Representational Frameworks and Conceptual Change in the Science of Heat: The Contributions of James Thomson to the Diagrammatic Approach of Critical Points*

Estructuras de representación y cambio conceptual en la ciencia del calor: contribuciones de James Thomson al enfoque diagramático de los puntos críticos

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Abstract

Scientific concepts are not static entities; rather, they evolve under the influence of forces such as experimental discoveries, ontological debates, and the heuristic power of representational structures. This article explores the role of representation in thermodynamics, especially in James Thomson's analysis of the critical points discovered by Thomas Andrews. We argue that, although Thomson took advantage of the heuristic resources of diagrams to introduce crucial notions such as instability, his analysis of critical points does not converge on an operational definition, as is the case in Gibbs' approach. Following this path, it is possible to trace the evolution of the concept of the state of substances in the science of heat. Finally, we situate Gibbs' work within a methodological tradition that values the representational elements of science, illustrating how representational choices fundamentally shape scientific concepts and problem-solving algorithms.

Keywords: critical points - diagrams - representation - heuristics - conceptual changes

Resumen

Los conceptos científicos no son entidades estáticas; más bien, evolucionan bajo la influencia de fuerzas como los descubrimientos experimentales, los debates ontológicos y el poder heurístico de las estructuras representacionales. Este artículo explora el papel de la representación en la termodinámica, especialmente en el análisis de James Thomson de los puntos críticos descubiertos por Thomas Andrews. Argumentamos que, si bien Thomson aprovechó los recursos heurísticos de los diagramas para introducir nociones cruciales como la inestabilidad, su análisis de los puntos críticos no converge en una definición operativa, como ocurre con el enfoque de Gibbs. Siguiendo este camino, es posible rastrear la evolución del concepto de estado de las sustancias en la ciencia del calor. Finalmente, situamos el trabajo de Gibbs dentro de una tradición metodológica que valora los elementos representacionales de la ciencia, ilustrando cómo las elecciones representacionales configuran fundamentalmente los conceptos científicos y los algoritmos de resolución de problemas.

Palabras clave: puntos críticos - diagramas - representación - heurística - cambios conceptuales

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1. Introduction

The development of thermodynamics has always been associated with the evolution of its forms of representation. In this study, we examine the role of these representations in the elaboration of procedures—or algorithms—for solving problems, especially those aimed at characterizing the thermodynamic properties of substances. We show that the resources offered by each form of representation are intimately linked to the concepts of the theory: concepts such as "state of substance" express their content through these resources. Thus, the very conceptual structure of thermodynamics is, to some extent, conditioned by the limitations and possibilities of the available representations. In this article, we investigate how this dependence between representation and conceptual structure is manifested in the historical emergence of critical phenomena, focusing on the works of Andrews, James Thomson, Van der Waals, and Gibbs. Our aim is to show how different representational strategies—mechanical, diagrammatic, and geometric—shape the ways in which equilibrium states, phase transitions, and critical points are conceptualized.

More specifically, we argue that the appearance of critical phenomena in the nineteenth century forced a co-evolution between the concept of state and the representational spaces of thermodynamics. Mechanical models, diagrams, and geometric constructions did not simply illustrate a pre-given theoretical language; they contributed actively to the variation, selection, and stabilization of distinct notions of thermodynamic state. From this perspective, the mathematical characterization of critical points, from James Thomson to Gibbs, depends crucially on an evolving representational infrastructure.

Representation is a fundamental component in the complexity of scientific concepts. Following Toulmin, these concepts can be understood in terms of three aspects: (i) language, consisting of the vocabulary with which a concept's contents are described; (ii) representational techniques, which provide the structural means by which concepts are articulated, explored, and transformed; and (iii) procedures of application in science, expressed in the practical criteria by which scientists determine when, where, and how a concept or representation is legitimately used (Toulmin 1977, pp. 162-164). A scientific concept, therefore, is not a monolithic block. In the context of thermodynamics, this article examines the first two aspects—which are largely symbolic—with emphasis on their relationship and on their role in enabling the theorization of empirical knowledge.[1] In more detail, the representation techniques, hereafter referred to simply as *representations*, are outlined as follows:

> The representation techniques include all those varied procedures by which scientists demonstrate—i.e. exhibit, rather than prove deductively—the general relations discoverable among natural objects, events and phenomena: so comprising not only the use of mathematical formalisms, but also the drawing of graphs and diagrams, the establishment of taxonomic trees and classifications, the devising of computer programs, etc. (Toulmin 1977, pp. 161-162).

While the term *devising of computer programs* is traditionally understood within the context of computer science, the formulation of algorithms for problem-solving within a coherent conceptual framework (Simon 1977, p. 224) can be viewed from that same perspective. This activity results in the construction of procedures that employ the heuristic tools provided by the representation. The richer the heuristics of a representation's conceptual framework, the more and better problem-solving algorithms can be developed within that environment.[2]

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[1] The functional separation between language and representation is realized when a representation is capable of generating algorithms (or programs) independently of the conceptual foundations of the scientific theory. To account for this distinction, it is necessary to expand aspect (i) to encompass both the language of the theory and the language of the representation. There are cases, however, in which these languages combine symbiotically in the resolution of thermodynamic problems. The subsequent sections provide examples to illustrate this point.

[2] In cases where the language of representation can be distinguished from the theoretical language, the representation can be examined in its essential form, such as mechanism, geometry, or algebra.

2. Mechanical and diagrammatic representations of thermodynamics

With Sadi Carnot (1796-1832), the theory of heat acquired the status of the theory of the motive power of heat or thermodynamics. His primary objective was not merely to advance the theoretical understanding of heat but to investigate the mechanical power generated by thermal machines. Using the analogy with the water wheel that generates work from a waterfall—an ideal version of which had been proposed by his father, Lazare (Carnot 1803, p. 249)—he used the properties of heat to design a heat engine aimed at maximizing the mechanical work associated with the caloric transfer.[3] It was through this analogy that the notion of reversibility was incorporated into his theory. The designed ideal heat engine, with its fundamental components—such as the boiler, cylinder, piston, and condenser—represents the cornerstone of Carnot's theory.

By integrating the engineering of heat engines, the science of mechanical machines, and the physics of gases, Carnot established a new and original conceptual framework. Within this framework, his reversible heat engine acts as an algorithm capable of identifying the most efficient heat engine, regardless of the working fluid. The foundational role of mechanical machine science in this approach justifies referring to Carnot's representation as *mechanical*: his theory is expressed through a heat engine modeled after a mechanical machine (Lucena, Laranjeiras & Chiappin 2023). The language of representation is semantically identified with the language of mechanical machines and, therefore, is not reducible to pure syntax.

However, this framework lacks the mathematical tools necessary to formalize certain aspects of the theory. Building on this, Clapeyron (1799-1864) sought to provide an algebraic formulation of the ideal heat machine. He recognized the necessity of expressing Carnot's theory mathematically and identified the C function (Carnot function) related to the efficiency of heat machines. To this end, he used an instrument developed by James Watt—the pressure-volume ($p\times V$) diagram,[4] where the area enclosed by the cycle is numerically equivalent to the mechanical work produced—to represent the cyclic sequence of thermodynamic processes.

In a general diagram with x and y coordinates, every closed curve encloses an area that has a purely geometric meaning.[5] However, in physics, the meaning of this enclosed area depends on the diagram's coordinate system. This is the case in a $p\times V$ diagram, where the enclosed area corresponds to mechanical work. Thus, one of the main heuristic resources of diagrammatic representation is an emergent property of the language of representation and the concepts of the theory, according to which the mechanical work ($W = \int pdV$) is expressed by the integral of pressure over the volume change from V_i to V_f.

