

## *The Ehrenfest Classification of Phase Transitions: Introduction and Evolution*

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### **Abstract**

The first classification of general types of transition between phases of matter, introduced by Paul Ehrenfest in 1933, lies at a crossroads in the thermodynamical study of critical phenomena. It arose following the discovery in 1932 of a surprising new phase transition in liquid helium, the “lambda transition,” when W. H. Keesom and coworkers in Leiden, Holland observed a  $\lambda$ -shaped “jump” discontinuity in the curve giving the temperature dependence of the specific heat of helium at a critical value. This apparent jump led Ehrenfest to introduce a classification of phase transitions on the basis of jumps in derivatives of the free energy function. This classification was immediately applied by A.J. Rutgers to the study of the transition from the normal to superconducting state in metals. Eduard Justi and Max von Laue soon questioned the possibility of its class of “second-order phase transitions” – of which the “lambda transition was believed to be the arche type – but C.J. Gorter and H.B.G. Casimir used an “order parameter to demonstrate their existence in superconductors. As a crossroads of study, the Ehrenfest classification was forced to undergo a slow, adaptive evolution during subsequent decades. During the 1940’s the classification was increasingly used in discussions of liquid-gas, order-disorder, paramagnetic-ferromagnetic and normal-super-conducting phase transitions. Already in 1944 however, Lars Onsager’s solution of the Ising model for two-dimensional magnets was seen to possess a derivative with a logarithmic divergence rather than a jump as the critical point was approached. In the 1950’s, experiments further revealed the lambda transition in helium to exhibit similar behavior. Rather than being a prime example of an Ehrenfest phase transition, the lambda transition was seen to lie outside the Ehrenfest classification. The Ehrenfest scheme was then extended to include such singularities, most notably by A. Brain Pippard in 1957, with widespread acceptance. During the 1960’s these logarithmic infinities were the focus of the investigation of “scaling” by Leo Kadanoff, B. Widom and others. By the 1970s, a radically simplified binary classification of phase transitions into “first-order” and “continuous” transitions was increasingly adopted.

## 1. Introduction

Different phases of matter are generally distinguishable by their appearances (for example, liquid water is visibly different from crystalline ice) or the presence of boundaries between them (for example, a meniscus forms between the liquid and gas phases of alcohol), and by differences of internal organization (for example, of spin orientation in magnetic domains). The formal study of transitions between phases can be traced at least as far back as the experimental discovery of a precise set of values of thermodynamical parameters at which a liquid-gas transition occurs; in 1822, Charles Cagnard de la Tour characterized the transition between liquid and gas phases in alcohol by a triplet of values: the temperature, pressure and volume.<sup>1</sup> Subsequently, Thomas Andrews (1863) experimentally demonstrated that for a large set of fluids, liquid and gas phases can be continuously changed into one another around such a point, in phase transitions called “continuous” transformations for that reason.<sup>2</sup> Andrews then, working with CO<sub>2</sub>, named the definite point at which such a transformation occurs the “critical point” of the substance.<sup>3</sup>

This initial notion of the critical point – as a triplet of thermodynamical values – was somewhat primitive. Ten years later, Josiah Willard Gibbs (1873) introduced the phase diagram, a graph of thermodynamical variables (for examples, temperature and pressure) in which different regions correspond to different phases, using it to give a new, fuller definition of the critical point. In the phase diagram of Gibbs, the boundary between regions, where different phases coexist in thermodynamical equilibrium, was called “the phase co-existence curve”; Gibbs’s more satisfying definition of the critical point was: the location in a phase diagram where the phase coexistence curve terminates.<sup>4</sup> This definition proved applicable to a wide range of systems, from fluids to magnets. The same year, Johannes Diderik van der Waals (1873) arrived at the first equation of state (a mathematical description of a system in terms of its measurable

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<sup>1</sup> Cagnard de la Tour noticed that, for a volume of alcohol under a given pressure, as the temperature was increased beyond a well-defined value, the liquid phase became visible opalescent, expanded and then disappeared completely into the gaseous phase; see Brush (1976, Book 1, p. 257).

<sup>2</sup> “[G]aseous and liquid states ... are capable of passing into one another by a process of continuous change” (Andrews 1869, p. 589). Note, however, that this sort of transition is not to be confused with Fisher’s (much later) conception of a continuous transition; see Footnote 75.

<sup>3</sup> “The critical point affords a criterion for distinguishing a vapour from a gas” (Andrews 1869, p. 589); see Miller (1863) and Andrews (1869). Andrews measured the pressure below, at and above the temperature of transformation and showed that, as the critical point is approached, liquid becomes less dense and gas more dense. Transition points were also attributed a “critical temperature”,  $T_c$ , by John Hopkinson (1889), who discussed the “temperature at which the magnetism disappears which we may appropriately call the critical temperature.” Serious investigations of the transition between paramagnetic and ferromagnetic states of a metal began about 1890; see Hopkinson (1889), Curie (1895), and Keith and Quédec (1992).

<sup>4</sup> Gibbs [1873] 1984, p. 45.

thermodynamical properties), in this case for fluids, to yield a critical point.<sup>5</sup> An important study of a critical point in magnetic materials, specifically the critical temperature at which ferromagnetism disappears, was later carried out by Pierre Curie (1895).<sup>6</sup> Its precise location was first theoretically derived using Pierre Weiss's (1907) theory of ferromagnetism.<sup>7</sup> This critical point was soon named the "Curie point" by Weiss and Heike Kamerlingh Onnes (1910) despite the fact that it had not been precisely located by Curie. The stage was thus set for the detailed investigation of phase transitions in a broad range of systems.<sup>8</sup> This investigation would repeatedly involve the question of how best to *classify* phase transitions, that as will be seen here, lies at a crossroads of the study of critical phenomena.

Important experimental advances in the investigation of phase transitions were by 1910 taking place in Leiden, Holland. Kamerlingh Onnes had by then made the University of Leiden a center of research in the physics of matter at low temperatures.<sup>9</sup> He was first to liquify helium, in 1908, by cooling its gaseous phase (using liquid hydrogen) and compressing it below 100 atmospheres pressure, at the laboratory which now bears his name: *Kamerlingh Onnes Laboratorium der Rijksuniversiteit te Leiden*.<sup>10</sup>

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<sup>5</sup> The equation of state was presented in van der Waals's doctoral dissertation. The critical point was found by noting that, for a liquid-gas system, the first and second derivatives, with respect to volume, of the pressure are zero, since the curve of pressure versus volume (at constant temperature) has an inflection point.

<sup>6</sup> Curie identified only a *region* where ferromagnetism disappears; see Domb (1971) for a discussion of the term's history.

<sup>7</sup> This theory is also historically significant for its introduction of the "hypothesis of the molecular field" and is a prominent example of the "mean field theories" which play an important role in the modern pedagogy of condensed matter and thermal physics; see, *e.g.*, Kittel and Kroemer (1980, p. 288).

<sup>8</sup> During the next fifty years, it became increasingly clear that critical phenomena have a generality which transcends the particular systems in which they occur. Indeed, the Weiss theory, itself an extension of Paul Langevin's (1905) molecular theory of magnetism which added an internal magnetic field, was soon followed by the Lenz (1920) one-dimensional model and the Ising (1925) two-dimensional model of the ferromagnet. The Lenz-Ising model was eventually shown by Rudolf Peierls (1936) to be equivalent to the later Bethe (1935) theory of order-disorder transformations in alloys. Furthermore, Cernuschi and Eyring (1937) and others showed that the Lenz-Ising model could be applied to a system of atoms and holes in a lattice. This system, later referred to as the "lattice gas" by Lee and Yang (1952) was itself shown by them to be analogous to the gas-liquid system.

<sup>9</sup> Kamerlingh Onnes founded, with state funding, a world-renowned school for instrument makers and glass blowers and began publication of *Communications from the Physical Laboratory of the University of Leiden*. The latter has been referred to as "the bible of low-temperature physics for several decades" (Hoddeson *et al.* 1992, p. 144). Kamerlingh Onnes occupied the first Dutch chair in physics from 1882 until his retirement in 1922. He received his doctorate in 1879 from Groningen University, with a thesis entitled *Nieuwe Bewijzen voor Aswenteling der Aarde* (*New Proofs for the Axial Changes of the Earth*).

<sup>10</sup> Kamerlingh Onne's belief in the van der Waals "law of corresponding states," which he referred to as a "scaling law", guided the early Leiden research. The "law of corresponding states"

W. H. Keesom, who studied with van der Waals and became an assistant to Kamerlingh Onnes at the Leiden laboratory in 1900, was later to provide the data from which a crucial element in the first classification of phase transitions, the discontinuity of a second derivative of free energy, was first noted experimentally.<sup>11</sup> Research on helium during the 1920's set the stage for the definitive discovery by Keesom in 1932 of an unusual phase transition in liquid helium.<sup>12</sup> It was this discovery that raised the issues of how many types of transition there were and how they could be classified. In 1933, Paul Ehrenfest, also working in Leiden, introduced the first comprehensive scheme for classifying phase transitions, which here will be referred to as "the Ehrenfest classification."<sup>13</sup> The new helium transition was classified by the Ehrenfest scheme as a "second-order transition" and the ordinary phase transitions "first-order transitions."

Soon after the introduction of this classification of phase transitions, a dispute arose, in the context of transitions in superfluids and superconductors, as to whether second-order transitions as Ehrenfest conceived them were *thermodynamically possible*.<sup>14</sup> By the fall of 1934 such a possibility in superconductors had been established definitively

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referred to here is the van der Waals equation of state written in units of the critical values of pressure, temperature and volume.

<sup>11</sup> Keesom worked with Kamerlingh Onnes from 1908 to 1917, left Leiden but returned in 1923 as professor of experimental physics. He subsequently, became the director of the laboratory upon Kamerlingh Onnes's death in 1926; see Sect. 2 and Footnote 27.

