Chapter 5

Kelvin, Maxwell, Clausius and Tait: the correspondence of James Clerk Maxwell

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Abstract

The correspondence between Maxwell and Kelvin on many topics of mutual interest during the second half of the nineteenth century was terminated by Maxwell's untimely death in 1879. Much of what little there was on thermodynamics is no longer extant. Peter Guthrie Tait, Professor of Natural Philosophy at Edinburgh University from 1860 to 1901, provided the important link with Kelvin, Professor of Natural Philosophy at Glasgow University, not least because both held office in the Royal Society of Edinburgh. Tait was well aware of Kelvin's crucial contributions to the elucidation of the laws of thermodynamics in the early 1850s, and the need to harmonise them with the insightful contributions by Clausius during that decade; in particular, Clausius's introduction of the thermodynamic property entropy. Processes permitted by the Second Law of Thermodynamics could be charted by changes in the value of entropy. The following decade saw Maxwell introduce his kinetic theory of gases. Thereby Maxwell's interest, especially in the Second Law, was heightened because he felt that he could, overall, enhance Kelvin's dynamics of gases by incorporating explicitly statistical properties of distributions of molecular velocities in assemblies of molecules constituting the gases. Violations of the Second Law by subsets of molecules selected by an artifice soon to become known as Maxwell's Demon would be completely hidden because observations could be made only on a complete assembly. Curiously, Maxwell's first early encounters with entropy were seriously flawed, possibly because he was inadvertently misled by Tait whilst he was writing his own textbook on heat. The strong link between statistics and entropy became apparent later in the century, by which time Maxwell's distributions of molecular velocities had been extended by Boltzmann to distributions of their energies.

1 Introduction

1.1 The correspondence between Maxwell and Kelvin

The correspondence on thermodynamics between William Thomson (1824–1907) – Lord Kelvin from 1892 – and James Clerk Maxwell (1831–1879) was sporadic and not extensive. Losses have left it fragmented as well. Fortunately, some gaps are made good by correspondence between Maxwell and his lifelong friend Peter Guthrie Tait (1831–1901). All that is now available has been collated and presented by Professor Peter Harman in his comprehensive (three volume) *Scientific Letters and Papers of James Clerk Maxwell* [1]. In the introductions and copious footnotes Harman provides continuity and links to the wider literature. These provide a guide to the



interactions – direct and indirect – between Maxwell and the main players in the development of classical and, later, statistical thermodynamics in the second half of the nineteenth century. Within it there is to be found much of a nearly self-contained story of Maxwell's particular involvement in the development of the Second Law of Thermodynamics.

In the 1870s, some of the correspondence amongst Thomson, Maxwell and Tait was by postcard. Figure 1 is an example of one of the few which have survived. To save space, Thomson was T, Tait was T' and Maxwell was dp/dt. The last originated from the equation dp/dt = JCM, based on one in Tait's book *Sketch of Thermodynamics* [2] with the factors on the right labelled and arranged to give Maxwell's initials. Thus, Thomson to Maxwell was written 'T 2 dp/dt'.

1.2 Timelines for Kelvin and Maxwell

In the summer of 1871, Maxwell replied to a prompt from Thomson [4] for help with the preparation of his (Thomson's) Presidential Address to the British Association for the Advancement of Science to be held in Edinburgh in the autumn. In June 1871, Thomson had written: '... Where is the Address you undertook to write? It should be in the printers hands soon, so please don't delay longer. Send it to the Athenaeum Club London posting not later than next Wednesday. It must be *complete* (for press) on Dynamical Theory of gases, Diffusion & all who worked meritoriously on it, whether experimentally or theoretically and *their merits carefully weighed*. This last is de rigeur ...'. Maxwell's detailed reply to Thomson was understandably thorough. He had continued to work on fundamentals and applications of the kinetic theory of gases over the preceding 10 years. In addition, he was completing the writing of his *Theory of Heat* for publication in 1871 [5]. The preceding 20 years or so had witnessed the steady development of an understanding of classical thermodynamics arguably begun by Thomson and Rudolf J. E. Clausius (1822–1888), with Maxwell's contributions beginning about half way through.

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Figure 1: Thomson's reply, dated 4 January 1872, to a query from Maxwell. Reproduced by kind permission of the Syndics of Cambridge University Library, classmark Add. MSS 7655,I,a/24. The transcript in the Appendix is based on the version in Harman [3].