The procedure that associates area and mechanical work arises from the convergence of two distinct languages: the geometric language of representation and the physical language of theory. While diagrams are rooted in a consistent mathematical framework, the connection between area and driving force in the form $A=W$ (area equals mechanical work) is not solely derived from the language of representation. It is the interplay between geometric representation and physical semantics that enables the diagrammatic formulation of $A=W$. Therefore, from the intersection between the language of representation and the language of theory—particularly in the $p\times V$ diagram—emerges one of the most powerful conceptual tools of an entire period in the history of thermodynamics.

The diagrammatic representation of the reversible Carnot cycle enabled Clapeyron to derive three key results: a method to experimentally obtain numerical values for the Carnot function, an early form

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3 Carnot was a follower of the caloric theory (Newburgh 2009).

4 Diagrams correspond to Cartesian planes whose coordinates can be any relevant thermodynamic variable. However, the relationship between area and mechanical work is specific to the $p\times V$ diagram.

5 It is not entirely accurate to claim that geometry corresponds to pure syntax, as its axioms, theorems, and calculations possess inherent semantics and are interpreted in terms of real-world parameters such as lengths, areas, volumes, points, lines, planes, surfaces, angles, curves, coordinates, and functions. However, since physical theories often attribute semantic content to geometric and algebraic structures, we adopt this convention to avoid redundant phrasing and maintain conciseness.

of the Clapeyron-Clausius equation for state changes, and a qualitative understanding of the critical phenomena identified by Cagniard de la Tour.

Following Clapeyron, several prominent thinkers, including William Thomson (1824-1907), Clausius (1822-1888), Rankine (1820-1872), and Maxwell (1831-1879), employed diagrams and the Carnot cycle for a variety of purposes. Among the key outcomes were the integration of the law of conservation of energy, the mathematical formulation of what is now recognized as the second law of thermodynamics (the principle of entropy), and the construction of Maxwell's relations (Lucena & Chiappin 2017).

At the same time, this period witnessed a profound transformation in the field of thermodynamics. Beyond the ontological debates regarding the nature of heat (Cajori 1922, Roller 1957), there was a notable proliferation of diagrams used to represent thermodynamic processes, empirical data, and the properties of substances. This representation facilitated the implementation of algorithms for problem-solving by the calculation of the enclosed area of reversible cycles and the application of Carnot's principle (the efficiency of an ideal heat engine depends solely on the temperatures of the hot and cold heat reservoirs). Given the significance of these two tools—diagrams and cycles—the theory of the motive power of heat of this era can aptly be characterized as diagrammatic thermodynamics or the thermodynamics of cycles.

3. The heuristic power of diagrammatic representation

The transition from mechanical to diagrammatic representation has expanded the phenomenological scope of heat science. Broadly speaking, the mechanical representation facilitates the articulation of heat engine components, demonstrating that no heat engine can produce a greater mechanical effect than a reversible heat engine. That said, this representation offers limited analytical resources beyond this fundamental insight. When information about the pressure, volume, and temperature of the cylinder containing the working substance becomes available, the representation naturally evolves into a diagrammatic form.

A particular form of representation often shapes and directs specific lines of research. Therefore, while Carnot concentrated on the study of reversible machines, thinkers such as Clapeyron, through mathematizing thermodynamic theory via diagrammatic representation, began to explore the properties of substances. The main theoretical tool in this development was the equation derived by Clausius from Clapeyron's equation. This achievement was made possible by incorporating the hypothesis of the convertibility between heat and mechanical work (as proposed by Joule) along with the explicit form of the Carnot function.

Clausius assigned a central role to William and James Thomson (1822-1892) in laying the groundwork for the theorization of phenomena related to changes in the state of matter (Clausius 1867, p. 80). James Thomson applied Carnot's theory to analyze the transition from ice to water. He concluded that unless one accepts the idea of unlimited production of motive force, the characteristic melting temperature of ice must change with pressure. As indicated by the title of his 1849 paper, *Theoretical considerations on the effect of pressure in lowering the freezing point of water*, this work was largely theoretical and strongly based on Carnot's arguments (Thomson 1912, pp. 196-203). The experimental confirmation of these findings was reported by William a year later in his paper *The effect of pressure in lowering the freezing point of water experimentally Demonstrated* (Thomson 1882, pp. 165-9).

Despite the theoretical predictions and experimental confirmations conducted by the Thomson brothers, there was still no quantitative theory to explain the phenomenon. Clausius recognized that his mechanical theory of heat could effectively address this gap.

Based on Carnot's principle, the problem was approached in two steps. The first step involved determining the work produced, and the second focused on deriving the analytical form of the Carnot function. The initial stage was addressed through the infinitesimal representation of a Carnot cycle on a $p \times V$ diagram (Figure 1), where the enclosed area represents the work produced. In this diagram, processes *ab* and *cd* occur at constant pressure and temperature, as they correspond to phase transitions.

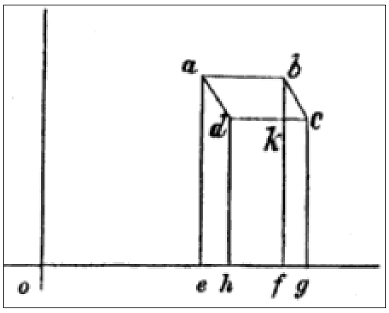

Figure 1: Carnot infinitesimal cycle in p×V diagram (Clausius 1867, p. 31).

In the current context, the process *ab* corresponds to the solidification of ice, where *oe* represents the volume of a certain portion of water (V_{water}) at 0ºC, and *og* represents the volume of the same portion in the solid state (V_{ice}) after releasing an amount of heat $m\lambda$ to the environment. This heat is considered negative. Identifying *bk* with the pressure difference dp, the area of the cycle is given by $(V_{ice} - V_{water})dp$. Simultaneously, through algebraic manipulations and considerations regarding the properties of ideal gases, Clausius demonstrated that the Carnot function for an infinitesimal cycle is expressed as $dT/A(a+T)$. Using this, Carnot's principle was reformulated to derive the Clapeyron-Clausius equation, which describes the phase transition between ice and water (Clausius 1867, pp. 30-31, 45-50, 81):

$$(1) \quad \frac{dT}{dp} = \frac{A(a+T)(V_{\text{ice}} - V_{\text{water}})}{m\lambda}$$

For a unit of mass, by substituting the value of A provided by Joule, along with the temperatures $a = 273$ and $T = 0$, as well as the experimental values of λ, V_{ice}, and V_{water}, the resulting calculation yielded $dT/dp = -0{,}00733$. This value closely approximated the result obtained by William Thomson, −0.0075 (Clausius, 1867, p. 81-2). This result indicates that the tangent line to the curve defining the transition region between solid and liquid at a temperature of 0ºC has a slope equal to the inverse of −0.00733. The restriction to the vicinity of the 0ºC point arises because the value of λ is not independent of temperature. From that point forward, the Clapeyron-Clausius equation would be used to construct the phase diagrams of various substances.

The strategy used to construct Equation (1) is remarkable. Rather than describing the phenomenon through a mechanical or algebraic model or explaining it via hypotheses about the nature of matter, it employs heuristically productive methods. At first glance, this may appear to be a simple analogy between the Carnot engine and the phase transition of matter. However, this perspective does not adequately account for either Carnot's theory or the role of diagrams. It overlooks the contribution of Carnot's theory, as the substance whose properties are being described serves as the working fluid of the ideal heat engine. Likewise, a purely mechanical representation of the heat engine is insufficient, since the $A=W$ algorithm—characteristic of diagrammatic representation—is essential.

4. The Critical Points

In this context of theoretical and technical advances, Cagniard de la Tour's discovery of the disappearance of the density barrier between the gaseous and liquid states of alcohol under certain conditions attracted renewed interest. This discovery occurred in 1822, during the experimental study of the acoustic behavior of fluids under high temperatures and pressures (Berche, Henkel & Kenna 2009). Cagniard de la Tour's results demonstrated that there is a critical limit to the expansion of a volatile liquid.

