Intensive and Extensive Properties: Thermodynamic Balance[1]

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Abstract: In equilibrium thermodynamics systems can be described in terms of properties which are either 1) intensive, 2) extensive, or 3) neither intensive nor extensive. While they can vary with spatial location in non-equilibrium systems, intensive properties are homogenous functions of degree (or order) zero ($k = 0$) and can be measured at any point. Temperature must always be intensive, as required by the laws of thermodynamics. This fundamental aspect of temperature is preserved whether dealing with equilibrium or non-equilibrium systems, as the latter can be analysed with local thermal equilibrium or reduced time intervals. As for extensive properties, given equilibrium, they are homogeneous functions of degree one ($k = 1$) and consequently, are both additive and dependent on spatial extent. Conversely, properties which are neither intensive nor extensive represent homogeneous functions of specific degree ($0 < k < 1$) which, while non-additive, remain dependent on some aspect of spatial extent. Importantly, the determination of whether some properties (e.g. length, surface area) are extensive or neither intensive nor extensive, remains system dependent. Since thermodynamic properties are homogenous functions, all thermodynamic expressions must be balanced. This requirement extends beyond simple dimensionality. The intensive or extensive character of any given thermodynamic expression must be preserved on either side. In this regard, the existence of properties which are neither intensive nor extensive provides significant insight into the validity of thermodynamic expressions. The inclusion of such properties within expressions can only be allowed when their presence results in thermodynamic balance. Otherwise, the resulting expressions violate the laws of thermodynamics. This is often manifested in temperature relations which are non-intensive.

Key words: Thermodynamic balance; intensive and extensive properties; non-extensive properties

1. INTRODUCTION
In 1961, P.T. Landsberg argued that the classification of thermodynamic properties as intensive or extensive was so fundamental to the study of thermodynamics that their existence should be recognized as the Fourth Law [1, 2]. He also argued that thermodynamic expressions must be balanced: "*…each side of a thermodynamic equation must contain extensive variables raised to the same power…*" and "*…thermodynamic equations must be homogeneous in the extensive variables…*" [1]. S. G. Canagaratna [3] has echoed the need for thermodynamic balance. However, textbooks on thermodynamics [4-10] generally provide only sparse information

relative to the treatment of intensive and extensive thermodynamic properties. Often, little can be gathered other than knowledge of their existence [2].[3]

Still, in 1972, Landsberg restated the central role of intensive and extensive properties in thermodynamics [11]. He summarized the laws of thermodynamics as follows: "*Zeroth Law – empirical temperature exists. First Law – internal energy exists. Second Law – entropy and absolute temperature exist. Third Law – states with T=0 do not exist. Fourth Law – for a class of non-equilibrium states, and for equilibrium states, extensive and intensive properties exist*" [11]. He also emphasized that those non-equilibrium states involving a theory of fluctuation and stability which do not follow these rules would not be thermodynamic in character [11]. Hence, Landsberg advanced that the Fourth Law was valid across all of thermodynamics. This included both equilibrium systems and those non-equilibrium systems which could be analysed by his "basic trick", wherein a system, which might have gradients in temperature, could be treated with subsystems in which the regular rules of thermodynamics applied [11]. Such arguments could be made whenever local thermal equilibrium methods were utilized.

Regrettably, while Landsberg's Fourth Law clearly had merit [1, 11], it has not been adopted by the scientific community beyond chemistry [3]. In large measure, this has been the result of a fundamental problem in properly classifying thermodynamic properties. For instance, the seminal work on the existence of intensive and extensive properties by R.C. Tolman [12], did not recognize that the characterization of a property as extensive (i.e. additive) depended on the nature of the thermodynamic system itself. The confusion in Tolman's work [12] arose because it was not focused on thermodynamics, but rather, attempted to identify fundamental properties across physics and mathematics. As a consequence, Tolman [12] identified length as an extensive property. However, in thermodynamics, length is usually not extensive (i.e. additive), unless the thermodynamic system is analogous to a wire. Despite such missteps, Tolman [12] clearly stated: "*We shall find it possible in agreement with the work of others to distinguish two general classes of quantity, those having extensive and those having intensive magnitude, and shall consider the methods necessary for measuring these two quite different magnitudes*" [12]. Tolman also properly recognized that extensive properties were fundamental. This arose because intensive properties were usually determined by sampling extensive properties.