William Thomson was a senior to James Clerk Maxwell by 7 years. From 1846, Thomson was well-established academically and scientifically following his appointment as Professor of Natural Philosophy at Glasgow University. Maxwell began 3 years of study at Edinburgh University in 1847 and moved to Cambridge University in 1850, graduating in 1854. During his undergraduate studies there, Maxwell had kept himself apprised of Thomson's overlapping researches on heat and electricity. These provided an entry to Maxwell's own research on electricity and magnetism. Shortly after graduating from Cambridge University, Maxwell wrote to Thomson on 20 February 1854, on behalf of himself and others, informing him of a 'strong tendency to return to Physical Subjects and several of us here wish to attack Electricity' [6]. He continued 'Suppose a man to have a popular knowledge of electrical show experiments ... how ought he to proceed in reading & working so as to get a little insight into the subject wh[ich] may be of use in further reading?' Thomson's letter of reply was accompanied by a reading list, and encouragement. In his editorial footnote to Maxwell's letter of thanks on 15 May 1855 [7], Harman commented, 'This [Thomson's] letter, like others from Thomson, is not extant.' Maxwell continued that he hoped to make use of Thomson's analogy between steady heat flow and electrostatic force. He added 'By the way do you profess to account for what becomes of the vis viva of heat when it passes thro' a conductor from hot to cold? You must either modify Fourier's laws [8] or give up your theory, at least so it seems to me.' (The concept of vis viva was introduced by Gottfried W Leibniz (1646-1716) [9] to describe a property of certain mechanical systems consisting of masses m each having its own speed v. The sum of terms mv^2 seemed to be conserved. By the middle of the nineteenth century, the name was usually given to $\frac{1}{2}mv^2$, an important quantity in mechanics, referred to as kinetic energy. Harman commented, 'Maxwell probes Thomson's concept of the dissipation of energy.' Maxwell was well aware of contributions by J.P. Joseph Fourier (1768–1830) to the theory of heat. While at Edinburgh University he had borrowed from the library Fourier's Théorie Analytique de la Chaleur, and his most recent biographer, Basil Mahon, noted that 'he was so smitten by Fourier's book that he bought his own copy for 25 shillings, a considerable sum in 1849' [10].

The issue had been raised by Thomson himself 6 years earlier in a footnote in his 1849 paper on Carnot's theory of the motive power of heat [11]. 'When 'thermal agency' is thus spent in conducting heat through a solid, what becomes of the mechanical effect which it might produce? Nothing can be lost in the operations of nature – no energy can be destroyed. What effect then is produced in place of the mechanical effect which is lost?' He had gone some way to answering his query in his 1851 paper on the dynamical theory of heat [12]. By that time studies on heat transfer had been extended to include, at least generally, properties of the material supporting the heat flow, intentionally excluded by Fourier in his theory. Energy considerations would lead Thomson a year later [13] to conclude that the conduction of heat through a body be accompanied by such transformations as to leave some of it dissipated and thereby irrecoverable but not lost. If, on this issue, Thomson replied to Maxwell in writing, there is no trace of that letter either.

Thomson had continued his research into the fundamentals and applications of thermodynamics beyond 1851, and his publications would have been available to Maxwell. However, by October 1856, Maxwell had moved to Aberdeen as Professor of Natural Philosophy at Marischal College. His father had died suddenly in the spring of that year, and Maxwell inherited the family estate, Glenlair, in Galloway in southwest Scotland. In 1858, he married Katherine Mary Dewar, daughter of the Principal of Marischal College. Whilst at Marischal College, from 1856 to 1860, the emphases in most of his letters to Thomson as have survived were on electricity, magnetism and optics.

2 Saturn's rings and the Adams Prize: Maxwell and Kelvin

Maxwell's pathway to Thomson's thermodynamics was mainly through the properties of gases in their own right rather than as dynamical systems such as integral parts of heat engines. With the benefit of hindsight, we can surmise that already, at Aberdeen, Maxwell had started an approach to an aspect of the Second Law of Thermodynamics, which can be traced back to his work there on the theory of the structure of the rings of planet Saturn.

The Adams Prize was instituted in 1848 to commemorate the prediction by John Couch Adams (1819–1892) in 1845 of the position of an as yet undiscovered planet. About a year later, in France, calculations by Urbain J.J. Leverrier (1811–1877) had led to essentially the same prediction. Unlike Adams's prediction, Leverrier's was quickly followed up, at the Berlin Observatory. From there, the new planet, to be called Neptune, was discovered late in 1846. In Britain, the Astronomer Royal, Sir George Airy, suggested that Adams be given priority for the prediction, and a squabble followed. The Adams Prize – to acknowledge brilliance in applications of mathematics – can be seen as part of Adams's compensation.