Michael Faraday successfully replicated the experimental findings of Cagniard de la Tour in the 1840s (Goudaroulis 1994), albeit in a primarily qualitative manner. Nearly three decades later, Thomas Andrews (1813-1885) provided a more rigorous empirical foundation for this phenomenon. In the introduction to his seminal work, *On the continuity of the gaseous and liquid states of matter*, Andrews highlights the experimental nature of his approach and acknowledges the significant contributions of Cagniard de la Tour, Faraday, and H. V. Regnault.

Although Thomas Andrews' landmark article was not published until the late 1860s, his investigations into the subject commenced in February 1861, influenced by James Thomson, who had served as a professor at Queen's College, Belfast, since 1857. In September of the same year, Andrews briefly presented his initial findings, focusing primarily on qualitative observations (Rowlinson 2003, pp. 143-144). It was not until 1869 that his renowned article was published. This work, characterized by its experimental rigor, detailed the apparatus used as well as the tables and diagrams derived from his research.

The substance utilized by Andrews was carbonic acid (carbon dioxide). However, the observed property is not unique to this compound. Any substance capable of existing in both gaseous and liquid states typically exhibits the same property. Andrews succinctly summarized the results of his findings as follows:

> On partially liquefying carbonic acid by pressure alone, and gradually raising at the same time the temperature to 88° Fahr., the surface of demarcation between the liquid and gas became fainter, lost curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited, when the pressure was suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering striae throughout the entire mass. At temperatures above 88° no apparent liquefaction of carbonic acid, separation into two distinct forms of matter, could be effected, even when a pressure 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results (Andrews 1869, pp. 575-576).

The data for carbonic acid were plotted (Figure 2) as continuous lines on a $p \times V$ diagram, with volume represented on the ordinate axis. These plots correspond to isothermal measurements at temperatures of 13.1°C, 21.5°C, 31.1°C, 32.5°C, 35.5°C, and 48.1°C (88°F = 31.1°C).

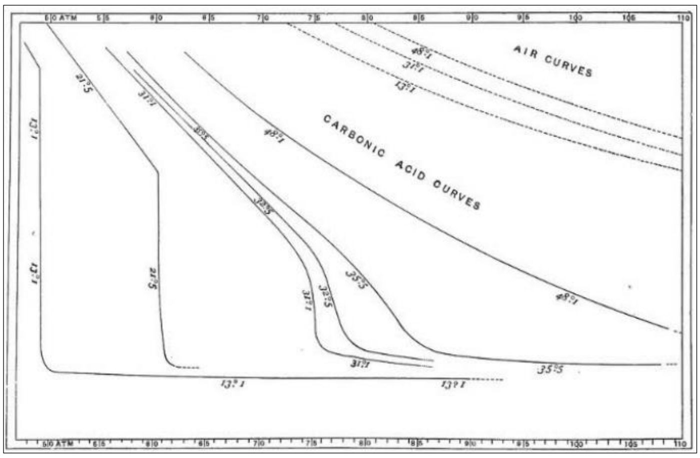

Figura 2: Andrews' diagram (Andrews 1869, p. 577).

An analysis of Figure 2 reveals that at a temperature of 13.1°C, carbonic acid exhibits a nearly constant volume even as the pressure increases significantly from 5 atm to over 10 atm. In contrast, at a pressure slightly below 5 atm, the substance undergoes a sudden change in volume, indicated by a vertical segment on the diagram. This vertical segment signifies a dramatic change in the density of carbonic acid, corresponding to the phase transition phenomenon. This transition, defined by a precise temperature and pressure pair, marks the change from the liquid to the gaseous state. The abrupt increase in volume along the vertical segment is due to the phase change of a portion of the carbonic acid from liquid to gas, resulting in a sharp rise in volume as heat is supplied to the system. The same behavior is observed at a temperature of 21.5°C, but at 31.1°C, the vertical segment becomes nearly imperceptible. Beyond this temperature, the curves no longer exhibit steps, indicating that the density of the substance varies continuously with pressure.

The coexistence of two distinct phases, characterized by different densities, is represented by a boundary that clearly separates each phase. According to Andrews' diagram, at approximately 31.1°C and 7.5 atm, this boundary disappears, signaling the complete transition of the substance from one density to another, with no intermediate coexistence of the two physical states. These values are referred to by Andrews as the critical temperature and pressure values, beyond which the density of carbonic acid changes continuously. From this, he concludes that:

> The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes (Andrews 1869, p. 587).

The view that the gaseous and liquid states represent distinct stages in a continuous series of transitions highlights the problem of abrupt changes below critical temperature and pressure values. To account for these abrupt changes, Andrews proposed that carbonic acid can exist in an unstable state by initiating a global change in its density. Under these conditions, small perturbations induce the substance to transition from the unstable condition to a stable state, where the change occurs abruptly and the two phases begin to coexist (Andrews 1869, pp. 587-588).

5. James Thomson and the characterization of Critical Points

From Cagniard de la Tour's phenomenological characterization to Thomas Andrews' establishment of a precise empirical basis, the concept of critical points has undergone significant evolution. Initially understood as the disappearance of the density difference barrier between the liquid and gaseous states, the critical point is now characterized in terms of specific thermodynamic variables (temperature, pressure, and volume). Nonetheless, from the perspective of mathematical physics, this empirical data is insufficient to fully describe the system's behavior near the singularity.

Addressing this shortcoming requires going beyond what is initially available and incorporating new insights that emerge during the search for a solution to this problem. In this process, diagrams play a crucial role: they reveal and integrate new information into the theoretical framework.

James Thomson developed the first explanations for the phenomenon and improved the necessary tools to integrate it into the established science of heat. Following his work on the effect of pressure on the solidification temperature of water, James maintained a strong interest in phase transition phenomena. His appointment as a professor of engineering at Queen's College Belfast fostered curiosity about these phenomena among some of his new colleagues, including Andrews. This shared curiosity naturally led to a collaborative relationship. Prior to Andrews' notable results, James offered his own interpretation of experiments by Faraday and Forbes in an 1859 paper. In this work, he revisited existing theories on ice near its liquefaction point and extended these interpretations to analogous phenomena:

> I think the general bearing of all the phenomena he has adduced is to show that the particles of a substance when existing all in one state only, and in continuous contact with one another, or in contact only under special circumstances with other substances, experience a difficulty of making a beginning of their change of state, whether from liquid to solid, or from liquid to gaseous, of probably also from solid to liquid. But I do not think anything has been adduced showing a like difficulty as to their undergoing a change of state, when the substance is present in the two states already, or when a beginning of the change has already been made. I think that when water and ice are present together, their freedom to change their state on the slightest addition of abstraction of heat, or the slightest change of pressure, is perfect (Thomson 1912, p. 228).

The concept of the perfect freedom of change stands in contrast to Faraday's assertion that the presence of ice compels the mixture to remain in the solid state. James Thomson clearly disagrees with this view, and in works published during the 1870s, he would cite this same passage again to assert that he was the first to advocate for this freedom. With the emergence of Andrews' initial findings—first presented as a brief note in the *Report of the British Association* in 1861 and later included in a chemistry textbook in 1863—he summarized the recent discovery in a personal, unpublished note dated June 1862:

> The experiments of Dr. Andrews show that there is a certain superior limit of temperature above which the fluid carbonic acid does not show any sudden transition from "liquid" to "gas", or rather does not arrive at any point of total heat beyond which it refuses to take more diffused through it, and sends all additions of heat only to parts of itself, leaving the remainder unchanged (Thomson 1912, p. 320-321).

The issue was framed as a dichotomy between the local and global distribution of heat: either the added heat diffuses uniformly throughout the substance, or it is localized in specific regions, leaving other parts unaffected. A global distribution of heat would result in a continuous increase in volume. In contrast, a localized distribution would introduce a discontinuity in this relationship.