The situation relative to intensive and extensive properties was further clouded in the classic reference by Redlich [13], who, while failing to properly describe non-extensive properties, surprisingly argued that "*the classification of intensive-extensive properties was…*" not "*…basic to the development of thermodynamics.*" He stated that "*the square root of volume is clearly neither extensive nor intensive; yet it is a well-defined property and all thermodynamic knowledge could be expressed if we replaced volume by the new variable. It would be awkward, cumbersome, and inefficient. But science could live with it. It is obviously wrong to say that only extensive and intensive variables exist*" [13]. The claim was obtuse at best, as the

square root of the volume of a sphere was not an additive property and its use would make it difficult to divide systems into subsystems and check for thermodynamic balance, a vital aspect of honouring thermodynamic laws. In addition, extensive properties are properly viewed as moving with mass or spatial extent. Volume is not utilized, for instance, when the thermodynamic system is the area of a monolayer. Consequently, the idea that the square root of volume could be used to redefine all of thermodynamic knowledge [13] is not tenable.

In any case, Redlich would simply be replacing the role taken by extensive properties with properties that were neither intensive nor extensive. He would have accomplished nothing relative to altering the fundamental intensive nature of temperature, the central aspect of all of thermodynamics. This is a key point for any treatment of thermodynamics for it is by the measurement of temperature that thermodynamics exists. Yet, in order to measure temperature at a given point, it is clear that temperature itself must be intensive. The idea that thermal equilibrium exists in the 0th law is directly requiring that temperature always be intensive. Otherwise, the 0th law itself could not exist.

Redlich was correct insofar as properties which are neither intensive nor extensive exist. Yet, he did not appreciate how they should be treated and what properties, in fact, behaved in this manner. Thus, he argued that surface area and boundary length are extensive [13]. In doing so, much like Tolman [12], he failed to realise that the extensive (or non-extensive) nature of these two properties depends on thermodynamic setting. At the same time, Redlich [13] recognized that thermodynamic coordinates (including intensive properties, extensive properties, and properties which are neither) and forces are fundamental to the development of thermodynamics: "*But the characterization of a property as a coordinate or force is indeed fundamental. Without these concepts we cannot define work and energy; thus, thermodynamics simply would not exist*" [13]. Unfortunately, Redlich did not appreciate the importance of intensive and extensive properties relative to establishing thermodynamic balance and guiding the derivation of thermodynamic expressions.

Recently, S.H. Mannaerts has presented a detailed account of extensive quantities [14]. The work is noteworthy for its detailed compilation of references relative to the treatment of intensive and extensive properties [14]. Regrettably, there are aspects of Mannaerts work which serve to highlight that the treatment of thermodynamic properties remain somewhat shrouded with confusion.

Mannaerts tries to argue that there is a fundamental difference in presenting extensive properties as additive or as proportional to mass [14]. Yet, the IUPAC has already determined that additivity will be the measure of extensivity for independent non-interacting subsystems [15]. He suggests that thermodynamic "*quantities are either constants or variables*" [14]. However, thermodynamic quantities should never be regarded as constants, given that the later never contribute to thermodynamic character. Thermodynamic quantities can, however, assume a constant value. Mannaerts also attempts to argue that in dividing a system in two that "*entropy is not halved either (Gibbs paradox)*" [14]. However, it is well-known that the Gibbs paradox is eliminated when the indistinguishability of the particles is considered.