<sup>12</sup> The progress at Leiden during the 1920's will be discussed in Sect. 2. One reason why this transition went unnoticed for so long is that helium itself was first discovered in the *sun* – as its name suggests. Helium wasn't known to exist until 1868, when spectrographic observations of the sun's chromosphere during a solar eclipse (see Janssen 1868, Rayet 1868, Haig 1868 and Herschel 1868) revealed a previously unobserved spectral line (the D<sub>3</sub> line). Furthermore, it wasn't until 1895 that helium was with certainty isolated on earth; this was accomplished by Ramsay (1895a, b) by boiling the mineral cleveite and observing the spectral properties of the emitted gas in a Geissler tube (see also Keesom 1942). It had been for that reason beyond the scope of experimentation. The name "helium" was introduced *circa* 1871 (for example, in Kelvin's presidential address to the British Association in August, 1871; see also Thomson 1871).

<sup>13</sup> Paul Ehrenfest succeeded H. A. Lorentz at Leiden, with the latter's recommendation, as professor of theoretical physics in 1912. Ehrenfest received his Ph.D. under Ludwig Boltzmann in 1904 and had been living in St. Petersburg since 1907. See Klein (1970) for a detailed scientific biography of Ehrenfest, covering the years up to 1920.

<sup>14</sup> Superfluids are fluids which, among other behaviors, move without friction. Superfluidity in helium II was not observed experimentally until 1938; see Kapitza (1938), Allen and Misener (1938) and Allen and Jones (1938). Superconductors are metals that are capable of conducting electrical current with no electrical resistance. Superconductivity had been discovered in 1911 by Kamerlingh Onnes (who liquified helium for the first time in 1908 and subsequently used it to cool other materials) and his coworkers, most notably Gilles Holst, who actually performed these measurements at his request; see London (1950, p. 10) and Casimir (1977a, p. 170). This group observed superconductivity when mercury was cooled to near 4.2 K: the electrical resistance of the material disappeared completely, dropping immediately and discontinuously to zero; see Kamerlingh Onnes (1911a, b) and Gavroglu and Goudaroulis (1984, 1988a, b).

using a newly introduced idea, that of an order parameter;<sup>15</sup> the classification of phase transitions was quickly becoming a locus of attention for those studying critical phenomena. Questions then arose regarding the existence of genuine physical *examples* of each of the Ehrenfest classes of transitions.<sup>16</sup> Although the liquid-helium transition was the most well known example of a second-order transition, by 1936 it was suspected of not satisfying the Ehrenfest definition of a second-order phase transition.<sup>17</sup> Nonetheless, second-order transitions continued to be viewed by most as phase transitions.<sup>18</sup> Furthermore, the value of the Ehrenfest classification for the study of many *model* systems had become clear.<sup>19</sup>

The situation changed, however, in the 1940's when Lars Onsager (1944) made the remarkable theoretical advance of exactly solving the problem of the two-dimensional Ising model in the absence of an applied magnetic field.<sup>20</sup> A phase transition was predicted by this model, but one with a free energy derivative that becomes *infinite* rather than discontinuous.<sup>21</sup> Regions of this kind are now said to contain "logarithmic divergences" or "logarithmic infinities."<sup>22</sup> This clearly pointed out for the first time the inadequacy in the original Ehrenfest classification system. Despite the solid experimental confirmation of logarithmic infinities during the 1950's in the work of K. R. Atkins and M. H. Edwards (1955), the Ehrenfest scheme remained in widespread use. Neither subsequent questions regarding the well-definedness of such transitions nor the failure

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<sup>15</sup> The concept of an "order parameter" had just been introduced by F. Bloch (1932) in his *Habilitationschrift* – written after a year as *Assistant* to Werner Heisenberg. This work has been described as presenting "an exceptional wealth of formalism, which has become part of the fabric of the modern theory of condensed matter physics and collective phenomena" (Hoddeson *et al.* 1992, p. 139). One example of an order parameter is, for fluid systems, density in the liquid phase minus density in the gas phase; another, for magnetic systems, is magnetization. These are first derivatives of the relevant thermodynamical fields (*e.g.* the Gibbs free energy field, for fluids) or conjugate densities (*e.g.* the Helmholtz free energy field, for magnets).

<sup>16</sup> Confusion also arose regarding *use* of the term "second-order transition" that originated with the Ehrenfest scheme. For example, it was applied by some to situations where the specific heat of a material rises rapidly but where no phase transition actually occurs, such as happens in certain glasses and polymers; see Tempereley (1956; pp. 20–21) for a retrospective view of this.

<sup>17</sup> Keesom (1936).

<sup>18</sup> For example, Pippard (1957, Chapter 9) and Münster (1970, p. 193). One who dissented from this view was E. A. Guggenheim (1949, pp. 276–288).

<sup>19</sup> For example, idealized Bose-Einstein fluids – model fluids consisting entirely of identical particles obeying Bose-Einstein statistics (see London 1938a, b) – were understood to undergo Ehrenfest "third-order phase transitions" (see Sect. 2) and London's (1939) model for liquid helium was thought to yield Ehrenfest second-order transitions.

<sup>20</sup> The one-dimensional version of the model had been solved exactly by Ising (1925), who noticed no phase transition. Ising had, however, mistakenly claimed that there would be no phase transition in the two or three-dimensional cases.

<sup>21</sup> Laszlo Tisza (1951) first suggested, much later, that the specific heat of helium might also become infinite; see Fairbank and Kellers (1966).

<sup>22</sup> See Fairbank and Kellers (1966). During the 1960's, logarithmic infinities became the focus of theoretical developments such as those of B. Widom (1965) and Leo Kadanoff (1966a, b).

of the helium transition to fit the Ehrenfest scheme proved fatal to it.<sup>23</sup> A. Brian Pippard (1957), in a move securing the long-term viability of the Ehrenfest classification, extended the scheme to include logarithmic infinities.<sup>24</sup> Extended Ehrenfest schemes of this kind have been used regularly in textbooks ever since, though alternative schemes are also often used.<sup>25</sup>

Here, I shall investigate the introduction of Ehrenfest classification, its reception and its revision, its role in the theory of critical phenomena and its relationship to other classification schemes in their historical contexts. Since the classification of phase transitions lies at the crossroads of many aspects of the theory of critical phenomena, understanding the evolution of the Ehrenfest scheme is fundamental to understanding the history of the study of critical phenomena itself. It is shown here how and why the scheme survived and was extended, and in what way it was finally explicated.<sup>26</sup> In Sect. 2, I present the Ehrenfest classification as originally formulated, after surveying the pertinent experimental background. I show how: (i) Ehrenfest created his scheme after considering the visual representation of the data of Keesom (1933) and (ii) Ehrenfest derived an analog of the Clausius-Clapeyron equation for “second-order transitions.” In Sect. 3, I discuss several significant exchanges regarding the new classification and show how they led to a better understanding of the newly discovered phase transitions. In Sect. 4, I trace the realization of the limitations of the Ehrenfest classification and its subsequent extension. I show that, from the long-term historical perspective there were three stages in the evolution of the Ehrenfest scheme, the first lasting from its introduction in 1933 until roughly 1950, the second occurring during the 1950s, and the last taking place from roughly 1960 onwards. In Sect. 5, I make several observations regarding the history of the Ehrenfest classification and its role in the study of critical phenomena.

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<sup>23</sup> The first comprehensive alternative scheme, that of Tisza (1951, 1961), was conceived in 1951 as an application of a new theory of phase transitions. Tisza’s (1961) *tour de force* then placed the classification of phase transitions on a new, more fundamental thermodynamical basis. Although considered by many, *e.g.*, H. Callen (1960) and A. Münster (1970), to be a superior scheme, its influence was not widespread. Callen’s (1960) text on thermodynamics emphasized the Tisza version at the expense of Ehrenfest’s, but the Ehrenfest version was already dominating usage. L. D. Landau and E. Lifshitz (1938) sketched a less detailed scheme much earlier but it lay largely dormant (amongst English speakers, at least) until about 1970, when its approach was revived due to the influence of M. E. Fisher (1967) and others; see Sect. 4.

<sup>24</sup> Pippard’s (1957, Chapter 9) survey of phase transitions proved influential.

<sup>25</sup> For example, Landsberg (1961), Buchdahl (1966) and Stanley (1971).

<sup>26</sup> Since Ehrenfest died on September 25, 1933, shortly after the introduction of the classification, he had no opportunity to revise it. Many later workers made their own revisions to accommodate valid criticisms or hybridized Ehrenfest’s scheme with other schemes; see Sect. 4.

## 2. The Introduction of the Ehrenfest Classification

Unlike previously observed phase transitions, the transition in liquid helium confirmed by Keesom and coworkers had no associated latent heat and showed no visible surface of demarcation between phases.<sup>27</sup> The inference that a phase transition was taking place in liquid helium was based on evidence that had accumulated since the observation in 1925 by L. I. Dana and Kamerlingh Onnes (1926) of a sharp maximum in the pressure-temperature curve near 2.2 K. By 1927, M. Wolfke and Keesom (1927, 1928), measuring the dielectric constant of liquid helium, had noted a rapid change in galvanometer reading as their sample was cooled, which suggested the occurrence of a phase transition.<sup>28</sup> Without observing any change in appearance of the liquid, Wolfke and Keesom hypothesized there to be two phases of liquid helium, that they called “liquid helium I” and “liquid helium II,” the former above the critical temperature and the latter below it.<sup>29</sup> Keesom and other coworkers then made measurements of the heat capacity, using a thermally isolated calorimeter.<sup>30</sup> Finally, in 1932, Keesom and K. Clusius obtained data points which appeared to rise to a finite maximum value and then jump to a much lower value – about one third that of the maximum.<sup>31</sup> They accordingly assigned

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<sup>27</sup> Kamerlingh Onnes and Boks (1924), van Urk, Keesom and Kamerlingh Onnes (1926), Dana and Kamerlingh Onnes (1926), Wolfke and Keesom (1927, 1928), Keesom and Wolfke (1927, 1928), Keesom and Clusius (1931), Keesom and Keesom (1932) and Keesom (1933). During the period immediately after Kamerlingh Onnes’s retirements in 1922, Keesom and W. J. de Haas shared the laboratory’s directorship. Keesom was responsible for the cryogenic plant and studies of the properties of helium and other gases, as well as the thermal properties of solids. De Haas was in charge of studies of electric, magnetic, and optical properties of materials at low temperatures. Keesom assumed the full directorship upon Kamerlingh Onnes’s death in 1926. A study of the methodology of this laboratory under Kamerlingh Onnes has been made by Gavroglu and Goudaroulis (1988a).