A month later, still in personal notes yet, James Thomson transformed his intuition into a hypothesis based on the observation of liquids being heated above their boiling point. He proposed that the steps in the $p \times V$ diagram (Figure 2) could be smoothed into continuous *S*-shaped curves, suggesting a direction for empirical investigation. Some intervals within these curves would represent possible, but unstable, fluid states (Thomson 1912, pp. 322-324). These notes formed the basis for the papers he would develop after 1871, once he gained access to detailed quantitative data from his colleague Andrews. In 1869, James formulated the Andrews' data into a tangible model in a three-dimensional domain. The resulting curved surface illustrates the full range of possible carbonic acid states in the $T \times p \times V$ space (Thomson 1912, pp. 277, 282).

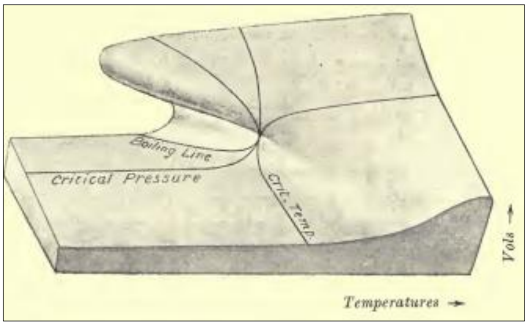

Figure 3: James solid model (Thomson 1912, p. 271).

After 1871, James Thomson published five articles on the subject. The ideas outlined in his earlier notes re-emerged, now bolstered by substantial experimental references. The first three articles were published almost simultaneously. In the first, titled *Considerations on the abrupt change at boiling or condensing in reference to the continuity of the fluid state of matter* (November 1871), James reintroduced Andrews' diagram, now incorporating his theory of continuity between the fluid states of matter, depicted by the dotted lines on the isotherms at 13,1°C and 21,5°C (Figure 4).

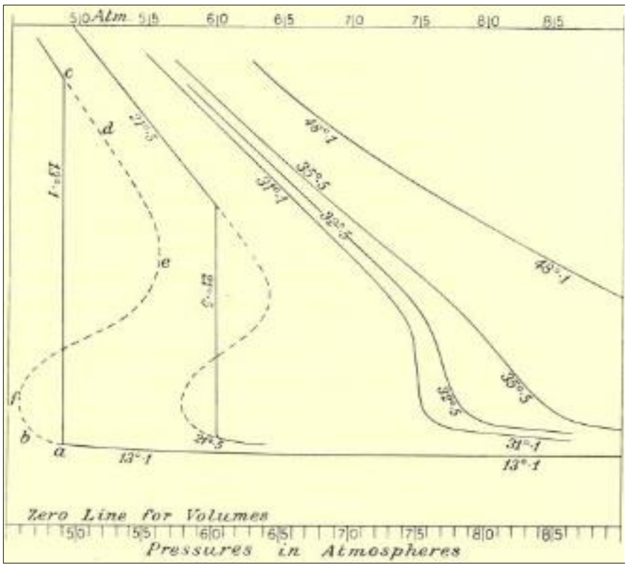

Figure 4: James' diagram (Thomson 1912, p. 281).

James Thomson acknowledges the immense difficulty of experimentally verifying the continuous range from *e* to *f*. Even if such verification were feasible, the resulting states would be inherently unstable. Crucially, however, this expedient allows us to explore the mathematical characteristics of the critical point. The first curve with an empirically accessible inflection point is that of 31.1 °C at a pressure of 7.5 atm.[6] For lower temperatures, the inflection point remains experimentally inaccessible. By inverting the coordinates in Figure 4, the condition $(d^2p/dV^2)_T = 0$ applies to the critical point insofar as it represents an inflection point. Above this temperature, an infinite series of isotherms still exhibits a change in concavity; this change disappears completely, and the isotherms assume a uniform upward concavity, only from a temperature of 48.1 °C onwards.

Prior to this, yet in unpublished notes, James Thomson intuitively sketched the isobaric curves in $V{\times}T$ (Figure 5). Nonetheless, the inflection point of the isotherms and isobars—$(d^2T/dV^2)_p = 0$ and $(d^2p/dV^2)_T = 0$—is not sufficient for determining the critical values of temperature and pressure. These equations generate a continuous series of temperature and pressure values that satisfy the inflection point condition; accordingly, additional conditions are necessary.

[6] While James Thomson himself introduces the concept of geometric inflection to describe critical points, he does not fully explore the mathematical implications that could be derived from it (Thomson 1912, p. 283).

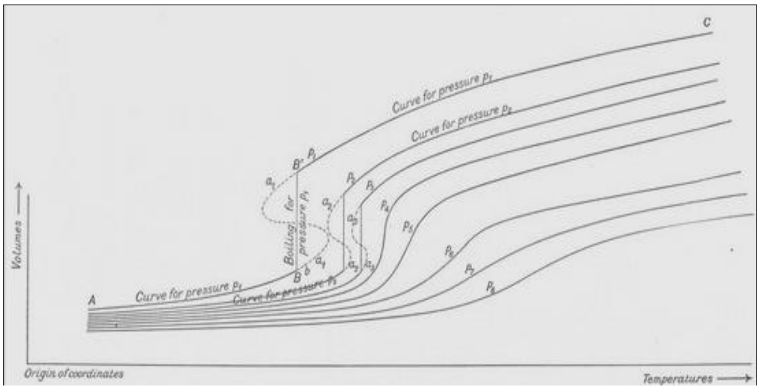

Figure 5: James' $V{\times}T$ diagram (Thomson 1912, p. 322).

In the context of diagrams, this condition is imposed by Maxwell, as a correction to James Thomson isotherms (Figure 4) in *On the Dynamical Evidence of the Molecular Constitution of Bodies* (Maxwell 2003, p. 425), which was published in March 1875, after the works of Van der Waals and Gibbs.

In the vertical segments of the isotherms shown in Figures 2 and 4, the gaseous and liquid phases of the substance coexist. The repositioning through the single-phase continuation (indicated by dotted lines) is highly accurate, ensuring that the areas between the single-phase continuation on either side of the two-phase line are equal. In a letter to G. Tait written a year earlier, Maxwell admitted that he had not previously recognized this fundamental property of single-phase isotherms and expressed regret for this oversight:

> In James Thomson's figure of the continuous isothermal show that the horizontal line representing mixed liquid and vapour cuts off equal areas above and below that curve. Do this by Carnots cycle. That I did not do it in my book shows my invincible stupidity (Maxwell 2002, pp. 155-156).

Within the area bounded by the line segments *aa'a''Cc''c'c*, as illustrated in Figure 6, the isotherms take on two forms: the horizontal dashed line, represented as *abc*, and the curves resembling the line *adec*, both part of the T_1 isotherm. In the first mode of extending the T_1 isotherm, the substance exists in both liquid and gaseous states within the region defined by *aa'Cc''c'c*. In the second mode, which cannot be achieved experimentally between points *d* and *e*, the substance would exist in only one state—either liquid or gas—at each point along the curve.

The points on the line *aa'Cc''c'c* represent states where the substance is on the verge of undergoing a phase change. At these points, any heat exchange will move the substance into or out of this region. Consequently, this line represents processes equivalent to adiabatic transformations. Therefore, following Maxwell's suggestion, a Carnot cycle can be formed between points *aa'c'c*. This cycle can be represented in its isothermal processes using both the dashed lines and curves similar to *adec*. Since the performance of the Carnot engine depends solely on the temperatures of the two isotherms, the mechanical work done remains the same whether we follow the two horizontal dashed isotherms or the equivalent continuous curves.

