

Clausius' *disgregation* and other disappeared thermodynamic quantities: conceptual relics or meaningful epistemic junctions?

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Abstract: The present paper is based on the analysis of some foundational works by Clausius (namely the Sixth and Ninth Memoires) and analyses the stepwise process that led Clausius to translate the qualitative statement of the Second Law of thermodynamics into mathematical expressions. The epistemic role of the thermodynamic quantities that were part of Clausius' formal system is discussed. In particular, we analyse the meaning of *disgregation* and other pre-modern quantities that stem from Clausius' microscopic model of matter, as essential precursor of entropy.

Keywords: Disgregation, Entropy, Second Law of Thermodynamics.

1. Historical hints

Clausius is legitimately considered the father of modern thermodynamics, whose date of birth may be identified with 1850 (Uffink 2001), the year of publication of Clausius' first paper on the mechanical theory of heat (Clausius 1850). A correct comprehension of Clausius' work needs a short mention of the historical landscape of his time. Clausius' work started where Carnot's work finished: he reaffirmed the validity of Carnot's theorem, rejecting at the same time the old theory of *calorique*. Carnot (1796-1832) lived at the time of the industrial revolution and his investigation was pushed by engineering concerns, as a crucial problem for the time was the improvement of the efficiency of steam engines. James Watt (1736-1819) managed to get a 5-7% yield (Müller 2007) and, in the 1820s, the improvement had gone as far as 18%: the aim of Carnot's investigation was to establish how far such improvement could possibly go. The problem was crucially relevant from the economical viewpoint, as witnessed by Carnot's own words:

To take away today from England her steam engines would be to take away at the same time her coal and iron. It would be to dry up all her sources of wealth, to ruin all on which her prosperity depends, in short, to annihilate that colossal power (Carnot 1824, p. 40).

Carnot died in 1832, when he was only 36-years-old. Müller underlines that “had he lived longer, it seems likely that he might have anticipated Clausius’ work by nearly 30 years” (Müller 2007, p. 55).

At the end of 1840s, Clausius, Thomson and other authors took over from Carnot’s work and started a debate that marked the birth of modern thermodynamics. Specifically, their discussion was focused on Carnot’s most relevant result, represented by his theorem that states:

The motive power of heat is independent of the agents employed to realize it; its quantity is fixed solely by the temperature of the bodies between which is effected, finally, the transfer of the calorique (Carnot 1824, p.68).

2. A stepwise process

In 1850, Clausius published the first formulation of what would later be known as the Second Law of Thermodynamics, in the form of a qualitative statement: “Heat cannot by itself flow from a colder body to a warmer one” (Clausius 1872, p. 136). Since then, the aim of Clausius’ work was to build up a formal system that could enable the translation of this qualitative statement into a mathematical language.

The process that led Clausius to the mathematical formalization of the Second Law was gradual and occurred through the logical extension of Clausius’ treatment from cyclic to non-cyclic processes. The analysis of Clausius’ original works (Clausius 1867, 1872) discloses that such an extension relied on the elaboration of a proto-microscopic model of matter. In fact, the treatment of cyclic processes was grounded on the concepts of *uncompensierte Verwandlung* (i.e. uncompensated transformation) and *Aequivalenzwerth* that were macroscopic quantities, still related to a macroscopic view of the thermodynamic system. The *Aequivalenzwerth*, or equivalence value, corresponds to the quantity Q/T , where Q is the amount of heat transmitted at a temperature T . It is related to the uncompensated transformation that, according to Clausius’ own words, corresponds to:

the equality $N = \int \frac{dQ}{T}$ where dQ is the heat element that is exchanged between the transforming system and the heat reservoir. And T consequently represents the absolute temperature. About this quantity, I have demonstrated that it can only be positive, or at least null at the boundary condition represented by a reversible cyclic process (Clausius 1872).

3. Clausius' microscopic model of matter

In his writings, Clausius reports that, since the elaboration of his first paper on the mechanical theory of heat, he had been thinking of a microscopic description of matter, where heat is connected to the motion of “constituent particles”:

We shall forbear entering at present on the nature of the motion which may be supposed to exist within a body, and shall assume generally that a motion of the particles does exist, and that heat is the measure of their vis¹ (Clausius 1967, p.18).