Mannaerts tries to argue that surface area is extensive according to the additivity rule, but not extensive according to the proportionality rule. He writes: "*If we have a droplet with surface area A' and another droplet with an area A'', then together they have a surface area A= A' + A. This is formal addition*" [14]. Yet, in establishing the extensive nature of surface area, one is not concerned with formal addition, but in the merging of the two subsystems. The area of the new system will be smaller than the sum of these two, as Mannaerts himself recognizes [14]. Yet, that is why surface area is never extensive when dealing with the sum of two drops. It is only when dealing with two planes for instance that surface area is extensive. Mannaerts' argument only adds confusion relative to establishing the extensive nature of surface area, as he has not properly treated the additivity rule [14]. The surface area of a spherical body is not a homogeneous function of degree 1 and it is therefore never extensive, as will be seen below.

Mannaerts also presents a proof that temperature is extensive using what he casts as a *"reductio ad absurdum"* [14]. First, he advances the internal energy expression for an ideal monoatomic gas, *U=m(3RT/2M)*, where *U* is the internal energy, *m* is the mass, *R* is the universal gas constant, *T* is the temperature, and *M* the molar mass. He then argues that since 1) *U* is proportional to *m*, and 2) *U* is proportional to *T*, then by 3) the transitivity of proportion, 4) *T* is extensive. The arguments contained therein are improper, as Mannaerts himself recognizes [14]. The proportionality terms between internal energy and mass, or internal energy and temperature are not the same. The first is intensive overall while the second is extensive. As a result, the arguments advanced are invalid and only act to confuse the inexperienced reader. This occurs despite the fact that Mannaerts interjects that "*the error arises from the improper us of the word 'proportional'*" [14], as he never explains precisely the nature of the error. It can never be argued that temperature can be made to appear extensive through claims of "*Reductio ad absurdum*" [14]. The author also argues that "*a vacuum is an obvious violation of both PRs, but not of the additivity rule*". The argument does not belong in this paper. A vacuum is not a thermodynamic system.

Finally, Mannaerts argues that some intensive thermodynamic quantities are additive. He invokes partial pressures as one of the examples and concludes that "*Most intensive variables not additive*" [14]. Yet, intensive properties are never additive. That is a feature of extensive properties. The confusion arises in not appreciating that each partial pressure represents a specific intensive property, distinct from all other partial pressures. When summing partial pressures, one is not summing the same intensive property. Rather, different intensive properties are added together leading to a new intensive property, namely the total pressure. Each partial pressure remains intensive and never additive onto itself. It is false to claim that intensive properties can be additive in the context of determining thermodynamic character. Again, intensive properties are never additive, that is a feature of extensive properties.

As a result of these considerations, and given the lack of clarity relative to the nature of intensive and extensive properties, it is appropriate to highlight how these properties, along with properties which are neither intensive nor extensive, must be identified and treated. Once this has been accomplished, the question of thermodynamic balance can be addressed using a variety of examples taken from across the physical sciences. The central role that Landsberg's Fourth Law [1, 11]

relative to thermodynamic properties and their balance can then be fully appreciated [16].

II. INTENSIVE, EXTENSIVE, AND NON-EXTENSIVE PROPERTIES

Tolman [12] writes: "*In order to decide whether a given quantity has extensive or intensive magnitude it is sometimes helpful to see if the simultaneous presence of two systems, each having a definite quantity of the kind in question, can be regarded as giving a larger system with twice the quantity; if so that quantity has extensive magnitude*". A similar scenario is advanced by Redlich [13]. Importantly, this scenario establishes that extensive properties scale linearly with system size and therefore, must be additive.

Alternatively, for simplicity, one could consider two identical homogenous spheres, B_1 and B_2, in thermal equilibrium. The two spheres could be combined to create a larger sphere, B_T. Those properties like mass, M, volume, V, internal energy, U, and entropy, S, which are doubled in forming B_T are extensive, as they are additive for subsystems (e.g. $M_T = M_1 + M_2$). Mathematically, they can be viewed as homogeneous functions of degree 1. Thus, if mass M can be viewed as some function of x, y, and z, this function is considered homogenous in the first degree since when multiplying the arguments of the function by a quantity λ, the following holds:
$M(\lambda x, \lambda y, \lambda z) = \lambda^k M(x, y, z)$, where $k = 1$ [9]. All extensive properties can be viewed in the same manner. They are homogenous functions of degree 1 and are therefore additive across subsystems [15]. This is a central feature in macroscopic thermodynamics.