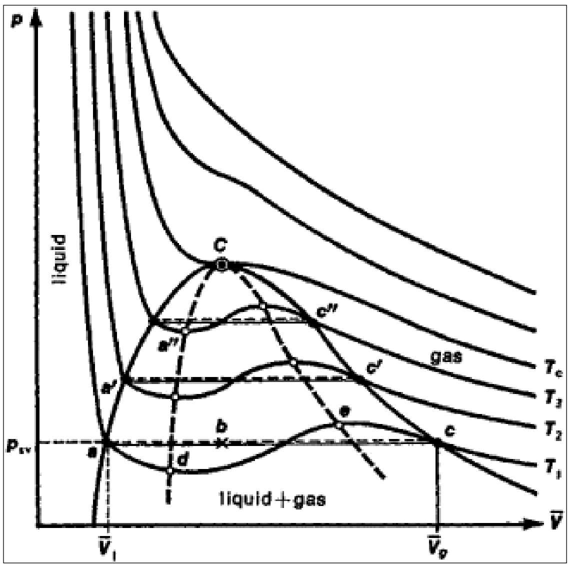

Figure 6: Maxwell's diagram (Maxwell 2002, p. 157).

Moreover, in a $p \times V$ diagram, the work done is equal to the area enclosed by the cycle. Hence, for each isothermal curve, the areas above and below the dashed line must be equal. As we approach the critical point C, this reasoning implies that the isotherm T_C not only inflects but also becomes horizontally inclined on C, meaning that the derivative $(dp/dV)_T$ is zero. The conjugate relationship $(dT/dV)_p = 0$ can be derived using James' method to establish isobaric curves in a $T \times V$ diagram.

When Andrews' empirical basis is expanded with the hypothesis of continuity of fluid states and Maxwell's argument, representing these results in $p \times V$ and $T \times V$ diagrams makes the mathematical characterization of critical points more transparent: $(dT/dV)_p = 0$, $(dp/dV)_T = 0$, $(d^2T/dV^2)_p = 0$ and $(d^2p/dV^2)_T = 0$. This point exhibits both an inflection and an infinite expansion coefficient, which is associated with the condition $(dV/dT)_p \rightarrow \infty$.

In isobaric lines where the pressure exceeds the critical pressure ($p_c = p_4$), only inflection points can be identified, and these do not correspond to states of infinite expansion. On the other hand, in isobaric lines with pressures below p_c, inflection points are also present; however, they represent states of unstable equilibrium. These points specifically appear along the dotted sections of the isobaric lines in Figure 5.

With regard to the mathematical formalization of critical points, the hypothesis of single-phase continuity of fluid states, adjusted by Maxwell's rule of equal areas, acts as a passive constraint that, imposed on Andrews' empirical foundation, prefigures the answer to the question of how to mathematically conceptualize this new phenomenon (Fleck 2010, pp. 133, 144).

Although the hypotheses and arguments added by James Thomson to Andrews' empirical framework increasingly prefigured the answer within the question, making it explicit was never their primary objective. Their focus was on understanding the phenomenon through the continuity of liquid and gaseous states rather than formulating an operational definition.

At an epistemological level, different motivations drive the activities of members of a scientific community. The pursuit of understanding (whether of events, processes, or phenomena) and the drive for application (of concepts, laws, or theories) mobilize distinct cognitive strategies. When researchers fail to recognize these distinctions, psychological obstacles may arise, preventing them from perceiving what, in a different teleological context, would already be prefigured within the question.

It is true that the objectives of 'understanding' and 'application' can be distinguished, but they cannot be entirely separated, as in many cases, one naturally leads to the other: understanding facilitates application, while the (need for) application often necessitates understanding. However, employing this distinction to analyze James Thomson's case allows us to revisit Toulmin's framework as a means of introducing order into the conceptual complexity inherent in scientific disciplines.

James Thomson's work, based on Thomas Andrews' results, contributed to a significant evolution in the concept of states of matter and, consequently, of critical points. Moreover, incorporating the set of equations $(dT/dV)_p = 0$, $(dp/dV)_T = 0$, $(d^2T/dV^2)_p = 0$ and $(d^2p/dV^2)_T = 0$ into the analysis would represent an even deeper understanding of these phenomena. This set of equations possesses an undeniable operational character—one that pertains to an aspect of the concept of the critical point that can only be fully realized within the context of application.

In the scientific domain, the application of knowledge is often associated with experimental validation or technological development. This is not the sense in which we claim that James Thomson did not seek to apply the concept of the critical point. It is not as though he aimed to conduct experiments similar to those of Andrews to establish an empirical basis for other substances or to develop techniques based on this property of matter. Rather, the application in question is theoretical, given the inherently operational nature of any set of differential equations. Proposing $(dT/dV)_p=0$ as a step in characterizing the nature of a substance's state implies that the function $T=T(p,V)$ must be explicitly known; otherwise, the set of equations remains practically ineffective. The task of deriving equations of state or identifying broader principles from which these equations could be derived was not one that James Thomson pursued.

In the second work of his 1871 series, James Thomson explores the properties of the $T{\times}p$ diagram, outlining the lines of physical state change for matter that converge at a single point. He called this the triple point, which serves as the origin for the three phase-change boundaries. One of these (the liquid-gaseous state line) terminates at the critical point (Thomson 1912, pp. 289-290). The third article in the series offers no major novelties.

In 1872, in an article entitled *On the relations between the gaseous, liquid, and solid states of matter* (1872), he again examines the relationship between pressure and condensation temperature. A noteworthy addition to his discussion is the characterization of states not merely as stable or unstable. Instead, he defines a state as corresponding to an equilibrium state of the system, which is subsequently classified as either stable or unstable. It is crucial to recognize the timing of the introduction of the term *equilibrium*. The systematic use of equilibrium does not occur in the works of Clausius or William Thomson. Gibbs' approach to thermodynamics, conversely, explicitly focuses on the properties of substances in equilibrium.

In 1873, he presented a text titled *A quantitative investigation of certain relations between the gaseous, liquid, and solid states of water substances*. In this work, he uses a mathematical approach based on his brother's formulation of the second law of thermodynamics (Thomson 1882, pp. 185-187) to accurately determine the slope of the phase change curves from the triple point (Thomson 1912, p. 307).

These are James Thomson's main contributions to the theorization of critical phenomena and phase transition. In summary, the problem of critical points is originally formulated using the $V{\times}p$ diagram, which is then inverted to $p{\times}V$ to facilitate analysis of the inflection characteristics. Due to dimensional constraints, the $V{\times}T$ diagram is also necessary to analyze the behavior of isobaric curves, which must similarly be inverted to $T{\times}V$. Finally, James Thomson's contribution lies in his global description of substance behavior, incorporating curves of abrupt state change, the triple point, and the critical point that marks the termination of the curve separating the liquid and gaseous states.

The modification of diagrams throughout the problem-solving process (characterization of critical points) enriches the original empirical basis. The search for insights to elucidate the original problem necessitates exploring alternative diagrams. However, when information is transferred from one diagram to another, some data is preserved while other elements are adapted to the new context. There is a selection of information dictated by the diagram in use. Only a higher-dimensional space, such as the

T×*p*×*V* space, can store both the original empirical data and the information added throughout the search for a solution (Simon 1977, pp. 321-323).

Using Toulmin's approach, the characterization of critical points is discussed in relation to the well-established concepts of "state" and "change of state of substances" (Toulmin 1977, p. 202). Innovations are introduced to accommodate questionable or controversial concepts within the problem framework. The conventional understanding of the abrupt transition between liquid and gaseous states can no longer be regarded as the sole mode of transformation between these two states of matter. The possibility of a continuous transition between fluid states emerges. However, what determines whether a given transformation is abrupt or continuous? More fundamentally, why does this process typically occur abruptly?

At this point, we observe a densification (complexification) of the concept of "state". Continuous transformation generally occurs through unstable states, meaning that small impurities or variations in the heat transfer regime interrupt the transformation, leading the substance to a stable state of abrupt change in which the liquid and gaseous phases coexist. The necessity for this disturbance suggests the existence of a viable domain of unstable states. These states would persist indefinitely if no perturbation occurred; consequently, another term is required to qualify them. It is here that the notion of equilibrium is added to that of the substance's state.