<sup>28</sup> In this early experiment, a galvanometer in the arrangement for maintaining compensation in the apparatus was seen to move suddenly at about 2.2 K. As Keesom later remarked, “...while the temperature was changing slowly, the galvanometer made a sudden important move, so that the idea of phase transformation going on in the liquid helium was definitely urged upon [the observer]” (Keesom 1942, p. 212).

<sup>29</sup> The first report of a *visible* difference between these two phases, by McLennan, Smith and Wilhelm (1932) was not made until about four years later; a liquid helium column was observed to bubble, then change appearance as the bubbling stopped, at which point the curvature at the edge of the meniscus appeared negligible. In 1923, J. C. McLennan had started an important center for low temperature research in Toronto.

<sup>30</sup> Successive, very small amounts of heat were added to the helium sample, each changing its temperature by roughly one tenth of one Kelvin (and by somewhat smaller amounts in the vicinity of 2.19 K) both at constant pressure (the saturation vapor pressure) and at constant volume. From such experiments a characteristic helium heat capacity curve slowly emerged. See Dana and Kamerlingh Onnes (1926), Keesom and Clusius (1932) and Keesom and Keesom (1932). Leo Dana was visiting Leiden from Harvard and returned to America shortly after these first observations were made.

<sup>31</sup> Keesom and Clusius (1932).

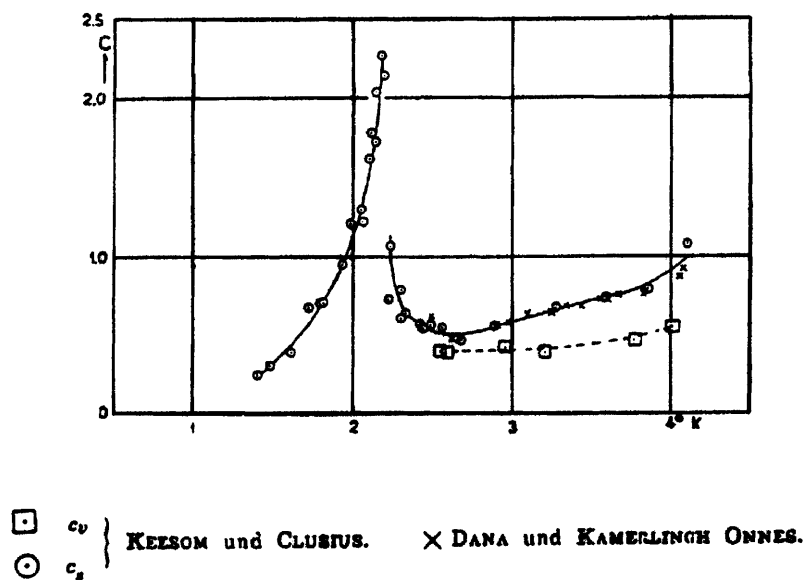


Fig. 1. The curve of heat capacity,  $C$ , versus temperature in  $K$  for liquid helium

a discontinuous curve to the data (see Fig. 1). Because its shape resembled the Greek letter “ $\lambda$ ,” this new transition was called the “lambda transition.”<sup>32</sup>

In 1933, Keesom first derived an important expression for the rate of change of pressure with respect to temperature, in terms of heat capacity. He began by considering a thermodynamic cycle in which there is no net change in entropy (see Fig. 2). Keesom noted that, since no latent heat was observed in passing along the lambda curve, the total change in entropy can be written as:

$$\left(\frac{\partial S}{\partial T}\right)_{p_{II}} dT + \left(\frac{\partial S}{\partial p}\right)_{T_{II}} dp - \left(\frac{\partial S}{\partial T}\right)_{p_I} dT - \left(\frac{\partial S}{\partial p}\right)_{T_I} dp = 0, \quad (2.1)$$

(where  $T$  is temperature,  $S$  is entropy,  $p$  is pressure and the subscripts  $I$  and  $II$  refer to values for the phases, helium  $I$  and helium  $II$ , respectively). He then used the identities  $\left(\frac{\partial S}{\partial T}\right) = \frac{c_p}{T}$  and  $\left(\frac{\partial S}{\partial p}\right) = -\left(\frac{\partial v}{\partial T}\right)$  (where  $c_p$  is the heat capacity at constant pressure and  $v$  the volume) to eliminate the derivatives of entropy in Eq. (2.1), and solved for the rate

<sup>32</sup> In later experiments, measurements of the specific heat were made with added precision, over temperature intervals as small as 0.0067 K – again by reading galvanometer deflections – confirming previous experimental results; see Keesom and Keesom (1932) and Keesom (1933). In the 1932 paper of Keesom and his daughter Anna Petronella Keesom the term “lambda point” was first used, with the comment: “According to a suggestion made by Prof. Ehrenfest we propose to call that point, considering the resemblance of the specific heat curve with the Greek letter  $\lambda$ , the lambda point”; Keesom and Keesom (1932, p. 742).



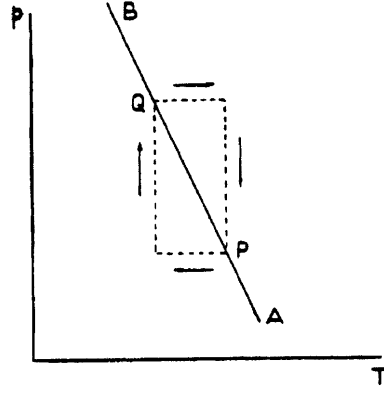


Fig. 2. The cycle, in the plot of pressure,  $p$ , versus temperature,  $T$ , considered by Keesom (1933)

of change of pressure with respect to temperature. Evaluating the result at the transition point yielded:

$$\left(\frac{dp}{dT}\right)_\lambda = \frac{c_{pII} - c_{pI}}{T \left\{ \left(\frac{\partial v}{\partial T}\right)_{pII} - \left(\frac{\partial v}{\partial T}\right)_{pI} \right\}}. \quad (2.2)$$

Introducing the relative expansion coefficient,  $\alpha = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p$ , Keesom wrote Eq. (2.2) more compactly as

$$\left(\frac{\partial p}{\partial T}\right)_\lambda = \frac{\Delta c_p}{Tv\Delta\alpha} \quad (2.3)$$

(where  $\Delta$  indicates the change of values across the transition point, *e.g.*  $\Delta c_p = c_{pII} - c_{pI}$ ). Interpreting the heat capacity curve, Fig. 1, as discontinuous enabled “the jump in the expansion coefficient to be calculated from the inclination of the lambda curve in the  $p - T$  diagram and the jump in the specific heat” (Keesom 1933, p. 149). This result was published, in English, in the Dutch publication *Verhandelingen der Koninklijke Akademie van Wetenschappen te Amsterdam* in 1933.<sup>33</sup>

The Ehrenfest classification of phase transitions was presented, in German, in the same volume. It was introduced expressly to accommodate the difference between the helium transition and transitions previously observed in other fluids: the lack of any entropy difference or volume difference as the transition point was passed. Ehrenfest took a simple, yet strict mathematical approach to the problem. He considered surfaces

<sup>33</sup> This paper was published as part of the proceedings of the meeting of the Dutch Royal Academy of Science of February 25, 1933. They also were published the same year in *Communications from the Physical Laboratory of the University of Leiden* (as was regularly done with articles by those working at the Laboratory) as Supplement 75a. Ehrenfest’s paper, mentioned directly below, was Supplement 75b.

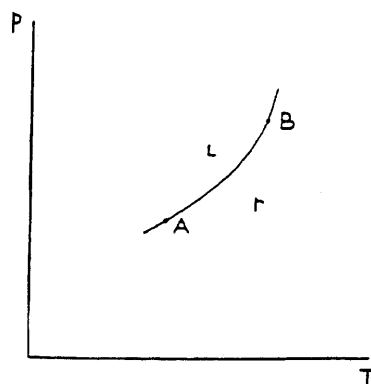


Fig. 3. A typical curve connecting two points, A and B, in the pressure–temperature plane, corresponding to a surface of constant Gibbs free energy. L and r signify the regions to the left and right of this curve

of constant Gibbs free energy,  $Z(T, p) \equiv G = U - TS + pv$  (where, again,  $T$  is temperature,  $S$  is entropy,  $p$  is pressure,  $v$  is volume and  $U$  is energy), which possess continuous derivatives away from transition points: in the  $p - T$  plane these appear as curves (see Fig. 3). When at least one first derivative of  $Z$  is discontinuous, so that the  $Z$ -surface “is *kinked*” (“*geknickt ist*” in his words), these kinks in  $Z$  were called “first-order discontinuities” (“*Discontinuität erster Ordnung*”; see Fig. 4a).<sup>34</sup> “Second-order discontinuities” (“*Discontinuität zweiter Ordnung*”) were said to arise when neither  $Z$  nor any of its first derivatives are discontinuous but there is a jump in a second derivative (see Fig. 4b). Ehrenfest similarly noted a general class of “distinct higher-order discontinuous curves” (“*Discontinuitäts-Curven verschieden hoher Ordnung*”). Phase transitions were then classified into “orders” on the basis of the behavior of the Gibbs free energy. Ehrenfest called phase transformations where  $G(\equiv Z)$  has first-order discontinuities “first-order phase-transitions” (“*Umwandlungen erster Ordnung*”); for these – the ordinary phase transitions – there is a jump in entropy,  $S = -\left(\frac{\partial G}{\partial T}\right)_p$ , or volume,  $v = \left(\frac{\partial G}{\partial p}\right)_T$ , at the transition point.<sup>35</sup> Similarly, he called those transitions with associated second-order discontinuities “second-order phase transitions” (“*Umwandlungen zweiter Ordnung*”); for these – as appeared at the time to be the case for liquid helium – there is *no* change in entropy or volume as the transition point is passed (since these first derivatives are continuous) but there *is* a change in heat capacity,  $c_p = \left(\frac{\partial^2 G}{\partial T^2}\right)_p$ , or other second derivatives. Ehrenfest similarly mentioned “higher-order phase transitions”

<sup>34</sup> There was no elaboration of the meaning of “*discontinuität*,” *i.e.* jump, but from the context of his discussion it can be assumed that Ehrenfest intended the ordinary sense of the term used in calculus.