Conversely, those properties like temperature and pressure which remain unaltered when combining the two smaller spheres are considered intensive. Intensive properties are independent of system size. Mathematically, they are homogeneous functions of degree 0, as they are usually partial derivatives of homogenous functions of order 1 in the extensive coordinates. Thus, if temperature T can be viewed as some function of x, y, and z, when multiplying the arguments of the function by a value λ, then the following holds: $T(\lambda x, \lambda y, \lambda z) = \lambda^k T(x, y, z) = T(x, y, z)$, as $k = 0$ [9]. Intensive properties are clearly not additive and all such properties can be viewed in the same manner.

However, some properties like the radius of the sphere and its surface area are neither extensive nor intensive. They can be described as homogeneous functions, but not of the first or zeroth order. For instance, relative to a sphere, the radius R is a homogenous function of degree 1/3, because $R(V) = (3/4\pi)^{\frac{1}{3}} V^{\frac{1}{3}}$ so that $R(\lambda V) = (3/4\pi)^{\frac{1}{3}} \lambda^{\frac{1}{3}} V^{\frac{1}{3}} = \lambda^{\frac{1}{3}} R(V)$. In this respect, it is clear that if one takes the cube of the latter, an extensive property will be obtained, with the same behavior as volume $(\lambda^{1/3} R(V))^3 = (3/4\pi) \lambda^{3/3} V^{3/3} = (3/4\pi) \lambda V$. Hence although R is not extensive, R^3 is extensive.

Similarly, the area of a sphere, $A = 4\pi R^2$, can be considered a homogeneous function of degree 2/3, such that $A(\lambda V) = \lambda^{2/3} A(V)$, where $k = 2/3$, because $A(V) = 4\pi (3V/4\pi)^{\frac{2}{3}}$, so $A(\lambda V) = 4\pi (3\lambda V/4\pi)^{\frac{2}{3}} = \lambda^{\frac{2}{3}} 4\pi (3V/4\pi)^{\frac{2}{3}} = \lambda^{\frac{2}{3}} A(V)$. Again, the area of a

homogenous sphere is not extensive. However, if this area is multiplied by radius, an extensive property will be obtained, which once again behaves like volume:

$$\frac{1}{3}A(\lambda V)\cdot R(\lambda V)=\frac{1}{3}\lambda^{\frac{2}{3}}A(V)\cdot\lambda^{\frac{1}{3}}R(V)=\frac{\lambda}{3}4\pi\left(\frac{3V}{4\pi}\right)^{\frac{2}{3}}\left(\frac{3V}{4\pi}\right)^{\frac{1}{3}}=\lambda V\ . \tag{1}$$

Finally, a thermodynamic system can be considered which is limited to an area built from a monolayer. In this case, the area A is the spatial extent of the system, not volume, the homogeneous mass of the system remaining extensive with this area, so that mass per unit area is intensive. Area and mass move together here: halving the area, for example, halves the mass, and conversely. In this case, length L becomes a property which is neither intensive nor extensive. It is a homogenous function of degree ½ such that $L(\lambda A)=\lambda^{1/2}L(A)$, where k = ½. It is evident that if the length is squared, an extensive property, like area, will be obtained. For instance, consider a homogeneous square monolayer of side L. The area of the square monolayer is $A = L^2$. Hence, $L(A)=A^{\frac{1}{2}}$. Since A is the spatial extent of the monolayer system, A is extensive: then $L(\lambda A)=(\lambda A)^{\frac{1}{2}}=\lambda^{\frac{1}{2}}A^{\frac{1}{2}}=\lambda^{\frac{1}{2}}L(A)$. Likewise, the perimeter of the homogeneous square monolayer is P = $4L$. Hence $P(A)=4A^{\frac{1}{2}}$, so $P(\lambda A)=4\lambda^{\frac{1}{2}}A^{\frac{1}{2}}=\lambda^{\frac{1}{2}}P(A)$. Similarly, the area of a homogeneous circular monolayer is $A = \pi R^2$. The 'length' or 'perimeter' of this circular system is the circumference C = $2\pi R$. Hence $C(A)=2\pi\left(\frac{A}{\pi}\right)^{\frac{1}{2}}$ and,