The attempt to characterize critical points necessitates the evolution of the concept of state to encompass stable and unstable equilibrium states of matter. Indeed, the concept of "state" (C^{S}) evolves through the multiplication of variants—concepts of stable state (C^{SS}), unstable state (C^{US}), equilibrium stable state (C^{ESS}), equilibrium unstable state (C^{EUS}), non-equilibrium stable state (C^{NSS}), non-equilibrium unstable state (C^{NUS})—from which certain aspects are selectively emphasized as significant for thermodynamics (Toulmin 1977, p. 203-205).[7]

While this evolution can be approximated by a longitudinal process tracing the genealogy of the concept of "state", such a model fails to distinguish two complementary aspects of conceptual change: variation and selection. When James Thomson extends the single-phase continuation (dotted lines) in Figure 4, he introduces a variation to the abrupt transformation, proposing an unstable alternative to the conventional process of state change. However, within this continuation, certain states are forbidden; their existence cannot be empirically verified. This results in a selection of variants, where the rationality behind this selection transcends mere logical analysis of the concepts involved. Instead, it fully manifests within the theoretical framework that operationalizes the new concept of "state": the thermodynamics of equilibrium substances (Gibbs) and the domain of non-equilibrium thermodynamics.[8]

[7] Some of these variations are discarded or considered nonexistent due to their inherent inconsistencies. In Figure 7, in addition to C^{S}, we include two other concepts to illustrate the variation and selection of concepts within the science of heat: C^{X} and C^{Z}. The first arises within the framework of classical thermodynamics and is relevant to both equilibrium and non-equilibrium thermodynamics of substances. It could correspond, for example, to the concept of energy. The second corresponds to a concept discarded before classical thermodynamics. A concept that suffered a similar fate to C^{Z} is that of caloric.

[8] The application of the evolutionary model of variation and selection to conceptual change aims, among other objectives, to encapsulate Ludwik Fleck's proposition that ideas emerge from collective authorship (Fleck 2010, p. 177). In this work, the mathematical delineation of critical points—fully realized in the frameworks of Van der Waals and Gibbs—draws on pivotal contributions by Andrews and Thomson, as well as substantial, albeit indirect, influences from Maxwell, Clausius, Clapeyron, and Carnot.

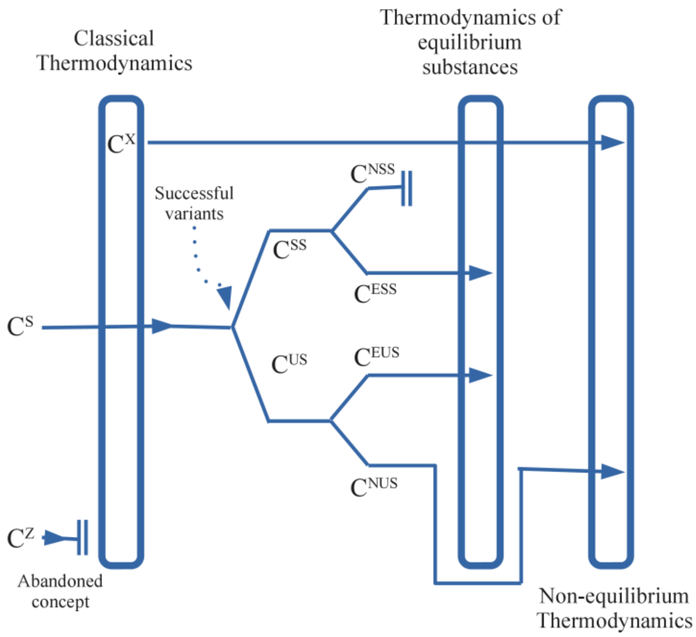

Figure 7: Evolutionary Scheme for the Concept of Substances' State.

6. Critical points in Van der Waals and Gibbs

As a counterpoint to the scientific investigation strategy based on the heuristic resources of representations, we can cite the alternative approach in this area: the research of Van der Waals. The research program (Lakatos 1978, pp. 202-203) of this author is linked to Newtonian physics, which generally ascribed the elastic behavior of real gases to repulsive forces between molecules (Klein 1974, pp. 31-35). Van der Waals critically examined this model, but then another problem emerged:

> We have therefore to explain why it is that particles attracting one another and only separated by empty space do not fall together: and to do this we must look around for other causes. These we find in the motion of the molecules themselves, which must be of such a nature that it opposes a diminution of volume and causes the gas to act as if there were repulsive forces between its particles (Van der Waals 1988, p. 128).

The treatment of gas particle motion follows a mechanistic reductionism. Among the relevant concepts borrowed from Mechanics, the notion of equilibrium, expressed in terms of potential energy (Van der Waals 1988, pp. 155-156), is combined with Clausius' virial theorem (Klein 1974, p. 39) and assumptions about the size of gas molecules and the forces between them. This synthesis allows Van der Waals to derive his equation of state:

$$(2)\quad \left(p + \frac{a}{V^2}\right)(V - b) = RT$$

In comparison to an ideal gas, the pressure p must be increased by a factor related to the constant a, while the volume V must be decreased by a value expressed by another constant, b. When written as a polynomial in V, Equation (2) takes the form of a cubic expression. This detail did not escape the attention of Van der Waals. He references James Thomson's article, as evidence to support his equation of state for carbonic acid (Van der Waals 1988, p. 196). By arranging these isotherms in a $p \times V$ diagram, Van der Waals applies the conditions $(dp/dV)_T = 0$ and $(d^2p/dV^2)_T = 0$ to determine the critical temperature, volume, and pressure as functions of the parameters in Equation (2) (Van der Waals 2004, pp. 191-194).

While Andrews and James Thomson sought to phenomenologically clarify the concept of a critical point, Van der Waals saw his equation of state as an opportunity for application. Within this framework, the mathematical characterization of critical points emerges as a significant challenge: an operational definition or algorithm to identify critical points is an integral part of scientific research. Despite integrating this new phenomenon into a theoretical framework, the calculated results did not align well with experimental observations (Van der Waals 2004, pp. 205-207). These discrepancies do not undermine Van der Waals' research. As noted by both Klein and Rowlinson, Van der Waals' primary goal was not a theoretical explanation of Andrews' findings, but a demonstration of his equation of state's effectiveness:

> His discussion of the last gas [carbon dioxide] is curtailed since he had fortunately become aware of Andrews' results. These were to provide him with a much more convincing demonstration of the power of his equation than he had been able to find from the rather inconclusive comparison with Regnault's results (Rowlinson 2004, p. 177).

As a research methodology applied to thermodynamics, this program was not well received by all physicists in the field (Rowlinson 2004, p. 173). However, it was later recognized as highly significant for Physics, culminating in the awarding of the Nobel Prize to Van der Waals. During this occasion, he expressed his belief in the existence of molecules with finite sizes:

> It will be perfectly clear that in all my studies I was quite convinced of the real existence of molecules, that I never regarded them as a fragment of imagination, nor even as mere centres of force effects. I considered them to be the actual bodies (Van der Waals 1967, pp. 254-265).

In the context of modern physics, which is inherently focused on molecular hypotheses and speculations regarding fundamental particles, Andrews' findings might serve as an invitation for scientists to formulate theory-driven explanations about the nature of matter. During that period, however, the use of molecular hypotheses was considerably contested and far from universally accepted among scientists. From this perspective, Van der Waals' work should not be regarded as an isolated response to a single stimulus; it does not represent what Klein refers to as a "tidy story". He argues that "tidiness is no more desirable in a historical narrative than it is characteristic of the way things happen in this world" (Klein 1974, p. 30). Instead, the episode of Van der Waals' theory is best understood within a long and complex history that acknowledges the methodological influences of scholars such as Clausius and Laplace, whose roots are grounded in Newtonian principles: "These remarks immediately set Van der Waals' thesis in a much broader and richer historical scene than the tidy sketch conjectured above" (Klein 1974, p. 31).