<sup>35</sup> Ehrenfest used the letter “ $G$ ,” rather than “ $Z$ ,” to represent the Gibbs free energy in the physical rather than merely mathematical context.

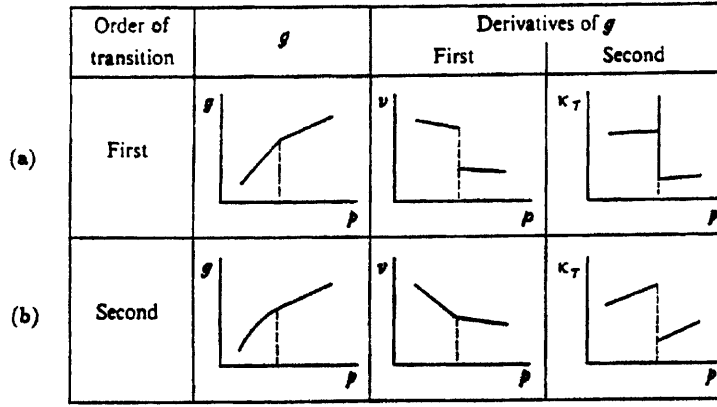


Fig. 4a, b. The behavior of the Gibbs free energy  $G$  and its derivatives during (a) first-order transitions, and (b) second-order transitions

(“*Phasenumwandlungen höherer Ordnung*”) but studied only the first and second-order phase transitions specifically.<sup>36</sup>

Having laid out this classification scheme, Ehrenfest (1933) addressed the question of the analog for second-order transitions of the Clapeyron equation

$$\frac{Dp}{DT} = \frac{Q}{T(v_r - v_l)} \quad (2.4)$$

(where  $Q$  is the latent heat, the subscripts  $r$  and  $l$  refer to the phases to the right and left of the critical temperature respectively, with temperature increasing to the right, and  $D$  indicates a total derivative).<sup>37</sup> The Clapeyron equation, which holds in the case of the usual, first-order transitions, cannot be applied to second-order transitions because it becomes indeterminate: the right-hand side becomes zero over zero, since there is both no latent heat and zero change in volume.

Ehrenfest proceeded as follows. Because the change in the Gibbs free energy, ( $G$ ), energy, ( $U$ ), the entropy change, ( $S$ ), and the volume change, ( $V$ ), are all in second-order transitions, the change in the Gibbs free energy was written:

$$((G)) = Dp \left( \left( \frac{\partial G}{\partial p} \right) \right) + DT \left( \left( \frac{\partial G}{\partial T} \right) \right) = 0 \quad (2.5)$$

<sup>36</sup> This scheme was to dominate the classification of phase transitions for the next twenty years. Later authors discussed higher-order transitions more explicitly; see, for example, Pippard (1957, p. 147).

<sup>37</sup> From here on, the Clausius-Clapeyron equation will be referred to simply as the “Clapeyron equation”; Clausius (1850) made minor changes in Clapeyron’s (1834) result to arrive at this particular form of the equation; see Partington (1949, p. 181).

(where pairs of doubled parentheses indicate a second-order change), much like the entropy in Eq. (2.1). Solving for the ratio of changes in pressure and temperature, Ehrenfest obtained:

$$\frac{Dp}{DT} = - \frac{\left(\left(\frac{\partial G}{\partial T}\right)\right)}{\left(\left(\frac{\partial G}{\partial p}\right)\right)}. \quad (2.6)$$

After writing the derivatives of  $G$  with respect to  $T$  and  $p$  in terms of derivatives of  $v$ , this became:

$$\frac{Dp}{DT} = - \frac{\left(\left(\frac{\partial v}{\partial T}\right)\right)}{\left(\left(\frac{\partial v}{\partial p}\right)\right)}. \quad (2.7)$$

Writing the (zero) entropy change in terms of derivatives with respect to  $T$  and  $p$ , he similarly found the analog to the Clapeyron Eq. (2.4):

$$\frac{Dp}{DT} = - \frac{\left(\left(\frac{\partial S}{\partial T}\right)\right)}{\left(\left(\frac{\partial S}{\partial p}\right)\right)} = \frac{(c)}{T \left(\left(\frac{\partial v}{\partial T}\right)\right)}. \quad (2.8)$$

This is exactly the relation Keesom (1933) observed to hold for his heat-capacity measurements (but presented in a different notation from Keesom's Eq. (2.3)). Equations (2.6–2.8) constitute Ehrenfest's theory of second-order phase transitions.

Ehrenfest remarked that the second-order transitions are similar to the transition of a magnet to the ferromagnetic phase. Unlike the case of ordinary phase transitions, in this case it seemed to him impossible to have two coexisting “spatially beside one another” (“*raumlich nebeneinander*”) and Ehrenfest remarked that the “would very much like to be able better to formulate and understand this characteristic difference in relation to the ‘usual’ phase transition.”<sup>38</sup> In a postscript, Ehrenfest mentioned on-going research by A. J. Rutgers, explicitly applying these results to superconductors.<sup>39</sup> The question of phase coexistence and the application of these results were central to further discussions, which began immediately, of second-order phase transitions.

<sup>38</sup> The original German reads “*Ich würde sehr wünschen diesen charakteristischen Unterscheid gegenüber der ‘gewöhnlichen’ Phasenumwandlung besser formulieren und durchschauen zu können.*” Others would soon seek answers to this question; see Sect. 3.

<sup>39</sup> As C. J. Gorter later recalled, “Keesom, who had attracted Ehrenfest’s attention to this problem, applied the formalism to the transition line between helium II and helium I and Rutgers suggested (at Ehrenfest’s colloquium) its application to superconductivity”; see Gorter (1964, p. 4). For more on Ehrenfest’s Wednesday evening colloquium, see Casimir (1977b, pp. 76–77). Rutgers had obtained his Ph. D. under Ehrenfest at Leiden in 1930. His thesis was concerned with the theory of thermoelectricity in crystals; see Casimir (1977b, p. 80).

### 3. Initial Reception and First Application of the Classification

The experiments of Keesom and the classification scheme of Ehrenfest gave rise to vigorous thermodynamical study of this new class of phase transitions. There were three immediate reactions to Ehrenfest's (1933) paper. First, Otto Halpern (1933) tried to explain, by a simple thermodynamical argument involving no explicit calculations, Ehrenfest's claim of a lack of coexistence of phases during second-order transitions. Second, Rutgers (1934) published his aforementioned work applying Ehrenfest's approach to superconductors. Third, the duo of Eduard Justi and Max von Laue (1934) questioned the well-definedness of Ehrenfest's second-order phase transitions.

Halpern's (1933) argument was based on three assumptions: (i) there are two possible phases 1 and 2, each without any discontinuous properties, (ii) only phase 1 is stable on one side of the transition point, on the other side only phase, 2, and (iii) at the transition point the two phases 1 and 2 have equal values of  $Z$ ,  $s$ ,  $v$  (and so also of the internal energy  $E$ ). On the basis of these assumptions, he directly concluded that there can be no phase coexistence in second-order phase transitions since two phases can be simultaneously stable only if there is a discontinuity in  $E$ . In response, E. A. Guggenheim (1934) showed this reasoning to fail by *reductio ad absurdum*. He argued that Halpern's assumptions, which he gave the form (i)–(iii) describe a “hybrid transition point that is thermodynamically impossible,” as follows. He considered the behavior of the Gibbs free energy,  $Z_i$ , as temperature is varied and pressure is kept constant, expressing  $Z$  in a Taylor series expansion to second-order in temperature:

$$Z_i = Z_i^0 - S_i^0(T - T^0) - \frac{c_i^0}{2T^0}(T - T^0)^2 \quad (3.1)$$

(where the superscript 0 indicates the critical-point value, the subscript  $i = 1$  or  $2$  indicates the phase and  $\bar{T}$  lies between  $T^0$  and  $T$ ). Assumption (iii) gives  $Z_1^0 - Z_2^0 = 0$  and  $S_1^0 - S_2^0 = 0$ . Evaluating Eq. (3.1) at the critical temperature then gave

$$Z_1 - Z_2 = -\frac{c_1^0 - c_2^0}{2T^0}(T - T^0)^2. \quad (3.2)$$

But since assumption (i) states that there is no discontinuity in  $c_1$  and  $c_2$ , it follows that  $Z_1 - Z_2$  does not change sign at  $T^0$ . Hence, whichever phase is stable below  $T^0$  must remain stable above  $T^0$ , in contradiction to Halpern's assumption (ii). Guggenheim thus showed that Halpern's simple argument did not properly address Ehrenfest's coexistence query.