$$C(\lambda A)=2\pi\left(\frac{\lambda A}{\pi}\right)^{\frac{1}{2}}=\lambda^{\frac{1}{2}}2\pi\left(\frac{A}{\pi}\right)^{\frac{1}{2}}=\lambda^{\frac{1}{2}}C(A). \tag{2}$$

Consequently the radius R of the circle is not extensive either.

In the case of a surface with constant positive Gaussian curvature [4] $\mathcal{G}$ = $1/\beta^2$ such that $A = 4\pi\beta^2$, defining the 'length' or 'perimeter' of this system as the 'great circle' C = $2\pi\beta$, then $C(A)=2\pi\left(\frac{A}{4\pi}\right)^{\frac{1}{2}}$ and so,

$$C(\lambda A)=2\pi\left(\frac{\lambda A}{4\pi}\right)^{\frac{1}{2}}=\lambda^{\frac{1}{2}}2\pi\left(\frac{A}{4\pi}\right)^{\frac{1}{2}}=\lambda^{\frac{1}{2}}C(A). \tag{3}$$

In both examples $[C(A)]^2$ moves as λA, i.e. $[C(A)]^2$ is extensive with the area defining the homogeneous monolayer system.

III. THERMODYNAMIC BALANCE
Thermodynamic equations must be dimensionally correct with respect to units. In addition, they must be balanced in the degree of properties. This concept is

fundamental to all work in thermodynamics. Without verified thermodynamic balance, a mathematical expression, for either temperature or entropy for instance, is invalid.

Much like Landsberg[1] before him, Canagaratna [3] noted: "*if one side of an equation is extensive (or intensive), then so must be the other side*". The importance of thermodynamic balance cannot be overstated, as irrespective of the nature of a thermodynamic expression, or the setting to which it is being applied, temperature must *always* be an intensive property. To argue otherwise violates the Zeroth, First, and Second Laws making it impossible to even speak of thermodynamics.

However, in order for temperature to remain intensive when appearing in an expression where temperature is the dependent variable, any non-intensive property in the expression must be divisible by another property in the expression of the same degree. This would result in an intensive property to thermodynamically balance to temperature. It is clear that rules must exist for establishing thermodynamic balance. These rules can be summarized as follows:

1. Only system properties contribute to thermodynamic balance.
2. The quotient of two properties within the same state, that are homogeneous to the same degree, is an intensive property.
3. The degree of a product of two homogeneous properties within the same state is given by the sum of their respective degrees.

From these simple rules, a few considerations arise. First, physical constants such as the universal constant of gravitation G, Planck's constant h, Boltzmann's constant k_B, and the Stefan-Boltzmann constant σ, while important for balancing the units (a question of proper dimensionality) of an expression, play no role in establishing thermodynamic balance. For instance, in the expression $E = Nk_BT$ both the energy, E, and the number of particles N, are extensive. Their quotient, by rule 2 is intensive, and so is temperature. As a result, this equation is balanced and, in accordance with rule 1, k_B played no role in establishing this balance. Second, it is clear by rule 3 that the product of two intensive properties is intensive, even if it has a constant value. By the same token, if one raises an intensive property to an exponent, the result remains intensive. Conversely, according to rule 3, the product of two extensive properties is never extensive, as the degree of the resulting property is now 2. Similarly, if one raises an extensive property to an exponent, the result is never extensive. Again, extensive properties must be additive. Finally, note that properties which are neither intensive nor extensive, but which have degree values between 0 and 1 ($0 < k < 1$), can result in an extensive property according to rule 3 when they are multiplied, provided that the sum of their degrees is equal to 1. Also, according to rule 2, if two such properties are divided, the resulting quotient can be intensive if the properties are homogenous to the same degree.