The topic for the fourth Adams Prize, announced in 1855, was 'The Motions of Saturn's Rings and, in particular, the question of their stability'. Maxwell worked intensively on the topic in 1855 and 1856 during his tenure of the Chair of Natural Philosophy at Marischal College. His, the only, submission was outstanding and he was awarded the prize. It was written up and published as a monograph in 1859 titled On the Stability of the Motion of Saturn's Rings [14]. This was described by his biographer Ivan Tolstoy [15] as 'ninety quarto pages of mathematics and carefully polished prose ... a bravura performance which, perhaps more than anything he had yet published, made him a star in the eyes of his contemporaries.' While preparing the monograph, Maxwell kept in touch with Thomson (who had been one of the examiners for the prize). In an update on 14 November 1857, Maxwell commented on progress in the consideration of various configurations of matter constituting the rings [16]. He remarked, 'The general case of a fortuitous concourse of atoms each having its own orbit & excentricity is a subject above my powers at present, but if you can give me any hint as to the point of attack I will go at it.' In the monograph, the remark is extended 'When we come to deal with collisions among bodies of unknown number, size, and shape, we can no longer trace the mathematical laws of their motion with any distinctness.' Maxwell returned to this viewpoint when within a few years he turned his attention to the kinetic theory of gases.

3 Molecular model for a gas: Maxwell and Clausius

3.1 Description of model

In the meantime, in 1858 Clausius had published a paper on, amongst other things, the average distance travelled by gas molecules between consecutive collisions, their mean free path [17]. Maxwell noticed the translation in the Philosophical Magazine in 1859. His reworked analysis differs significantly from Clausius's in that he allowed for a distribution of molecular velocities rather than work with just an average value. In Maxwell's 1860 paper [18], he presented what became known as the Maxwell Distribution of molecular velocities.



With a display of audacity rather than bravura, Maxwell kept the derivation brief: four equations derived in 2 pages in Part I of the complete 33-page paper. In the introductory preamble, he remarked: 'In order to lay the foundation of such investigations [of properties of matter, especially when in the gaseous form] on strict mechanical principles, I shall demonstrate the laws of motion of an indefinite number of small, hard, and perfectly elastic spheres acting on one another only during impact.' Extending this basic assumption, he continued: 'Instead of saying that the particles are hard, spherical, and elastic, we may if we please say that the particles are centres of force, of which the action is insensible except at a certain small distance, when it suddenly appears as a repulsive force of very great intensity. It is evident that either assumption will lead to the same results.'

After setting out the key parameters of such collisions – velocities and angles of rebound in particular – Maxwell continued: 'If a great many equal spherical particles were in motion in a perfectly elastic vessel, collisions would take place among the particles, and their velocities would be altered at every collision; so that after a certain time the *vis viva* will be divided among the particles according to some regular law, the average number of particles whose velocity lies between certain limits being ascertainable, though the velocity of each particle changes at every collision.' He had moved to a starting point which was thus a description of an isolated sample of gas that had settled into an equilibrium state.

The paper continued with 'PROP. IV. To find the average number of particles whose velocities lie between given limits, after a great number of collisions among a great number of equal particles'. For a sample of N particles, whose velocity v has components x, y and z in each of three mutually perpendicular directions (Maxwell's notation) with all three components governed by the same function f, the analysis led to, in sequence, four equations. Here, Nf(x)dx is the number of particles with x in the narrow range x to x+dx, and correspondingly for velocity components y and z. The number with actual velocity in the range v to v+dv is NF(v)dv.

 $f(x) = (1/a\sqrt{\pi})\exp(-(x^2/a^2)) \qquad F(v) = (4/a^3\sqrt{\pi}) v^2 \exp(-(v^2/a^2))$ mean value of v is $2a/\sqrt{\pi}$ mean value of v^2 is $(3/2)a^2$

The factor $-1/a^2$ replaced one of the arbitrary constants in the introductory analysis. Thus, Maxwell excluded the unrealistic steady increase with velocity of the number of particles and made the later analysis immediately amenable to well-known mathematical results. The value of a^2 increases with the temperature and decreases with the molecular mass of the gas. The paper continues: 'It appears from this proposition that the velocities are distributed among the particles according to the same law as the errors are distributed among the observations in the theory of the 'method of least squares'. The velocities range from 0 to ∞ , but the number of those having great velocities is comparatively small. In addition to these velocities, which are in all directions equal, there may be a general motion of translation of the entire system of particles which must be compounded with the motion of the particles relatively to one another. We may call one as the motion of translation and the other the motion of agitation'.