Like Ehrenfest's origin 1933 piece, the direct extension by Rutgers of Ehrenfest's results into the realm of superconductivity also received attention.<sup>40</sup> Rutgers (1934)

<sup>40</sup> As H. B. G. Casimir (1977a) recalled: “Rutgers took a very bold step: he applied Ehrenfest's thermodynamics of transitions of the second kind to a superconductor. he argued as follows ... . If we apply thermodynamics, assuming that in superconductor the magnetic induction  $B$  is zero, then one can derive the equation [for ((c))]" (Casimir 1977a, p. 176); see Eq. (3.5) below.

began by reproducing part of Ehrenfest's original derivation of the relation (Eq. 2.8) between the jump in specific heat and the slope of the transition curve, for the case of a superconducting system. Not surprisingly, Rutgers's result had the form of Ehrenfest's relation (Eq. 2.6):

$$\frac{dH}{dT} = - \frac{\left(\left(\frac{\partial Z}{\partial T}\right)\right)}{\left(\left(\frac{\partial Z}{\partial H}\right)\right)} \quad (3.3a)$$

(where  $Z$  is the Gibbs free energy and  $H$  is the applied magnetic field). Since  $dZ = -\eta dT - \sigma dH$  (where  $\eta$  is the entropy and  $\sigma$  is the magnetic moment), this is

$$\frac{dH}{dT} = - \frac{((\eta))}{((\sigma))}, \quad (3.3b)$$

the right hand side of which is indeterminate.<sup>41</sup> Rutgers applied L'Hôpital's rule to Eq. (3.3b) to obtain

$$\left(\frac{dH}{dT}\right)^2 = - \frac{\left(\frac{\partial \eta}{\partial T}\right)_s - \left(\frac{\partial \eta}{\partial T}\right)_n}{\left(\frac{\partial \sigma}{\partial H}\right)_s - \left(\frac{\partial \sigma}{\partial H}\right)_n} \quad (3.4)$$

because  $\left(\left(\frac{\partial \eta}{\partial H}\right)\right) = \left(\left(\frac{\partial \sigma}{\partial H}\right)\right) = 0$ . Further, assuming that the magnetic induction,  $B$ , remains zero in the superconducting phase he arrived at the compact expression

$$\left(\frac{dH}{dT}\right)^2 = \frac{4\pi d((c))}{T}, \quad (3.5)$$

the analog for superconductors of Ehrenfest's relation (Eq. 2.8) known as "Rutgers's formula."<sup>42</sup>

Reacting to Rutgers's result, in a paper actually published before Rutgers's article, Gorter (1933a) showed this result to be "identical to the statement that the second law of thermodynamics applies to the magnetic disturbance, in spite the fact, that the dying out of the persistent currents in the superconductor appeared at first to be an irreversible phenomenon" (Gorter and Casimir 1934a, p. 308).<sup>43</sup> Gorter considered a cyclic process in the (externally applied) magnetic field – temperature ( $H - T$ ) plane (see Fig. 5). He then used the first law of thermodynamics in light of observations by Keesom and Kok (1934)

<sup>41</sup> Evaluating the right hand side of Eq. 3.3b leaves one with 0/0, as was the case with Eq. (2.4), because there is no change of entropy or magnetic moment.

<sup>42</sup> For an example of this usage, see London (1950, p. 20).

<sup>43</sup> "Rutgers applied in an intuitive way a formula Ehrenfest had derived for transitions of the second kind ... and Gorter worked out this idea in greater detail" (Casimir 1977b, p. 339). Gorter recalled that: "Rutgers suggested ... its application to superconductivity. This induced me to consider this ... problem in some more detail" (Gorter 1964, p. 4). The work of Gorter mentioned is that in Gorter (1934a). The experimental work confirming this result, mentioned by Casimir, is that of Keesom and Kok (1934) and Keesom and P. H. van Laer (1938). This work is also discussed in Keesom (1942); see Gavroglu and Goudaroulis (1984) for a history of work on superconductivity as it relates to the current subject.

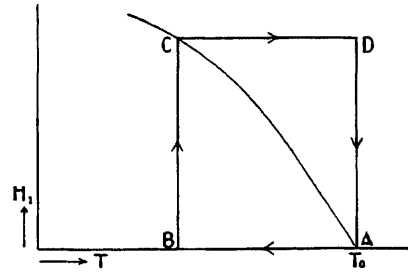


Fig. 5. The cycle, in the plot of external magnetic field,  $H_1$ , and temperature,  $T$ , considered by Gorter (1934a)

that the heat of transformation at the point (A in Fig. 5) of highest temperature and lowest field is zero. Assuming that the susceptibility of the “normal” (non-superconducting) metal phase is zero and noting that there is zero change in entropy for this cycle, this gave:  $dQ = dE - H_1 d\sigma$  (where  $Q$  is heat,  $E$  is system energy,  $\sigma$  is entropy and  $H_1$  is the value of the applied magnetic field). The direct application of the second law of thermodynamics to the cycle then yielded Rutgers’s formula, Eq. (3.5). In this sense Gorter showed Rutgers’s result to follow from second law of thermodynamics (together with the above-mentioned background assumptions).<sup>44</sup>

Gorter claimed these results showed that normal and superconducting phases *can* co-exist next to one another in space (see Gorter 1933a, p. 383).<sup>45</sup> This conclusion contrasted with Ehrenfest’s hypothesis that there is no phase coexistence in second-order phase transitions. Gorter and H. B. G. Casimir then together showed that, for certain shapes such as that of the sphere, one part of the conductor could be in the normal phase while another is superconducting.<sup>46</sup> They also speculated as to the mechanisms

<sup>44</sup> Gorter (1934a). This is discussed in Gavroglu and Goudaroulis (1984, pp. 141–144) who, it should be noted, failed to state that lambda transitions are not second-order phase transitions in Ehrenfest’s sense.

<sup>45</sup> In a note to *Nature*, Gorter (1933b) also suggested that the assumption  $B = 0$  made by Rutgers is a *general* characteristic of superconductors. This hypothesis was to be of great significance in the study of superconductivity. W. Meissner and R. Ochsenfeld (1933) showed that the state of the magnetic field in the interior of a metal in a superconducting state is zero whether the superconducting state was reached in an external magnetic field or not; before this discovery it was predicted (by classical electromagnetism) that reaching a field-free state would require being brought to a superconducting state in a *field-free* environment. Gorter sent a copy of his 1933(b) paper to Meissner with the note: “It is remarkable, apropos of my thermodynamic considerations, that Dr. Casimir as well as I had, before your measurements, conjectured that  $B = 0$  ...” (Hoddeson, *et al.* 1992, p. 500); see also Dahl (1986, 1992).

<sup>46</sup> Gorter’s (1933a) results were initially obtained for ellipsoidal geometries. It is an important fact that Gorter and Casimir (1934a) extended these results to general geometries. Both Gorter and Casimir were recent Ph.D.’s: Gorter received his degree under de Haas in 1932; Casimir received his degree under Ehrenfest in 1931 and had recently returned to Leiden from a stint working under

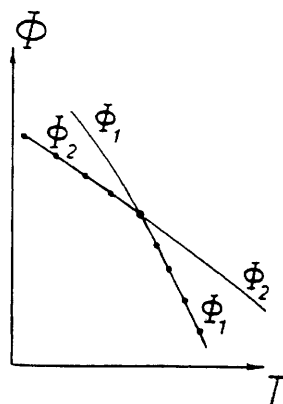


Fig. 6. Two curves of constant Gibbs free energy,  $\Phi_1$ , and  $\Phi_2$ , involved in a first-order phase transition. The dotted portion of each line indicates the stable surface at each temperature,  $T$ , according to Justi and von Laue (1934)

underlying phase coexistence, namely the formation of “superconducting rings inside the body.”<sup>47</sup>

The third reaction to Ehrenfest’s 1933 work was to the classification scheme itself: Eduard Justi and Max von Laue (1934) argued that Ehrenfest’s notion of a second-order transition was *thermodynamically impossible*. Since second-order transitions were the primary new class considered by Ehrenfest and the only new class an example of which was believed to have been observed at all, this was a significant challenge to the Ehrenfest classification.<sup>48</sup> In following Justi and von Laue’s argument, one is to extend across all values of  $T$  a pair of surfaces of constant  $G$ , that correspond to curves in the  $p - T$  diagram each representing a phase, for a system which putatively undergoes a second-order transition. By the definition of a second-order transition, these curves osculate at the critical point *rather than crossing* as in an ordinary phase transition of the first-order (see Fig. 6). There are then two possibilities in the case of the second-order transition: either the curves touch and separate, or they merge at the critical point in a “fork” (see Fig. 7a, b). In either case, the lower of the two curves will correspond to the stable phase. In the first case, there can be no phase transition because the system will always be found in the lower, therefore stable phase; no equilibrium will obtain between phases. In the second case, there certainly is only one phase beyond the point of osculation, so that, again, there cannot be any transition since the system will always have been in the lower phase.

Wolfgang Pauli. Gorter held a position at the Teyler Foundation in Haarlem, Holland from 1931 to 1936.

<sup>47</sup> This idea is discussed in London (1950, p. 15).

<sup>48</sup> The paper of Justi and von Laue (1934) was received by the *Physikalische Zeitschrift* on September 14, 1934.