Sixteen years after writing the article on Van der Waals, Klein published another piece titled *The Physics of J. Willard Gibbs in His Time*. In this article, he establishes a motivational connection between the results of Andrews and the work of Gibbs. However, this time he suggests a tidy outline:

> It seems to me that Andrews' discovery—a new, unexpected and general feature of the behavior of matter, as yet totally unanalyzed—would have been just the sort of thing to capture Gibbs' attention as that promising new professor of mathematical physics sought for a suitable subject on which to work (Klein 1990, p. 43).

According to the structure of the argument constructed by Klein to analyze the historical context of Van der Waals' work, it is impossible to reconnect Gibbs' articles to a research tradition. This would be a *creatio ex nihilo* from Andrews' inspiring breath. We disagree with this statement. The relationship between Andrews' results and Gibbs' theory cannot be described as a "tidy story" either. If Andrews' results indeed had a profound impact on Gibbs, revealing the limitations of classical thermodynamics in addressing the new phenomenon, the reformulation of this theory incorporates new elements while maintaining a connection to an alternative tradition in mechanics. Gibbs' theory and its relationship to this tradition will be explored in a separate work.[9]

For now, it suffices to observe that the final version of Gibbs' thermodynamics is based on variational principles. This formulation presents essential parallels with Hamilton's approaches to mechanics and geometric optics. These theories, in turn, dialogue with Lagrange's analytical mechanics, incorporating d'Alembert's dynamic equilibrium condition in the form of the principle of virtual work. Finally, the principle of virtual work is a reformulation of Stevin's principle, which is a generalized expression of the lever principle attributed to Archimedes (Dugas 1988, p. 127, Salençon 2018, pp. 1-18). This methodological framework offers a distinct alternative to Newtonian mechanics, prioritizing kinematic constraints over the notion of force (Lanczos 1970, p. 77). It is within this tradition—characterized by a focus on the structural form of theories—that Gibbs' contributions can be situated.

Although the concept of expressing natural laws through minimization principles is not new—consider Fermat's principle of least time—the application of theories based on these abstract principles, has significantly impacted various fields of physics. This approach proved to be both fertile and powerful in fields such as geometric optics, mechanics, and thermodynamics, enabling the development of theories characterized by greater logical coherence and enhanced heuristic potential, while encompassing a broader phenomenological scope. In James Thomson and Gibbs, critical points are analyzed not through a theory of matter, but by the heuristic resources of the representations (Lucena & Chiappin 2017, pp. 302-314).

Furthermore, Gibbs' theory, from a representational perspective, constitutes the culmination of a sequence of intellectual challenges and solutions within this field (Toulmin 1977, p. 148). This lineage of inquiry can be traced from Carnot's exploration of the maximum-efficiency heat engine, through aspects of Clausius' investigations—such as those culminating in Equation (1)—to James Thomson's efforts to characterize critical points, and ultimately to Gibbs' proposal to devise a geometric representation that integrates the phenomenology of critical points into thermodynamics. This sequence of problems reflects a persistent quest for representational frameworks endowed with progressively greater heuristic capacity. Certainly, this is a common pattern in the history of science. However, when faced with experimental and ontological challenges, the heuristic power of representations as a resource for problem-solving is frequently neglected. Thermodynamics is one of the best branches of physics for discussing and valuing this dimension of scientific theories.

In short, Carnot's heat engine was initially rendered diagrammatically to facilitate the mathematization of the theory, yielding outcomes such as Clausius' Equation (1). Subsequently, the $p \times V$ diagram emerged as an increasingly prevalent tool for investigating and elucidating the properties of substances. However, Thomas Andrews' experimental findings necessitated the adoption of additional diagrams—namely $V \times p$, $T \times V$, $V \times T$, and $p \times T$—to grapple with the complexity of emerging phenomena. A pivotal aspect of Gibbs' challenge was to identify a representational space capable of cohesively capturing the empirical data concerning substances, effectively synthesizing the disparate information previously isolated across multiple diagrams.[10]

This characteristic attracted the attention of Duhem, for whom the physical theory is a natural classification of empirical laws, free from metaphysical commitments about matter, prioritizes the pursuit of mathematical representations that continually expand their heuristic potential to accommodate the

[9] Among other aspects, we also defer to that future work the task of detailing the relationship between the language of representation and the language of theory in the Gibbs program. This relationship is expected to assume a different configuration compared to what we have examined regarding thermodynamics in the two representations explored in the present work: the mechanical and diagrammatic representations.

[10] Gibbs organizes the empirical basis of the equilibrium states of a substance through a thermodynamic surface in $U \times S \times V$ (energy, entropy, volume) space. This fundamental surface allows for the geometric description of all accessible states of the system. Through analysis of its tangent planes, Gibbs identifies the triple point, the critical point, the regions of phase coexistence, and system instabilities. The concavity of the surface—an essential property of thermodynamic functions—ensures that the equilibrium processes associated with this empirical basis obey the variational principles: energy tends to a minimum, and entropy to a maximum.

ongoing discoveries of experimental physics (Chiappin & Lucena 2024). The works of Andrews and James Thomson serve as a conceptual framework for organizing the empirical foundation of critical phenomena, but it is Gibbs who ultimately constructs the new representation of thermodynamics. In contrast to Duhem's strategy, Van der Waals incorporates critical points into his equation of state, grounding them in the existence of finite molecules and the nature of their interactions. His objective is inseparable from the development of a theory of matter.

7. Conclusion

Since the time of Clapeyron, diagrammatic representations have functioned as a valuable heuristic tool for articulating and refining thermodynamic concepts. Clausius employed the relationship $A=W$, derived through an infinitesimal Carnot cycle, to formulate Equation (1). This approach enables the expression of the cycle's area using differentials and the construction of the first derivative of pressure with respect to volume to elucidate phase transitions in matter. However, this method precludes the incorporation of second derivatives into the analysis of natural phenomena. Consequently, without alternative algorithmic strategies within this framework, such diagrams fail to establish a substantive connection—beyond simple mathematical characterization—among the variables describing critical points.

A more robust representation from a heuristic perspective is necessary. James Thomson partially suggests a new representation by proposing a set of possible states for carbonic acid arranged in the configuration space $T \times p \times V$. Maxwell employed the same approach ($A=W$) to establish the rule of equal areas.

Given the lack of algorithms more suited to the problem, researchers are left with two paths: improving the language referring to the critical point and investigating routes to new representations, or entering the field of explanation through theories of matter. James Thomson took the first one. He introduced the concepts of equilibrium, stability, and instability in the analysis of states of matter by various diagrams. Based on Thomas Andrews' data, it seems that James Thomson refined and enriched the terminology surrounding the new phenomenon and explored the possibility of an alternative representation. However, he neither developed an alternative algorithm nor established a representation with practical heuristic features.

In an alternative approach, Van der Waals develops an equation of state based on molecular concepts. He not only adapts the Clapeyron equation for ideal gases but also estimates the size of molecules and the strength of interactions between them. The aim here is to explain experimental laws —"to strip reality of the appearances covering it like a veil, in order to see the bare reality itself" (Duhem 1981, p. 7). The reproduction of part of Andrews' results immediately conferred prestige and aroused the interest of the scientific community in Van der Waals theory.

Conversely, Gibbs' approach, published in the same year as Van der Waals' thesis, takes a different direction. He revisits James Thomson's ideas without committing to a specific theory of matter. The strength of Gibbs' proposal lies in the choice of configuration space and the geometric framework used to represent the set of physical states of the substance.

In Gibbs' perspective, the thermodynamics of Clausius and William Thomson, along with the study of critical phenomena, should be unified into a single theory. This attempt at unification necessitated the adoption of a new and more powerful representation. In this context, convexity plays a crucial role in relation to the stability of the system. Thus, Gibbs not only integrates the empirical findings of Thomas Andrews but also incorporates the empirical laws derived from the diagrammatic method. Most importantly, he establishes a representation, in which convexity leads to a fundamental law expressed as a variational principle: the principle of equilibrium and stability.