3.2 Summary of selected predictions from model

Maxwell summarised the illustrations in the last few paragraphs of the final PART III of the paper, beginning with those in PART I: 'We have now followed the mathematical theory of

the collisions of hard elastic particles through various cases, in which there seems to be an analogy with the phenomena of gases.' These began with the relations amongst the thermodynamic coordinates (pressure, temperature and density) and continued with the phenomena of internal friction (viscosity) with the mean free path (the average distance between consecutive collisions) having particular importance. It contained the counter-intuitive prediction that the coefficient of viscosity be independent of density. PART II illustrations were on diffusion for which he had modelled a bulk gas as a large number of parallel strata and treated the net movement of molecules between strata. He added a temperature gradient in the final illustration, the conduction of heat through a gas. Clausius was soon to point out Maxwell's unsatisfactory specifications of the strata [19], which was acknowledged and acted on in Maxwell's preparation [20] of his later paper, in 1867, 'On the Dynamical Theory of Gases [21]. In particular, for thermal conductivity Maxwell had overlooked the variation of kinetic energy with the layerto-layer variation in temperature. The distributions of velocities could not, therefore, be of the isotropic motion of agitation as Maxwell had assumed. Conduction of heat through a gas was the least satisfactory because it also highlighted a conflict between theory and experiment in thermodynamics, pointing to an inadequacy in modelling of molecular structure. Maxwell had replaced molecular mass M in the treatment of diffusion by $\frac{1}{2}Mv^2\beta$, where, following Clausius, β is the unknown factor by which, because of rotational motion, the energy is greater than just the kinetic energy $\frac{1}{2}Mv^2$. However, Maxwell edged the topic one stage further, introducing the final illustration, thus: 'The energy of a single particle is composed of two parts - the vis viva of the centre of gravity, and the vis viva of the various motions of rotation round that centre, or, if the particle be capable of internal motions, the vis viva of these'.

In the concluding PART III of the paper immediately preceding the summary, Maxwell addressed the allocation of energy to the rotational motion of 'perfectly elastic bodies of any form'. He argued that his statistical treatment was valid also for the rotational motion, and so he chose $\beta = 2$ and looked to experiment for judgement. This allocation was part of what became known as equipartition of energy. The crucial test was made using the link between β and the ratio γ of the specific heat of a gas at constant pressure to its specific heat at constant volume: $\beta = 2/(3(\gamma - 1))$ For air $\gamma = 1.408$, hence an experimental value for β of 1.634, in conflict with Maxwell's choice of 2. (Alternatively, $\beta = 2$ leads a predicted value for γ of 1.333 in disagreement with experiment.) On this issue, Maxwell concluded his paper: 'Finally, by establishing a necessary relation between the motions of translations and rotation of all particles not spherical, we proved that a system of such particles could not possibly satisfy the known relation between the two specific heats of all gases.'

3.3 Experimental check and some further developments

It was after he moved to the Chair of Natural Philosophy at King's College in London, in 1860, that he confirmed experimentally the counter-intuitive prediction that the viscosity of a gas would be independent of the pressure [22]. The measurements – a joint effort by Maxwell and his wife Katherine – were made between 1863 and 1865 with apparatus, a viscometer, assembled in the attic of Maxwell's London house in Palace Gardens Terrace, in Kensington. In his 1867 paper, Maxwell addressed the issue of the law of force between colliding molecules. His conclusion is best described from his own abstract [23] of the paper: 'the action between the molecules is supposed to be that of bodies repelling each other at a distance, rather than of hard elastic bodies acting by impact; and the law of force is deduced from [his own] experiments

on the viscosity of gases to be that of the inverse fifth power of the distance, any other law of force being at variance with the observed fact that the viscosity is proportional to the absolute temperature [22]. In the mathematical application of the theory, it appears that the assumption of this law of force leads to a great simplification of the results, so that the whole subject can be treated in a more general way than has hitherto been done.'