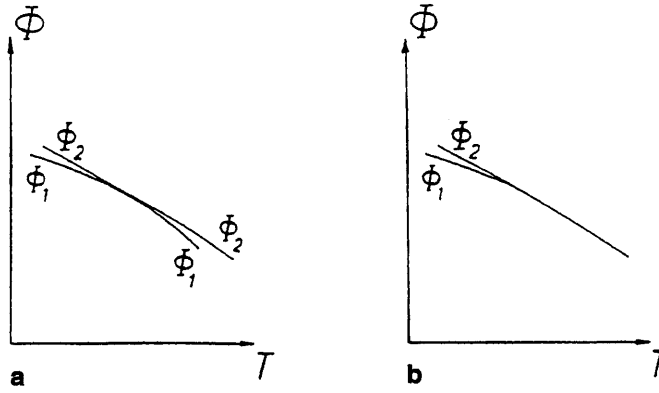


Fig. 7a, b. Pairs of curves of constant Gibbs free energy,  $\Phi_1$  and  $\Phi_2$ , involved in a second-order phase transition: (a) for the case of touching curves; (b) for the case when the curves merge a in “fork”

At the September, 1934 meeting of the German Physical Society in Bad Pyrmont, von Laue raised this objection in the context of the transition between normal and superconducting phases. Gorter pointed out to von Laue that, although he and Casimir had not addressed themselves to the Justi-Laue criticism of the Ehrenfest scheme, they effectively had just shown in a short communication that, for superconductors, the curves of Justi and von Laue are not *themselves* well-defined.<sup>49</sup> This was accomplished as follows. Gorter and Casimir (1934b) introduced a parameter corresponding to the fraction,  $x$ , of electrons in the normal phase.<sup>50</sup> If one follows the curve of the (lower temperature) superconducting phase upward from  $T = 0$ , where  $x$  is 0, this monotonically increasing order parameter becomes 1 at the critical temperature,  $T = T_c$ . Extending the curve of the superconducting phase above the temperature of osculation requires the fraction of particles in the superconducting phase,  $1 - x$ , to be *negative*, a physical absurdity. Thus, the curve representing the superconducting phase cannot be extended beyond the critical temperature. The system must therefore change phase from the initially stable superconducting phase to the remaining normal phase after the point of osculation.

<sup>49</sup> “Laue and Justi had just attacked the possibility of Ehrenfest’s transitions of the second order arguing that the free energies, or Gibbs functions, of the two phases would osculate in the transition point so that above and below the osculation point the same phase would be stable. Now this question was just answered by ... Casimir and myself” (Gorter 1964, p. 5). Gorter attended the Bad Pyrmont meeting together with Keesom despite concerns about the new political climate in Germany; see Gorter (1964).

<sup>50</sup> This was one of the first uses of the concept of the “order parameter” to solve a physical problem. It was also an element in Gorter and Casimir’s “two-fluid” theory – one of the first of such theories of superconductivity.

The Gorter-Casimir counter-argument was readily accepted and reproduced in subsequent textbook discussions on the subject.<sup>51</sup> Indeed, von Laue's own later text, *The Theory of Superconductivity*, contains a discussion of the failure of the requisite phase curve to exist, indicating his own acceptance of Gorter and Casimir's position.<sup>52</sup> By the mid-1930s, the Ehrenfest classification and theory of second-order phase transitions were, it was felt, solidly established as adequate to the task of capturing the new sort of phase transition first observed in liquid helium and superconductors. A subsequent thermodynamical study even extended Ehrenfest's results to "diffuse transitions," where one cannot speak of a specific transition point; results for the case of diffuse transitions analogous to those Ehrenfest and Rutgers had obtained for the second-order transitions were achieved, showing that work to be broadly and practically applicable.<sup>53</sup>

#### 4. Acceptance, Extension and Final Formulation

The Ehrenfest classification was first successfully advocated in journals; then textbooks presented the classification in its entirety, including the higher-order transitions, at times at greater length than that of Ehrenfest's (1933) own presentation. Mounting theoretical and experimental evidence, however, eventually showed the lambda transitions to fall outside the original Ehrenfest scheme. This led to extensions of the scheme during the 1950s.<sup>54</sup> The extended classification came into widespread use, and the original Ehrenfest scheme was hybridized with alternative schemes during the 1960s.<sup>55</sup> I will show that there were three stages in this evolution of the Ehrenfest classification: (i) initial acceptance, while growing uncertainty regarding the nature of the helium lambda transition was considered insufficient to put the scheme in question (before roughly 1950), (ii) extension of the classification, in order to accommodate the sort of singularities accompanying the two-dimensional Ising model and the helium lambda transition (from roughly 1950 to 1960) and (iii) final acceptance of the extended scheme and the formulation of hybrid schemes (after 1960).

Immediately after its publication, the Ehrenfest classification was much discussed in journals, as we have seen in the previous section. In 1935, it was treated in a review article by P. W. Bridgman, who said: "The great variety of phenomena offered by ... small scale anomalies shows that a classification of transitions into 'first, second, third' etc. kinds is to a certain extent at present a matter of convenience, reflecting more or less

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<sup>51</sup> For example, Roberts and Miller (1951).

<sup>52</sup> Von Laue (1952, p. 108).

<sup>53</sup> Rutgers and Wouthuysen (1937a, b). One can, strictly speaking, only have a transition point when one is dealing with infinite systems at full internal equilibrium. When either of these ideal conditions is not met to a good approximation the transition is considered diffuse.

<sup>54</sup> One of the most influential was that of Pippard (1957).

<sup>55</sup> That of Fisher (1967) is an important example.

closely the experimental accuracy” (Bridgman 1935, p. 22).<sup>56</sup> By 1937 an early textbook presentation was given (Epstein 1937). The first alternative to Ehrenfest’s classification, the Landau-Lifshitz classification, appeared in 1938 in the first edition of the now classic text of L. D. Landau and E. Lifshitz, *Statistical Physics*. Its distinctions, based on symmetry considerations, were fewer but overlapped considerably with Ehrenfest’s.<sup>57</sup> The Landau-Lifshitz classification had far less influence on early discussions than did the Ehrenfest scheme.<sup>58</sup>

During the 1940’s, elements of the Ehrenfest classification were questioned. Keesom (1942), in his seminal text *Helium*, questioned the apparent discontinuity at the liquid helium phase transition.<sup>59</sup> He believed that thermal agitation (which is always present at non-zero temperatures) ensures a “rounding off” the helium specific heat curve so as to render it continuous.<sup>60</sup> Soon added to this was Lars Onsager’s (1944) discovery of a solution to the two-dimensional Ising model problem, which pointed out a lacuna

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<sup>56</sup> The small-scale anomalies Bridgman found in solids were sharp, reversible discontinuities (within experimental limitations) in derivatives of volume and energy (Bridgman 1935, p. 22). He, like the scientific community in general, had cautiously accepted the Ehrenfest classification, being mindful of current experimental limitations. On the lambda transition, Bridgman wrote: “Ehrenfest ... proposed that such discontinuities [as observed in liquid helium] should be called ‘transitions of the second kind,’ a name that has apparently been accepted” (*ibid.*, p. 21). Ehrenfest called these “second order transitions,” but the two terms did not differ in meaning. In referring to “transitions of the second *kind*,” Bridgman used, as many later would, a variant of Ehrenfest’s original terminology.

<sup>57</sup> The Landau-Lifshitz scheme remained the only alternative to the Ehrenfest classification before 1950. Landau and Lifshitz (1938) identified “two possible kinds of transition associated with a change of symmetry of a body. In the first of these the probability distribution representing the system changes abruptly together with the sudden change from one symmetry to another. Transitions of this kind are those between two phases of different symmetries, and at the actual transition point (which we shall call the *phase transition point*) we have two bodies in different states, in equilibrium ... . The other kind of transition is one in which although a number of symmetry elements appear or disappear abruptly, the probability distribution in the lattice differs only very slightly before and after the transition... . We shall call this sort of transition a *Curie point*; it is sometime called a ‘phase transition of the second kind,’ or a  $\lambda$ -point ... . [It] usually occurs for transitions between ordered and disordered states” (Landau and Lifshitz 1938, pp. 204–205). The phrase “phase transition of the second kind” again appears to be a reference to Ehrenfest’s term “second order phase-transition.” At the time, Landau and Lifshitz’s “Curie point” appeared to be coextensive with Ehrenfest’s second-order transition, though the manner of distinguishing classes was different. Also, probably because of an overlap with Ehrenfest’s, Landau and Lifshitz’s scheme was perceived by at least one later author to be extension of the Ehrenfest classification; see Izuyama (1967).

<sup>58</sup> This remained so until the two schemes were hybridized; see, for example, Fisher (1967).

<sup>59</sup> Keesom (1942, p. 257).

<sup>60</sup> “[The] fluctuations may round off the ideal discontinuity ... the peak .. will appear to be rounded off at the top” (Keesom 1942, pp. 260–261); see also Keesom (1936, Section 6e). Notably, a similar claim was forwarded by theorists decades later, in particular by J. M. Blatt, S. T. Butler and M. R. Schafrath (1955, 1956).

in the Ehrenfest classification: the solution implied the presence of infinities at phase transitions, whereas only phase transitions involving jump discontinuities were recognized by the Ehrenfest scheme. However, many at the time considered the Lenz-Ising model to be over-simple in its treatment of interatomic forces, so an immediate reworking of the entire classification was not widely felt necessary. After World War II, E.F. Lype (1946) arrived at results differing (by a factor of 2) from Ehrenfest's equations for second-order transitions by approaching thermodynamic equilibria "of higher order" by Taylor series.<sup>61</sup> But Bridgman (1946) showed that this difference arose because Lype had, somewhat unusually, assumed that second-order equilibria occur at isolated points rather than along a curve.<sup>62</sup>

Jacob Frenkel (1946) was exceptional in flatly denying the reality of second-order transitions (in Ehrenfest's sense) during this period.<sup>63</sup> E. A. Guggenheim (1949) differed with Ehrenfest only as to whether higher-order transitions are genuine changes of phases.<sup>64</sup> The strong agreement between the experimental observations of Keesom and coworkers and Ehrenfest's analog to the Clapeyron equation continued to lead authors to accept Ehrenfest's characterization of the lambda transition.<sup>65</sup> The original Ehrenfest classification was generally assumed sufficient to cope with all observed phase transitions.<sup>66</sup> The outstanding issue remained how practically to classify transitions which

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<sup>61</sup> This line of investigation was later taken up by Fischer (1957).

<sup>62</sup> Bridgman noted that: "the difference ... between the results of Ehrenfest and of Lype is not to be attributed to any failure of mathematical rigor on the part of Ehrenfest, but on two different conceptions of the nature of physical phenomena, which are essentially incompatible with one another" (Bridgman 1946, p. 425). By that time, Bridgman had come to believe that "[e]xperimentally second-order transitions appear to exist" (Bridgman 1946, p. 427) and that the liquid helium transition is a "physical system to which Ehrenfest's assumptions apply" (*ibid.*, p. 426).

