads or tails, flip it, *and don't look at the result*, the change in the Shannon information is $-\ln(2)$. If this is multiplied by $-kN$ to represent N coins, we have exactly the entropy increase claimed by Nagle. This also agrees with my definition of the entropy under these conditions. If you do look at the coins after flipping them (or, for Nagle's experiment, look at which box each particle is in), the information change and the entropy change return to zero. No irreversibility is observed.

Note that if the particles initially in each box are painted different colors and the number of particles of each color is measured after the partition is replaced, my definition of the entropy leads to Eq. (3) with $M = 2$. This gives the correct increase in entropy due to mixing.

6. NAGLE'S "COMMENTS ON THE POSTULATES"

The postulates in my paper that Nagle refers to are actually thermodynamic postulates. I took them from Callen's book$^{(5)}$, and modified their order primarily to reflect their relative importance. They are complete as they stand. The additional postulates Nagle proposes are not wrong, just redundant. The expressions for the entropy derived from my definition satisfy them for every thermodynamic experiment Nagle considered.

The point of view I have taken is that statistical mechanics provides the more fundamental description. The properties of thermodynamic systems can be calculated on the basis of statistical mechanical postulates. My definition gives a function in statistical mechanics that has all the properties of the thermodynamic entropy. The thermodynamic postulates then become theorems of statistical mechanics.

I did not state all of my own assumptions explicitly in the (perhaps mistaken) belief that they would be regarded as obvious. However, since Nagle has disputed the validity of my assumptions and conclusions, I will list the most important points here.

- Thermodynamics provides a description of an experiment or set of experiments. They may be real experiments, computer experiments, or thought experiments, but always experiments.
- The information corresponding to the entropy is obtained through measurement in an experiment.
- The variables contained in the thermodynamic description of an experiment are the same as those measured in the experiment or set of experiments under consideration.
- The recognition of the incompleteness of available information in an experiment is essential to understanding the connection between statistical mechanics and thermodynamics.
- Probability theory provides an appropriate way of describing the information available from experimental measurement.

The first two of these points led to my emphasis on experimental quantities in the definition of the entropy. The third provides the direct specification of which variables the entropy depends on. The last two postulates are the basis for the probabilistic interpretation of the entropy in statistical mechanics that I have advocated.

7. NAGLE'S "CRITIQUE OF SWENDSEN'S METHODOLOGY"

Nagle begins the "critique" in his Section VI with the claim that the distribution in his Eq. 16, which has its maximum when all the particles are in the larger of the two volumes, is correct for distinguishable particles. Nagle states that, "one should place each particle into the larger subvolume if one wishes to maximize the entropy." As far as I can see, this procedure has nothing to do with equilibrium states in thermodynamics. The entropy is supposed to describe experiments; particle distributions are not normally altered to maximize a particular expression for the entropy.

Nagle also makes the claim that, "the additivity postulate … should not be expected to hold for BCD [Boltzmann Classical Distinguishable] particles because extensivity does not hold for them." Nagle's statement would seem to contradict his use of his Eq. (16), which gives the entropy of his composite system before the partition is removed as the sum of the Boltzmann entropies of the subsystems.

In the second paragraph of Section VI, Nagle considers an experiment involving the macroscopic observables N_1 and N_2 for the numbers of particles in a composite system. In his Eq. (17), he writes a distribution that is proportional to the probability distribution of the numbers of particles. By using macroscopic observables and considering a composite system directly, Nagle produces an expression for the entropy that is separable into additive entropies for the subsystems. Nagle does not mention it, but these entropies agree with my definition.

If a composite system is considered, the accessible volume of phase space as a function of the internal variables N_1 and N_2 is proportional to the probability distribution of these variables. The expression for the entropy obtained this way for this case is then the same as for my definition. It should also be noted that the Boltzmann entropy derived in this manner is inconsistent with the Boltzmann entropies of the subsystems (unless additivity is denied).

If the energy distribution is also considered, there is a difference corresponding to the use of a volume in phase space versus the hypersurface that comes from the probability distribution.

8. CONCLUSIONS

Nagle has made a number of direct statements about claimed defects in my definition of the entropy, which I should respond to.

In his Section III, Nagle states that my inclusion of an explicit factor of $1/N!$ in the derived expression for the entropy of distinguishable particles, but not for indistinguishable particles "is logically backwards and indicates a fundamental inconsistency." It should be noted, however, that he uses the factors in the same way. Nagle did not include an explicit factor of $1/N!$ for the indistinguishable case in his Section II; the factor of $1/N!$ came from the integrals, exactly as it did in my paper. Nagle did correctly include an explicit binomial coefficient in his Eq. (17) for the distribution of distinguishable particles. This is exactly the same source as the factor of $1/N!$ that Nagle disputes in my expression for the entropy of distinguishable particles. The entropy for a composite system obtained from Nagle's Eq. (17) is equal to that obtained from my definition to within an unimportant additive constant.

Nagle also asserts that the factor of $1/N!$ I had derived for distinguishable particles "really is *ad hoc*". To the contrary, I had given an explicit derivation of the result in Section 5 of my paper that did not use any *ad hoc* steps.

When my definition of the entropy is applied to Nagle's thought experiments, the contradictions he claimed to find are absent. My proposed definition of the entropy is self-consistent. It provides a clear probabilistic interpretation of the second law of thermodynamics and is consistent with all experimental observations of irreversibility, including those discussed by Nagle.

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