Also in the paper, he re-cast the final formula for thermal conductivity, rearranging the factors so as to eliminate β in favour of γ , and including the coefficient of viscosity explicitly – thereby winning the security of factors whose values were well known from experiment. He also referred, presciently, to the internal motions as 'oscillation, or vibration'. However, he was never able to fully address their significance. The issue was resolved by the early years of the twentieth century. The nuclear atom provided the lead-in to more realistic atomic and molecular physics, spectroscopic data could be related to frequencies – not directly to but not too distantly from the notion of frequencies of vibrations of Maxwell's 'internal motions' – and rapidly developing quantum theory provided overarching support. However, 'despite the problems with the kinetic theory, Maxwell never seriously doubted its validity or that of the velocity distribution he had derived. Amongst the most compelling of his reasons were the results of his studies of the viscosity of gases.' [24].

In his biographical study of Maxwell, C.W.F. Everitt [25] identifies the derivation of the velocity distribution in the 1860 paper as marking 'the beginning of a new epoch in physics.' In justification, he continues 'Statistical methods had long been used for analyzing observations, both in physics and in the social sciences, but Maxwell's idea of describing actual physical processes by a statistical function was an extraordinary novelty'. The distribution of molecular velocities is still known as the Maxwell Distribution. It quickly became key to further work on mainland Europe, by Clausius and Ludwig E. Boltzmann (1844–1906). There soon emerged the Boltzmann Distribution of molecular energies, crucial to the development of statistical thermodynamics.

4 Two laws of thermodynamics: Maxwell, Clausius, Kelvin and Tait

4.1 The First Law

P.G. Tait had been appointed Professor of Natural Philosophy at Edinburgh University – in preference to Maxwell – in 1860. There he followed assiduously developments in thermodynamics to keep his lectures on the subject up to date. In his book on thermodynamics, *Sketch of Thermodynamics*, whose first edition appeared in 1868 [2], Tait set out the developments historically. He challenged the attribution made in 1862 by John Tyndall (1820–1893) [26] to J. Robert Mayer (1814–1878) of the introduction in 1842 of the idea of conservation of energy, pointing to a mechanical equivalent of heat [27]. Mayer's intuition was strong but his interpretation of available experimental data was suspect and he made little of any link between heat and motion [28]. On the grounds that Mayer had failed to support his hypothesis satisfactorily, Tait insisted that credit should be given to James P. Joule (1818–1889) who had begun reporting on his measurements in 1843 [29]. Joule improved his experimental techniques systematically to measure the rise in temperature of water stirred by rotating paddles. This provided the direct link between mechanical work producing the motion of the paddles and the heat produced, permitting a value for the mechanical equivalent of heat to be found ever more accurately, as reported to the Royal Society in 1850 [30]. The debate became quite bitter [31]. Thomson's substantial and timely paper published in 1851 [12] contains many references to the work of both Joule and Mayer, and had led him to move on from a mechanical equivalent of heat to identify a thermodynamic property of substances, initially called mechanical energy, *e*, later changed to intrinsic energy and finally to internal energy, denoted by *U*. A sample heated externally and, whilst expanding, doing mechanical work on its surroundings would experience a change in its internal energy equal to the difference of the energies calculated from the heat and the work, although neither heat nor work on their own could serve as a thermodynamic property.

The year before, Clausius [32] had arrived at essentially the same thermodynamic property, which he represented by (thus introducing the symbol) U, in a treatment which avoided the use of the concept of energy. Instead, simplifying the more detailed discussion by Cropper [33], he argued that the effect of adding heat to a gas is the performance of external work done, if any, and an increase in the value of the property U which could be attributed to an increase in 'sensible heat' together with work done within the gas itself. Represent the net heat input *to* and net external work done *by* a system by ΔQ and ΔW , respectively. The accompanying change ΔU in U is found from $\Delta Q = \Delta U + \Delta W$. By 1865, the status of the concept of energy, and its conservation, having been established, Clausius accepted U as an energy and made his succinct statement of the First Law of Thermodynamics: 'The energy of the universe is constant' [34].

4.2 The Second Law

4.2.1 Background to Kelvin's approach

Tait was well aware of Thomson's abilities. They had collaborated on the writing of the famous 'Thomson and Tait', their *Treatise on Natural Philosophy* [35]. They corresponded and met frequently, not least in connection with the affairs of the Royal Society of Edinburgh. Tait was the General Secretary from 1879 to 1901, and Thomson served as President several times. Tait had followed Thomson's researches on the laws of thermodynamics, and they both acknowledged the clarifications from the contribution [36] in 1850 of W.J. Macquorn Rankine (1820–1872), Professor of Civil Engineering at Glasgow University, though Thomson did not show much enthusiasm [37] for Rankine's speculative modelling of molecular properties in terms of vortices.