<sup>63</sup> Frenkel stated that: "[S]uch transitions have never been observed and cannot correspond to a stable equilibrium between the corresponding phases." Adopting Landau and Lifshitz's (1938) classification, Frenkel was concerned primarily with changes in the degree of order.

<sup>64</sup> Guggenheim expressed the view that "there is a temptation to regard a *transition of the second order* as a kind of *phase change*. The expression *phase change of the second-order* has been used, but as it has in the past led to considerable confusion it is better avoided" (Guggenheim 1949, p. 283). He explicitly discussed transition of first, second and third order. Regarding the last, he added that "[i]t is possible, but not certain, that transitions of the third order exist" (Guggenheim 1949, p. 288).

<sup>65</sup> "This agreement, together with the discontinuity observed in the specific heat, establishes the phase change in liquid helium as a second-order transition" (Roberts and Miller 1951, 392–398). Roberts and Miller discussed the data of Keesom and Clusius (1932) and displayed the values of the variables for the left-hand side and right-hand side of the equation as verification of Eq. (2.3). They also noted that the superconducting transition in zero magnetic field is second-order in Ehrenfest's sense. This shows that by that time at least one genuine second-order transition was known to exist.

<sup>66</sup> As late as 1954 the lambda transition of helium was being called a second-order transition: "at the  $\lambda$ -point of liquid helium the derivative of the specific volume (or density) and the specific heat change discontinuously. Ehrenfest has suggested the name 'phase transformations of the

might involve infinities like Onsager's solution for the two-dimensional Ising model. Earlier concerns about not only the physical possibility of second-order transitions, but also their reality, had been laid to rest, however.

The second, pivotal stage of the evolution of the Ehrenfest scheme, from roughly 1950 to roughly 1960, involved its extension and reinterpretation to accommodate phase transitions falling outside its original taxonomy. The helium transition was increasingly suspected by careful observers of having an *infinite* free-energy second derivative, and so definitely not being an Ehrenfest second-order transition. This suspicion had grown since the discovery of an infinity in Onsager's (1944) solution. In 1951, Tisza suggested that the heat capacity at the lambda helium transition also approaches infinity. Tisza (1951) also presented his own classification of phase transition – the second alternative to Ehrenfest's – in conjunction with a new theory of phase transitions.<sup>67</sup> Despite the ready incorporation of infinite derivatives in Tisza's scheme, others sought to include such singularities by extending the well-known Ehrenfest scheme rather than seeking an alternative. Finally, K. R. Atkins and M. H. Edwards (1955) obtained experimental evidence of an infinity: a logarithmic term was shown to account for their data regarding the thermal expansion coefficient below the critical point. This sealed the fate of the Ehrenfest scheme in its original form: it would be supplanted by a broader scheme.

H. N. V Temperley (1956) offered the first extension of the Ehrenfest scheme, although he was uncertain as to whether transitions of the type envisioned by Ehrenfest existed; he preserved these and included transitions with associated infinities.<sup>68</sup> Tem-

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second order' for such phenomena and has shown that the transformations from the ferromagnetic to paramagnetic state at the Curie point and from normal conductivity to superconductivity are further examples" (Jackson 1954, p. 62). As noted previously, however, not Ehrenfest but Rutgers (1934) first explicitly treated transitions in superconductivity as second-order; Ehrenfest had only noted that these transitions were similar to his second-order transition. A similar presentation was given by A. H. Wilson (1957, pp. 272–281).

<sup>67</sup> Tisza's theory of phase transitions was yet more firmly grounded in the 1961 article "The Thermodynamics of Phase Equilibrium," wherein thermodynamics was given a new, broader axiomatic basis. Tisza's classification was more mathematically complex than Ehrenfest's, although it still made its distinctions on the basis of the behavior of the Gibbs free energy function.

<sup>68</sup> Temperley (1956) distinguished three classes of phase transitions, A, B and C, based on the behavior of the first derivatives of the free energy. A, when there is a finite change in 'one or both of the differential coefficients,' with respect to  $T$  or  $P$ , of the free energy (that is, Ehrenfest's first-order transitions which Temperley called, at time, "first-order transitions"); B, "Both of these first-order differential coefficients are continuous"; C, "The Taylor expansion becomes illegitimate for one or both phases" (Temperley 1956, p. 7). Temperley then went into great detail regarding the classes B and C. Class B was subdivided into two types, 1 and 2, the first being those when the first derivatives are continuous "along a finite length of the equilibrium curve" and the second being those where the first derivatives are continuous "only for a transition at ... one point, the remainder of the equilibrium curve corresponding to first-order transitions." Importantly, he commented on class B, type 2, that "[n]o such transition is known involving the variables  $P$  and  $T$ , but a quite analogous situation does occur for the transition of a superconductor to the normal state." (*ibid.*, pp. 9–10).

perely noted that there is “no reason, in principle, why some of the second or higher order differential coefficients” of the free energy “should not become ‘infinite’ ” and that the associated invalidation of the Taylor expansion “alone is enough to show that Ehrenfest’s proposed classification is incomplete” (*ibid.*)<sup>69</sup> However, A. Brian Pippard’s (1957) now classic text, *Elements of Classical Thermodynamics*, most clearly marked stage (ii) of the evolution of the Ehrenfest scheme by comprehensively extending the Ehrenfest classification. Like Temperley, Pippard supplemented the scheme to include transitions where infinities in free energy derivatives arise – such additional transitions he labeled “ $\lambda$  transitions” but, unlike Temperley, he retained Ehrenfest’s full “order” terminology.<sup>70</sup> Pippard also claimed that Ehrenfest’s third-order transitions include “the Curie points of many ferromagnets” and “the condensation of a perfect Bose-Einstein gas.”<sup>71</sup> He found “no thermodynamical reason why each of Ehrenfest’s types should not occur” (*ibid.*, pp. 138–140).<sup>72</sup> Pippard’s reinterpretation of the terms “first order,” “second-order,” etc., so as to incorporate the “lambda transitions” effectively extended the Ehrenfest scheme. Pippard’s text, and somewhat less so Temperley’s, completed the internalization of the Ehrenfest classification in extended form by the science of thermodynamics.<sup>73</sup> Though some had discomfort about using the (unextended) Ehrenfest

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<sup>69</sup> Temperley (1956) did not consider cases where anomalies arise at orders higher than the second since those with “the first discontinuity occurring in some still higher derivative ... would be extremely difficult to detect experimentally, because what are, in fact, usually observed experimentally are variations of *volume* and *heat content* with temperature and pressure, so that the plotting of such a curve ... already involves one *numerical differentiation* of the experimental results” (*ibid.*, p. 9). This is perhaps the greatest limitation of the Ehrenfest scheme in an empirical setting: the experimental error for such derived quantities is generally larger than for their directly measured counterparts.

<sup>70</sup> Pippard’s (1957) Chapter 9, “Higher-Order Transitions,” contains a presentation of the basic Ehrenfest scheme, together with a figure illustrating the behavior of the heat capacity in first, second and third-order transitions, as well as in “variants of the Ehrenfest classification.”

<sup>71</sup> “Now this classification of Ehrenfest’s, while having served a valuable purpose in pointing to a distinction between different types of transition, is of only limited application, since true second-order transitions are exceedingly unusual. It is probably true to say that of physically interesting systems (that is, excluding *ad hoc* models, of which we shall discuss one in detail) there is only one class, the superconducting transition, which bears any resemblance to an ideal second-order transition. On the other hand, there are many transitions known to occur in widely different varieties of substance which do not comfortably conform to Ehrenfest’s scheme” (Pippard 1957, 136–137). The “*ad hoc*” model, to which Pippard referred, was one sketched by Gorter to demonstrate the physical possibility of second-order transitions. Gorter and Casimir (1934b) initially gave almost no detail to this simple model. Gorter’s (1963) lectures given at the Tata Institute of Fundamental Research, Bombay, contained a fuller version, and Pippard’s (1957) own presentation of it was more elaborate yet.

<sup>72</sup> While Pippard anticipated no theoretical difficulties for an extended Ehrenfest scheme, he did state that many experiments would be needed to validate its new classes.

<sup>73</sup> Most significantly, Pippard (1957) adopted Ehrenfest’s method of using the derivatives of Gibbs free energy to determine classes.

classification scheme by this time, its utility compelled them to choose an extended version.

The third stage in the evolution of the Ehrenfest classification scheme, the use of the extended classification or of a hybrid classification, took place from roughly 1960 onwards.<sup>74</sup> One of the first texts of this period, Herbert Callen's (1960) *Thermodynamics*, presented both the Ehrenfest and Tisza classifications, with an emphasis on the latter, which Callen called "more generally applicable" (*ibid.*, p. 173). Unfortunately, one reason often given for such views was the failure of the lambda transition to find a place in the *unextended* Ehrenfest scheme. In an influential review article, Michael Fisher (1967) presented a classification of phase transitions nearly identical to that of Landau and Lifshitz, but including Ehrenfest's term "first-order transitions."<sup>75</sup> R. J. Finkelstein (1969), by contrast, followed the Ehrenfest terminology yet declared the scheme itself to be "not terribly relevant."<sup>76</sup> A. Münster (1969) presented the Ehrenfest classification in an extended version of his own, occasionally invoking Tisza's (1951, 1961) scheme.<sup>77</sup> Ultimately Münster (1970), like Fisher, lumped together all transitions

<sup>74</sup> Many followed Pippard (1957) in the continued use of the Ehrenfest terminology. For example, Callen illustrated "the specific heat of quartz in vicinity of second-order phase transition" (Callen 1960, p. 179). He succinctly presented the Ehrenfest scheme, thermodynamical relations for second-order phase transitions and even an analog of Clapeyron's equation for *third-order* phase transitions, ending with comment; "Unfortunately, no known cases of higher-order transitions of the Ehrenfest type have been found, except for the second-order transition of superconductors in zero magnetic field" (*ibid.*, p. 181). P. T. Landsberg (1961) also discussed first, second, and third-order phase transitions explicitly, including cases of both finite discontinuities and infinities; see Landsberg (*ibid.*, pp. 316–317). In these discussions, he referred to Pippard's (1957) text but failed to mention Ehrenfest's (1933) work at all. However, it was not always ignored -H. A. Buchdahl (1966) presented an extended Ehrenfest scheme and clearly identified it as such. He included the superconducting transition in zero magnetic field and  $\lambda$ -transition of helium among the second-order transitions, making clear that the lambda transition is second-order only in the *extended* scheme: "The salient point is that the mere classification of transitions according to 'order' in Ehrenfest's sense provides an incomplete characterization of the possible types of phase transitions: if a transition is of order  $m$  one must also say something about the actual nature of the discontinuity of the  $m$ th derivative of [the Gibbs free energy]  $g$  at the transition point ... whether [, for example,]  $c_p$  appears to go to infinity at the transition point ... or [is] merely one which is finite but very large" (*ibid.*, p. 182). The approach of J. Wilks (1967) was essentially the same.