IV. EXAMPLES OF THERMODYNAMIC BALANCE
As a simple example of the importance of thermodynamic balance, Clausius' definition of temperature, as stated in the Second Law, can be taken as follows: $T = \delta Q/dS$. In this case, both the infinitesimal change in heat δQ, and the associated change in entropy dS, represent homogenous functions of degree 1. Their ratio is thereby intensive according to rule 2. As a result, temperature remains intensive, as

must be the case. Note that δQ is always considered to be so small as to not alter the equilibrium state. The reason for this is now made plain. If the change in heat is allowed to be other than infinitesimal, it then becomes a path function, whereas δQ must act as a state function, and thereby acquires extensive character. This must be the case if temperature is to remain intensive.

Let us now consider another example as previously discussed [16], namely the Stefan-Boltzmann law as applied to describe the luminosity of a star:

$$L = \sigma A T^4 = \sigma 4\pi R^2 T^4 , \tag{4}$$

where L, R, T, A, and σ correspond to luminosity, stellar radius, temperature, surface area, and the Stefan-Boltzmann constant respectively. Since stars can be viewed as homogenous spheres, it is clear that R is a homogenous function of degree 1/3. By squaring R, a homogeneous function of degree 2/3 is obtained, corresponding to the degree of both the luminosity and the area functions. As a result, when luminosity is divided by R^2 or by A, one generates a quotient from functions of the same order. The functions themselves are not extensive, however, their quotient becomes intensive as they must according to rule 2. As a result, temperature in this expression remains intensive, as must be the case. The Stefan-Boltzmann Law is thermodynamically balanced.

When describing blackbodies in "*The Theory of Heat Radiation*" [17] Max Planck required that thermal equilibrium take place throughout the system of interest. In the case of a blackbody, this must include two subsystems, the bulk and the surface thereof. Temperature remains intensive throughout the entire system. This occurs even though surface properties, like surface area and luminosity, are not extensive, while bulk properties, like mass and volume, are extensive. Rule 2 ensures that temperature remains an intensive property in a manner which is independent of the extensivity of the system or subsystem in question. Returning to Clausius' formulation of the Second Law ($T = \delta Q/dS$), if a system could be described wherein dS is not properly extensive, then this lack of extensivity must also be found in δQ, such that temperature remains intensive.

The importance of properties which are neither intensive nor extensive can be further clarified by examining an expression for the change in free energy, ΔG, taken from the biological literature [18] for the interaction of cells with surfaces covered with nanorods. These surfaces were constructed with varying number densities of nanorods, χ, on 1 μm^2 surface areas. The free energy of the system can be evaluated using this expression [18]:

$$\Delta G_{bottom-top} = -w\left(1\ \mu m^2 + \chi 2\pi RL - \chi \pi R^2\right) + \sigma\chi 2\pi RL + \kappa\chi\pi R^{-1}L , \tag{5}$$

where w is the specific adhesion energy per unit area (an intensive property with units = Joules/μm^2 and $k = 0$), χ is the number density of nanostructures (NSs) on the surface (a pure number for each system), R is the radius of the nanorod (a property which is neither intensive nor extensive with units = μm and $k = \frac{1}{2}$), L is the length of the nanorod (a property which is neither intensive nor extensive with units = μm and $k = \frac{1}{2}$), σ is the surface tension of the cell (an intensive property with units = Joules/μm^2),

and κ is the bending modulus (an extensive property with units = Joules and $k = 1$). It is readily apparent that this equation is both dimensionally and thermodynamically balanced.