Clausius' microscopic conception of a thermodynamic system leads him to postulate the existence of quantities that he calls internal (dI) and external work (dW), quantity of heat exchanged with external bodies (dQ), and heat actually contained in the body (dH). Such distinction stems from considering that the constituent particles of the systems display two distinct modes of interaction:

The forces which here enter into consideration may be divided into two classes: those which the atoms of a body exert upon each other, and which depend, of course, upon the nature of the body, and those which arise from the foreign influences to which the body may be exposed. According to these two classes of forces, which have to be overcome (of which the latter are subjected to essentially different laws), I have divided the work done by heat into interior and exterior work (Clausius 1867, p.112).

An extensive explanation of the meaning of these quantities may be found in appendix A of Clausius' Sixth Memoir (Clausius 1867, pp. 250–256). Table 1 summarizes Clausius' description of the energetic of a thermodynamic system.

	INTERIOR QUANTITY		EXTERIOR QUANTITY		TOTAL QUANTITY	
WORK	<i>Interior work</i>	dI	<i>Exterior work</i>	dW	<i>Total work, i.e. the sum of interior and exterior work, performed by the heat in the change</i>	$dL = dI + dW$
HEAT	<i>Heat actually contained in the body</i>	dH	<i>Heat exchanged with the external environment</i>	dQ		
	ENERGY OF THE SYSTEM	$dU = dI + dH$				
A is “the thermal equivalent of a unit of work” (Clausius 1867, pp. 252-253)						

Table 1. Fundamental quantities of Clausius' formal system

A further enrichment of the formal system was boosted by the investigation of non-cyclic processes, whose treatment was based on the heat actually contained in the body

¹ That is kinetic energy, in the 19th century language.

(H) and the disgregation (Z). The meaning of the latter quantity is explained by Clausius in the following terms:

By disgregation is represented [...] the degree of dispersion of the body. Thus, for example, the disgregation of a body is greater in the liquid state than in the solid, and greater in the aeriform than in the liquid state. Further, if part of a given quantity of matter is solid and the rest liquid, the disgregation is greater the greater the proportion of the whole mass that is liquid; and similarly, if one part is liquid and the remainder aeriform, the disgregation is greater the larger the aeriform portion. The disgregation of a body is fully determined when the arrangement of its constituent particles is given; but, on the other hand, we cannot say conversely that the arrangement of the constituent particles is determined when the magnitude of the disgregation is known. It might, for example, happen that the disgregation of a given quantity of matter should be the same when one part was solid and one part aeriform, as when the whole mass is liquid (Clausius 1867, p. 226).

Disgregation (dZ) shares with *internal heat* (dI), and with the *heat actually contained in the body* (dI) and the *total work* (dL), the feature of being neither a macroscopic physical quantity nor an experimentally accessible one. This aspect would turn out to be crucial in determining the subsequent disappearance of all these quantities. Conversely, the quantities *external work* (dW) and *heat exchanged with the external environment* (dQ) have a precise macroscopic physical meaning (close to the concepts of work and heat of modern thermodynamics) and lasted over time, finding their place in modern thermodynamics treatments. We will briefly discuss this issue by analyzing the role and fate of disgregation within Clausius' efforts to attain a mathematical formulation of the Second Law of thermodynamics.

In his treatment of non-cyclic reversible processes, Clausius states that – at a given temperature – disgregation is “proportional to the work that the heat can thereby perform” and he points out that “the corresponding work must be proportional to the absolute temperature”² (Clausius 1867, p. 227). In formal terms this is expressed as: $dL = K T dZ$ where K designates a constant, dependent on the measure unit of Z , that can be chosen so that $K = 1/A$, being A the thermal equivalent of a unit of work.

For non-cyclic irreversible transformations, the relation between work, temperature and disgregation takes the shape of an inequality $dL \leq K T dZ$. Clausius argues as follows:

In case this [reversible condition] need not be fulfilled, the change of disgregation may be greater, provided it is positive, than the value calculated from the [total work L]; and if negative, it may be, when taken absolutely, smaller than that value, but in this case also it would algebraically have to be stated as greater (Clausius 1867, p. 245).