Nevertheless, it is essential to acknowledge the valuable contributions made by James Thomson. The monophasic continuity of the isotherms demonstrates a level of geometric insight that allows us to view the critical point as an inflection point. From this perspective, we can derive the relationships: $(dT/dV)_p = 0$, $(dp/dV)_T = 0$, $(d^2T/dV^2)_p = 0$, and $(d^2p/dV^2)_T = 0$. The representation developed by Gibbs aligns with James's approach. Gibbs could have formulated his theory directly in analytical terms, similar to the method established by Massieu (1869), but he chose to first construct it geometrically and then express it analytically. This decision shares the same motivation as that of James Thomson, who represented the empirical basis of Andrews' critical points as a thermodynamic surface (Figure 2). The key difference lies in Gibbs' choice to work in the space $U \times S \times V$ rather than the space $T \times p \times V$.

In particular, the analysis of the representational aspect of thermodynamics provides us with a substrate where the concept of state finds its natural habitat. Each representation associates its own characteristics with the concept, and this association densifies the concept itself as a consequence of the representation's heuristic power. In the context of Carnot's mechanical representation, the description of the behavior of the working substance in terms of expansion and contraction—especially in vaporization and liquefaction—allows us to discuss the state of the substance in terms of the physical state of matter (gaseous and liquid).

By contrast, the main purpose of the diagrammatic representation is to establish a univocal relationship between the state of the substance and the values of the thermodynamic variables. It is in this context that James Thomson develops his research on critical points and introduces, together with Thomas Andrews, the idea of stability/instability. The particularization into stable or unstable states is added to the infinite descriptive possibilities that the values of thermodynamic variables bring to the concept of state.

The fact attested by James Thomson—that some unstable states can exist while others cannot—evokes the idea of distinguishing them. The way to do this is to categorize instability through the term equilibrium. This densification of the concept of state has its genesis in the context of representation by diagrams. Ultimately, however, it is in Gibbs' thermodynamics and its representation of the states of substances by surfaces in the $U \times S \times V$ configuration space that a physics of equilibrium states becomes effectively operational.

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References

Andrews, T. (1861), "On the Effect of Great Pressures Combined with Cold, on the Six Non-Condensable Gases", *Report of British Association for the Advancement of Science* 31: 322-332.

Andrews, T. (1869), "On the Continuity of the Gaseous and Liquid States of Matter", *The Bakerian Lecture* XVIII: 575-590.

Bachelard, G. (2002), *The Formation of the Scientific Mind: A Contribution to a Psychoanalysis of Objective Knowledge*, Manchester: Clinamen Press.

Berche, B., Henkel, M. and R. Kenna (2009), "Critical Phenomena: 150 Years since Cagniard de la Tour", *Journal of Physical Studies* 13(3): 3001-3004

Cajori, F. (1922), "On the History of Caloric", *Isis* 4(3): 483-492.

Carnot, L. (1803), *Principes fondamentaux de l'équilibre et du mouvement*, Paris: Deterville.

Carnot, S. (1897), *Refletions on the Motive Power of Heat*, New York: John Wiley & Sons.

Chiappin, J.R.N. and J. Lucena (2024), "A concepção de Duhem de História da Ciência como história intelectual-teses historiográficas e metodologia da continuidade e da convergência", *Khronos* 17: 71-100.

Clapeyron, B.P.E. (1837), "Memoir on the Motive Power of Heat", *Journal de l'Ecole Polytechnique* XIV(153): 347-376.

Clausius, R. (1867), *The Mechanical Theory of Heat, With its Applications to Steam-Engine and to the Physical Properties of Bodies*, London: John Van Voorst.

Dugas, R. (1988), *A History of Mechanics*, New York: Dover Publications.

Duhem, P. (1981), *The Aim and Structure of Physical Theory*, New York: Atheneum.

Fleck, L. (2010), *Gênese e desenvolvimento de um fato científico*, Belo Horizonte: Fabrefactum.

Goudaroulis, Y. (1994), "Searching for a Name: The Development of the Concept of the Critical Point (1822-1869)", *Revue d'histoire des sciences* 47 (3-4): 353-380.

Joule, J. P. (1884), *Scientific Papers of James Prescott Joule,* London: The Society.

Lanczos, C. (1970), *The Variational Principles of Mechanics*, New York: Dover Publications.

Klein, M.J. (1974), "The Historical Origins of the Van der Waals Equation", *Physica* 73(1): 28-47.

Klein, M.J. (1990), "The Physics of J. Willard Gibbs in his Time", *Physics today* 43(9): 40-48.

Lakatos, I. (1978), *The Methodology of Scientific Research Programmes I*, Cambridge: Cambridge University Press.

Lucena, J. and J. R. Chiappin (2017), "A geometria como instrumento heurístico da reformulação da termodinâmica na representação de ciclos para a de potenciais", *Principia: An International Journal of Epistemology* 21(3): 291-315.

Lucena, J., Chiappin, J. R. and C. Laranjeiras (2018), "Gibbs' Rational Reconstruction of Thermodynamics According to the Heuristic Tradition of Descartes' Analytical Method", *Revista Brasileira de Ensino de Física* 41(1): 1-15.

Lucena, J., Laranjeiras, C. and J. R. Chiappin (2023), "The Mechanical Representation of Knowledge: From Descartes' Mechanized Geometry to Carnot's Heat Engine", *Transversal: International Journal for the Historiography of Science* 14: 1-19.

Massieu, F. (1869), "Sur les fonctions caractéristiques des divers fluides et sur la théorie des vapeurs", *Comptes Rendus* 69: 858-862.

Maxwell, J. C. (1872), *Theory of Heat*, London: Longmans, Green and CO.

Maxwell, J. C. (2002), *The Scientific Letters and Papers of James Clerk Maxwell*, Vol. III, Harman, P. M. (Ed.), Cambridge: Cambridge University Press.

Maxwell, J. C. (2003), *The Scientific Papers of James Clerk Maxwell*, Vol. II, New York: Dover Publications.

Newburgh, R. (2009), "Carnot to Clausius: Caloric to Entropy", *European Journal of Physics* 30(4): 713-728.

Roller, D. (1957), "CASE 3. The Early Development of the Concepts of Temperature and Heat. The Rise and Decline of the Caloric Theory", in Conant, J. B. (Ed.), *Harvard Case Histories in Experimental Science*, Vol. I, Harvard University Press, pp. 117-214.

Rowlinson, J. S. (2003), "The Work of Thomas Andrews and James Thomson on the Liquefaction of Gases", *Notes and Records of the Royal Society of London* 57(2): 143-159.

Rowlinson, J. S. (2004), *Cohesion, a Scientific History of Intermolecular Forces*, Cambridge: Cambridge University Press.

Salençon, J. (2018), *The Virtual Work Approach to Mechanical Modeling*, London: John Wiley & Son.

Simon, H. A. (1977), *Models of Discovery and Other Topics in the Methods of Science*, Dordrecht: D. Reidel.

Thomson, J. (1912), *Collected Papers in Physics and Engineering by James Thomson*, London: Cambridge University Press.

Thomson, W. (1882), *Mathematical and Physical Papers by sir William Thomson*, Vol. 1, Cambridge: Cambridge University Press.

Toulmin, S. (1977). Human Understanding: The Collective Use and Evolution of Concepts, Princeton: Princeton University Press.

Van der Waals, J.D. (1967), "The Equation of State for Gases and Liquids", in *Nobel Lectures in Physics, 1901-1921*, Amsterdam: Elsevier, pp. 254-265.

Van der Waals, J.D. (2004), *On the Continuity of Gaseous and Liquid States*, New York: Dover Publications.