When multiplied by the intensive property w, each of the terms in brackets has units of joules. The first term in brackets, $1 \, \mu m^2$ is extensive as it represents a constant area. The second term becomes extensive through the application of rule 3, by multiplying R and L (two homogeneous functions of degree ½), resulting in area, which is a function with $k = 1$ for this system. The third term becomes extensive by squaring R (here a homogeneous function of degree ½) resulting, once again through rule 3, in area, a function with $k = 1$. The fourth term gains its extensive character by invoking rule 3 once again and multiplying R and L (two homogeneous functions of degree ½), resulting in an area, which is a function with $k = 1$ for this system. Finally, the fifth term includes an extensive property, namely, the bending modulus, κ. However, it is being multiplied by the quotient of R and L which according to rule 2 is intensive. As such, according to rule 3, the fifth term is extensive. Consequently, each of the five terms in this expression is extensive, as they must be, since free energy, ΔG, in this case must be extensive.

IV. ENTROPY AND TEMPERATURE

Within the context of classical thermodynamics, thermodynamic entropy, S, is considered to be an extensive property which is a homogeneous function of internal energy, U, volume, V, and number of particles, N, such that $S(\lambda U, \lambda V, \lambda N) = \lambda^k S(U, V, N)$ and $k = 1$ [9]. Entropy is maximized in thermal equilibrium and is always additive [17].

However, if a statistical mechanic viewpoint is adopted, entropy is not always extensive. For instance, it is well-known that Boltzmann's classic expression ($S = k_B \ln W$, where W is the number of equiprobable microstates) is not extensive when the number of particles becomes very small ($N < 1000$). This was recognized by Boltzmann himself [20]. In fact, it is only through the use of the Stirling approximation that Boltzmann statistical entropy becomes extensive over a range of N values which is neither too small nor too large [21].

Some have argued that statistical entropy described by Boltzmann is only additive in the thermodynamic limit despite recognition that "*The extensive nature of thermodynamic entropy was already well established in the early part of the 19th century*" [22]. Consequently, statistical models can lead to findings which are contrary to established knowledge relative to thermodynamic entropy. Statistical results can be diametrically opposed [21, 22].

In very small systems, surface area and interfaces can no longer be neglected relative to the sample bulk [19]. These problems have long been recognized [23, 24]. Using computational approaches, it has been argued that temperature is no longer intensive in such systems [25]. Yet, in these cases, the object under review should no longer be considered a thermodynamic system. Small systems can get trapped in metastable states and unable to reach equilibrium. Therefore, their entropy cannot be properly defined, given that the measurement of entropy depends on equilibrium, the determination of which requires that temperature be intensive. This highlights the

point that systems must not be too small; otherwise they can no longer be viewed as thermodynamic systems.

V. CONCLUSIONS

Nearly 60 years have now past since Landsberg first emphasized the importance of intensive and extensive properties in thermodynamics. The Fourth Law which he formulated relative to their existence has been largely ignored by the physics community. Given the confusion which still exists concerning correct identification of properties as intensive, extensive, or neither, it is easy to understand why this has been the case.

Some insist that the radius of a sphere remains an extensive property. This becomes important in treating the thermodynamics of a star, for instance. However, the radius of a sphere is a homogeneous function of degree 1/3, as the volume of a star is a thermodynamic property of degree 1. It is clear that variables which are neither intensive nor extensive, like radius, do exist and they must be properly treated in balancing thermodynamic equations. The widespread failure of scientists to recognize these facts has led to numerous violations of thermodynamics [16, 26]. The radius of a sphere has a thermodynamic meaning because it determines the volume of a sphere. Since volume is a thermodynamic property homogeneous of degree 1, the spherical radius is a homogeneous function of degree 1/3 by virtue of the equality $V=4\pi R^3/3$. Since it is usual to classify extensive variables as homogenous functions of degree 1 and intensive variables as homogeneous functions of degree 0, then variables that are neither extensive nor intensive must also be related to their degree in order to ascertain thermodynamic balance.