Already in 1850 [32], Clausius had sought, independently, to extend conclusions being drawn from the description by N.L. Sadi Carnot (1796–1832) in 1824 [38], rescued by B.P. Emile Clapeyron (1799–1864) 10 years later [39], of an idealised version of a processes common to many heat engines which became known as the Carnot Cycle. This was before the acceptance of the First Law and so indestructible heat, as described in the caloric theory, played a dominant guiding role. The cycle, fully discussed in other chapters, is a closed cycle of four reversible stages, alternately isothermal and adiabatic. A working substance gas absorbed heat Q isothermally at the higher temperature t_1 of a constant temperature heat source, expanding to do work externally. The expansion continued with the gas thermally insulated, doing work adiabatically. Two compression stages followed, with work now being done *on* the gas. The first was isothermal at the lower temperature t_2 of a constant temperature heat sink, to which *all* the heat Q was released. The final compression, with the gas again thermally insulated, returned the gas to its

initial state. The net amount of work delivered was associated with the complete throughput of the heat *Q*, to comply with the indestructibility of caloric.

Further restricted to an infinitesimal temperature difference between source and sink, this reversible cycle would provide the maximum possible work output for a given heat input at the higher temperature. This upper limit on the efficiency of heat engines pointed to a more general law. Thomson [11] had referred to Carnot's admission that the foundations of his theory 'would require a most attentive examination'. Clausius [32] pointed out that accepting that work output was necessarily accompanied by heat flow was compatible with some of the heat input being transformed into the output work without the need to move to a new basic theory of heat. Thomson collated the various such contributions in his 1851 paper [12], in which he introduced the thermodynamic function mechanical energy, *e*. In the following year, he distinguished reversible from irreversible processes: in the latter, there can be no complete restoration of mechanical energy – part of it having been dissipated. This applied in particular to the conduction of heat in which a transformation of energy leads to part of it becoming irrecoverable. He therefore proposed, in 1852, an overarching law that 'there is at present in the material world a universal tendency to the dissipation of the mechanical energy' [13].

4.2.2 Alternative approach of Clausius

By 1854, Clausius – also seeking a general principle – had analysed an enhanced Carnot cycle [40]. The return adiabatic did not restore the working substance to its initial state. Instead it was followed by a reversible isothermal expansion having heat input q at the constant temperature t of a third heat source, with $t > t_1$, and the cycle was closed by a final reversible adiabatic expansion with the temperature decreasing to t_1 . The cycle thus comprised two identifiable transformations. One was of heat Q at t_1 to the same amount but now at t_2 . This was the necessary accompaniment to the other transformation of the net heat input, just q, to the external work wdelivered. Clausius's analysis was based on an 'equivalence value', in terms of heat flow and temperature, for each of these two mutually compatible transformations. Detailed analysis led to $Q(1/T_2 - 1/T_1) - q/T = 0$, where the three temperatures are now represented by their absolute temperature scale values. This he generalised firstly to any number (including infinitesimal) of reversible heat flows dQ at temperatures $T: \int dQ/T = 0$. In a later paper [34], Clausius continued the interpretation introducing a thermodynamic property entropy, denoted *S*, with dQ/T = dS. Allowing for irreversible processes as well, he extended the generalisation to $\int dS \ge 0$, with the equality valid for reversible processes only. Matching the brevity of his statement there of the First Law, he pronounced the Second Law of Thermodynamics in the form 'the entropy of the universe tends to a maximum'. Traced back to its origins - allowed processes identified by changes (if any) in thermodynamic properties – it correlates with Thomson's more easily visualised conclusion of 1852 in terms of dissipation of energy.

4.2.3 A merging of interpretations

Maxwell's letter to Tait on 1 December 1873 showed that there was still then some confusion about how entropy was related to available and unavailable energy [41]. Initially, Tait inter preted entropy as available energy, possibly confused by the over-use of the word transformation. Much earlier, in a letter dated 6 December 1867, Tait had sought Maxwell's opinion on his own

book, the *Sketch of Thermodynamics* to which Maxwell replied on 11 December 1867 [42]. Later, Maxwell erred by following Tait's lead in the treatment of entropy in the first edition, in 1871, of his own book [5]. It was quickly corrected in later editions.