<sup>75</sup> Fisher (1967) chose the term "continuous transition" for Landau and Lifshitz's "Curie point" (that is, for higher-order transitions) and commented: "The original classification of transitions, due to Ehrenfest, which essentially recognized only discontinuities in thermodynamic derivatives, rather than divergences, is inappropriate in the light of present theoretical and experimental knowledge. It seems best, therefore, to discard terminology such as 'second-order' or 'third-order' which is often confusing or uninformative" (*ibid.*, p. 617). This criticism echoed an earlier comment by Guggenheim (1949, p. 283).

<sup>76</sup> Finkelstein (1969, p. 52)

<sup>77</sup> In addition, he presented graphical examples fitting both the original and extended Ehrenfest schemes. Shortly thereafter, he was more critical of the scheme, while continuing to use Ehrenfest's "order" terminology; see Münster 1970.

other than first order, effectively using the same hybrid scheme.<sup>78</sup> In 1971, H. E. Stanley's then influential text, *Introduction to Phase Transitions and Critical Phenomena*, also used a hybrid Ehrenfest classification.<sup>79</sup> In this final stage, the Ehrenfest scheme was so dominant that even those who claimed to prefer some other classification found themselves holding onto *at least* Ehrenfest's terminology; attempts to move away from the Ehrenfest scheme inevitably resulted in hybrid classifications.

## 5. Discussion

I now make seven observations regarding the history of the Ehrenfest classification scheme:

(i) It is remarkable that, although the lambda transition of liquid does not belong to *any* of its classes, this phase transition led to the creation of the Ehrenfest classification. This is because the Ehrenfest classification became an important and permanent tool at a crossroads of the theory of critical phenomena. Its creation and evolution was tied to several advances in this realm, such as the understanding of the lambda transition, the understanding of superconductivity, and the solution of the two-dimensional Ising model. The liquid-helium lambda transition became one of the most important cases in the study of critical phenomena – its true (logarithmic) nature was not understood for more than ten years, either experimentally or theoretically. When the transition's true nature was discovered, an extended form of the Ehrenfest scheme, best exemplified by Pippard's (1957) exposition, was created to incorporate it.

(ii) The character of the lambda transition, of other “unusual” phase transitions found later and, in particular, of the various models proposed to explain them were in

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<sup>78</sup> Nonetheless, Münster included a separate discussion of “second order transitions.” He noted: “The Ehrenfest equations constitute an application of thermodynamics to a set of previously defined circumstances. Whether these circumstances correspond to those occurring in nature can only be decided by experiment or by statistical thermodynamics. Higher-order transitions were originally usually regarded as second-order transitions in the sense of the Ehrenfest definition. Numerical values for the discontinuity in the specific heat are often found in the older literature. It should, however, be obvious that these statements do not follow from the experimental results with anywhere near the same certainty as analogous problems involving first-order transitions.” (Münster 1970, pp. 194–198); *cf.* Footnote 69.

<sup>79</sup> Stanley's usage was, in fact, terminologically identical to Münster's (1970). The following comment from the introduction is most telling: “In this monograph we shall follow Ehrenfest in so far as we shall denote by ‘first-order transitions’ phase transitions in which the first derivative of an appropriate thermodynamic potential is discontinuous, while we shall denote by ‘higher order’ or ‘continuous’ transitions the characteristic behavior near the critical points of fluids and magnets for which the first derivatives are continuous while the second derivatives are either discontinuous or infinite. This classification, due to Fisher, is somewhat more general than Ehrenfest's (Stanley 1971, p. 16). This is actually closer to describing the extended Ehrenfest (1933) scheme than the Fisher (1967) scheme.



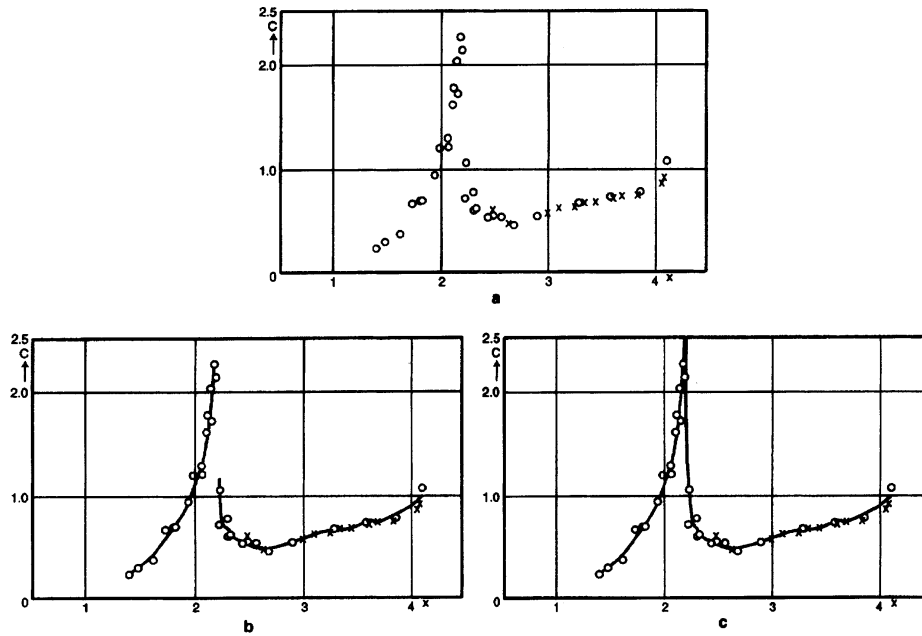


Fig. 8. (a) The data of Keesom and co-workers from which heat-capacity curves can be drawn. (b) The curve drawn by Keesom and Clusius and accepted by Ehrenfest. (c) The curve that would be drawn under the hypothesis that the heat capacity becomes infinite at approximately 2.19 K

part captured by the Ehrenfest scheme.<sup>80</sup> This, coupled with the new theoretical work (see (iii) below) gave the scheme great heuristic value. To this day, models for known phase transitions, especially those (such as that of Landau 1937) studied because of their mathematical tractability, are distinguished by Ehrenfest class.

(iii) The Ehrenfest scheme fulfilled the clear need, in 1933, of thermodynamics to accommodate “unusual” new transitions, allowing theoretical work on them to begin. Ehrenfest and Keesom immediately used it to arrive at concrete results, most significantly the appropriate analog for the Clapeyron equation. This and the work of others, like Rutgers and S. A. Wouthuysen (1937a, b) and Lype (1946) demonstrated its conceptual value.

(iv) It is important to note a general scheme was generated on the basis of just *one* “unusual” case, liquid helium. One likely motive for the creation of this general scheme on the basis of one unusual case was that it seemed probable that the scheme would be applicable to other known systems, such as superconductors. The work of Rutgers (1934) and others clearly bore this out.

<sup>80</sup> As Wilks has said, “Although this approach is now outmoded, it did in fact achieve a moderate degree of success” (Wilks 1967, p. 307).

(v) The precise form of the Ehrenfest scheme – based on the simple mathematical notion of discontinuity – limited it. In addition, the scheme overstepped the available empirical information (Fig. 8a) when it assumed that the new transitions involved “jumps” in the heat-capacity curve (Fig. 8b). With hindsight, it is clear that the data were also fully compatible with an infinite peak at the same temperature (Fig. 8c). As we have seen, however, this is not a case of a theorist pursuing mathematical formalism for its own sake: Ehrenfest’s mathematical discontinuities correspond precisely to the experimentalist Keesom’s (1933) own characterization of the data as showing “jumps.” Nonetheless, by giving a clear characterization of these observed jumps, the scheme provided a useful framework for continued research until the work of Onsager (1944) and Atkins and Edwards (1955) work forced its extension.

(vi) The Ehrenfest scheme was applied at the macroscopic rather than the microscopic level. Microscopic considerations appeared later, when Gorter and Casimir (1934b) invoked their “internal parameter,” the fraction of particles in the “normal,” non-superconducting state. The Ehrenfest classification provided the opportunity for theorists to use new concepts such as this order parameter to reach greater theoretical heights.

(vii) Tisza (1961) introduced his alternative classification of phase transitions in order to eliminate what he considered to be *ad hoc* assumptions, on the part of Pippard (1957) in particular, in the extended Ehrenfest scheme. He sought, more generally, to develop thermodynamics “beyond its usual scope from a new postulational basis.” The “*ad hoc* taxonomical considerations” of Pippard were those that allowed observed singularities to be considered similar to Ehrenfest’s discontinuities. It should be noted, however, that Tisza utilized a new theory of phase transitions in order to avoid these *ad hoc* moves. Though, it was ultimately on this basis that Tisza’s new classification was founded, its classes were still demarcated (like Ehrenfest’s) via the behavior of the Gibbs free energy. In this way, the Ehrenfest classification may be seen to have motivated yet another advance in the theory critical phenomena.

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