This expression can be introduced into Clausius' expression $dQ + dH + AdL = 0$ that represents a balance of *interior* and *exterior* energetic quantities. This step leads to:

² Clausius here refers to the total work dL .

$$\frac{dQ + dH}{T} + dZ \geq 0$$

that is, in Clausius' own words, “the extension of the second fundamental theorem” to not-cyclic changes, and dates 1862. This achievement was the starting point of a reflection that, three years later, would lead Clausius to introduce the most challenging of thermodynamics quantities: *entropy*. The story is told by Clausius himself, in a paper published much later, in 1872:

I wanted to obtain a quantity that was valid for any transformation of a system and whose value could change only in one sense. For this scope, in addition to both the already existing statements about transformation (i.e., the one concerning the transformation of work into heat and vice versa, and the one about the transfer of heat from a warmer system to a cooler and vice versa), I added a third one that regards the state change of a system and was formulated by means of a quantity Z , that I named the Disgregation of the system. With the aid of this quantity and of that indicated with H , the heat actually available in the system, instead of the above relation I could obtain the following more general instance:

$$\int \frac{dQ + dH}{T} + \int dZ \geq 0$$

The sum:

$$\int \frac{dH}{T} + \int dZ$$

is that to which I have given the name of Entropy of a system (Clausius 1872, pp. 145-146).

Interestingly, entropy S was not introduced for conceptual reasons: in fact, both the logical and formal architecture of Clausius' thermodynamics hold up even without this further step. Entropy entered the thermodynamic landscape face to a practical need: the fundamental equations of the mechanical theory of heat had to find an expression “more convenient for use”. The presence of quantities, such as Z and H , devoid of macroscopic physical meaning and thus not accessible experimentally, made the fundamental equations of the mechanical theory of heat unsuitable for practical applications (Clausius 1867, p. 327). Indeed, substituting the entropy definition into Clausius' inequality for non-cyclic changes, leads to:

$$\frac{dQ}{T} + dS \geq 0$$

that can be rearranged in the more familiar: $dS \geq \frac{dQ}{T}$ where the equality holds only in case of reversibility. In his Ninth Memoir, Clausius provides a “way for determining S ” in the case of reversible changes. In fact, the integration of the previous equation leads to:

$$S = S_0 + \int \frac{dQ}{T}$$

that is an exploitable expression of entropy. Interestingly, this expression is applicable to the exclusive case of reversible changes; hence Clausius left the problem of the operational treatment of irreversible non-cyclic processes totally open. Much later, this would become the main challenge of non-equilibrium thermodynamics.

4. Conclusions

In conclusion, a few remarks on the problem of the “disappeared” quantities. Table 2 summarizes the quantities employed by Clausius in the frame of his formal system and compares them to the quantities employed by current thermodynamics.

The current thermodynamic apparatus is clearly derived from the foundations built in by Clausius; nevertheless, it has got rid of a number of conceptual tools that were inherent to Clausius’ treatment. How could this have happened?

Z , H and I stand as pre-modern quantities and find their justification within the frame of Clausius’ microscopic model. Their epistemic value has been remarked by several authors (e.g. Gibbs, Horstmann) as these were the scaffolding of Clausius’ thermodynamic architecture (Gibbs 1906, vol. II p. 261; Kragh, Weininger 1996). Interestingly, none of them may be associated with a macroscopic physical meaning nor is measurable. This aspect turned out to be crucial in determining either their disappearance or their replacement, as was the case of entropy which, actually, replaced disgregation, being a more accessible quantity as Z (Pellegrino 2015). Notwithstanding, disgregation may claim a cognitive value as it helps in understanding the meaning of entropy.

In conclusion, we like to think of these pre-modern quantities as the construction lines traced to build up Clausius’ logical and formal thermodynamics apparatus, that finally vanished from the formal description without compromising its conceptual self-consistency.

Clausius’ Quantities		Current Quantities	
Interior work	dI	disappeared	
EXTERIOR WORK	dW	WORK	dW
Heat actually contained in the body	dH	disappeared	
Total Work	dL	disappeared	
HEAT ABSORBED BY THE SYSTEM	dQ	HEAT	dQ
Disgregation	dZ	disappeared	
ENERGY OF THE SYSTEM	dU	INTERNAL ENERGY	$dU = dQ - dW$
ENTROPY	dS	ENTROPY	$dS = dQ/T$

Table 2. An overview of Clausius’ thermodynamics quantities as compared to the current ones

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