Often, this has not been done in the literature. However, physics has paid a tremendous price. Failing to properly insist that temperature is always intensive, expressions have been advanced which are in direct conflict with the laws of thermodynamics [16, 26]. The solution for some has been to ignore the nature of thermodynamic properties altogether, in hope of evading the need for thermodynamic balance. Yet the Fourth Law and thermodynamic balance provides the sole means of verifying the physical validity of a given expression in thermodynamics. If these constraints are ignored, then physics loses its most important guides and walks incoherently in the field which is thermodynamics.

REFERENCES

[1] P. T. Landsberg, Monographs in Statistical Physics and Thermodynamics, Volume 2: Thermodynamics, With Quantum Statistical Illustrations, (Interscience Publishers, Inc., New York, 1961), p. 127-142.
[2] J. Dunning-Davies, 2007, arXiv:0706.4020v1 [physics.gen-ph].
[3] S. G. Canagaratna, J. Chem. Educ., Vol. 69, No. 12, 957-963 (1992).
[4] M. W. Zemansky, R. H. Dittman, Heat and Thermodynamics, (McGraw-Hill Book Company, 1981).
[5] Y. A. Cengel and M. Boles, Thermodynamics: An Engineering Approach, 5th Edition, (McGraw-Hill Book Company, 2005).
[6] F. W. Sears, An Introduction to Thermodynamics, The Kinetic Theory of Gases, and Statistical Mechanics, (Addison-Wesley Publishing Company, Inc., 1955).
[7] C. McMullen, A Guide to Thermal Physics from the Fundamentals thru Callen-Level Equilibrium Thermodynamics, (CreateSpace, ISBN: 1453772804, 2010).
[8] B. V. Karlekar, Thermodynamics for Engineers, (Prentice-Hall, Inc., New Jersey, 1983).

[9] H.B. Callen, Thermodynamics: An Introduction to the Physical Theories of Equilibrium Thermostatics and Irreversible Thermodynamics, (John Wiley & Sons, New York, N.Y., 1960).

[10] O. Redlich, Thermodynamics: Fundamentals, Applications, (Elsevier Scientific Publishing Company, Amsterdam, 1976).

[11] P.T. Landsberg, Nature, Vol. 238, July 28, 229-231 (1972).

[12] R.C. Tolman, Phys. Rev., Vol. IX, No. 3, 237-253 (1917).

[13] O. Redlich, J. Chem. Educ., Vol. 47, No. 2, 154-5 (1970).

[14] S.H. Mannaerts, Eur. J. Phys., Vol. 35, 035017 (2014).

[15] E.R. Cohen, et al. (Editors), Quantities, Units and Symbols in Physical Chemistry, IUPAC Green Book, Third Edition, Second Printing, IUPAC & RSC Publishing, Cambridge, p. 6 (2008).

[16] P.-M., Robitaille, S. J. Crothers, Physics Essays, Vol. 32, No. 1, (2019).

[17] M. Planck, The Theory of Heat Radiation, (P. Blakiston's Son & Co., Philadelphia, PA, 1914).

[18] N. Buch-Manson, S. Bonde, J. Bolinsson, T. Berthing, J. Nygard, and K.L. Martinez, Adv. Funct. Mater, Vol. 25, 3246-3255 (2015).

[19]R. H. Swendsen, Am. J. Phys., Vol. 79, No. 4, 342 (2011).

[20] K. Sharp and F. Matschinsky, Entropy, Vol. 17, 1971-2009 (2015).

[21] R. Riek and A.Sobol, J. Phys. Chem. Biophys. , Vol. 6, No. 2, 1000207 (2016).

[22] T. Salagaram and N. Chetty, J. Phys.: Conf. Ser., Vol. 454, 012074 (2013).

[23] T. L. Hill, J. Chem. Phys., Vol. 36, 3182 (1962).

[24] P. T. Landsberg, Thermodynamics and Statistical Mechanics, (Oxford, 1978).

[25] P. Mohazzabi and G. Ali Mansoori, J. Comp. Theoret. Nanosci., Vol. 2, No. 1, 138-147 (2005).

[26] P.M. Robitaille, Progr. Physics, Vol. 14, No. 3, 179-181 (2018).