In particular, Tait had noticed that expressions structurally similar to Clausius's were prominent in Thomson's researches. He insisted on giving Thomson priority over Clausius for the introduction of a thermodynamic function – Clausius's entropy – to which Clausius objected, resulting in a second controversy [43, 44]. When he had had time to consider the matter, Maxwell was more understanding of Clausius's attitude, pointing out in a letter to Tait on 13 October 1876 [45] that in 1854 Rankine [46] had arrived at an expression which he called the thermodynamic function, which was indistinguishable from Clausius's $\int dQ/T$. In that letter Maxwell wrote: 'There are many things in T[homson] which are equivalent to this, because T has worked at the subject and worked correctly, and all mathematical truth is one, but you cannot expect C[lausius] to see this unless it stands very plain in print. In short Rankines statements are *identical* with those of C but T's are only *equivalent*.'

Conventional statements of the Second Law in introductory thermodynamics rule out processes which Thomson and Clausius realised did not happen in isolation. The modern wording of two [47], which can be shown to be equivalent, are the 'Clausius' version 'It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body' and the 'Kelvin-Planck' version 'It is impossible to construct a device that, operating in a cycle, will produce no effect other than the extraction of heat from a single body at a uniform temperature and the performance of an equivalent amount of work.'

4.3 Impact of kinetic theory and Maxwell's Demon

4.3.1 The statistical approach of Maxwell

Maxwell was led to suggest that his statistical kinetic theory would fit harmoniously with the Second Law of Thermodynamics. He had to show that the assumption of identifiable velocities of all molecules at all instants could lead to a contradiction of the Second Law. Inverting, the validity of the Second Law would rule out the option of such detailed knowledge particle by particle, but not the option of a statistical specification. In that sense, the Second Law of Thermodynamics had to be regarded as statistical.

In treatments of the Second Law, one thermodynamic system has a heat source and a heat sink defining the ends of a volume filled by a sample gas. They are key to heat in and heat out, compatible with a steady temperature gradient between source and sink. Many observations all indicated that there would be a transfer of heat down the temperature gradient from the source to the sink. In his letter to Tait on 11 December 1867 [42], Maxwell simplified the system to two samples, A and B, containing the same number of molecules of the same gas at different temperatures, with A hotter than B. The samples were in contiguous vessels of the same size, completely closed with a diaphragm forming the side in common. A sliding door covered a hole in the diaphragm. So his system had at the outset a temperature difference, rather than a temperature gradient. He then proceeded 'To pick a hole – say in the 2nd law of thermodynamics, that if two things are in contact the hotter cannot take heat from the colder without external agency.'



He illustrated his reservations to Tait (Fig. 2) by introducing an agency to control energy changes accompanying the movement of molecules – through the hole in the diaphragm – from each vessel to the other. 'Now conceive a finite being who knows the paths and velocities of all the molecules by simple inspection but who can do no work, except to open and close a hole in the diaphragm, by means of a slide without mass. Let him first observe the molecules in A and when he sees one coming the square of whose velocity is less than the mean sq. vel. of the molecules in B let him open the hole & let it go into B. Next let him watch for a molecule in B the square of whose velocity is greater than the mean sq. vel. in A and when it comes to the hole let him draw the slide & let it go into A, keeping the slide shut for all other molecules. Then the number of molecules in A & B are the same as at first but the energy in A is increased and that in B diminished that is the hot system has got hotter and the cold colder yet no work has been done, only the intelligence of a very observant and neat fingered being has been employed.'

Maxwell then summarised his argument, shifting the scenario slightly: 'Or in short if heat is the motion of finite portions of matter and if we can apply tools to such portions of matter so as to deal with them separately then we can take advantage of the different motion of different portions to restore a uniformly hot system to unequal temperatures or to motions of large masses. Only we can't, not being clever enough.'

Tait added a pencilled postscript when he forwarded the letter to Thomson with the request 'to say what occurs to you about the enclosed *which return* speedily.' [48]. Thomson's annotation to the letter was 'Very good. Another way is to reverse the motion of every particle in the universe and preside over the unstable motion thus produced'. He was pointing to the feature of classical mechanics that the solutions to the equations determining the motion of a particle are equally valid for time *t* decreasing as well as, normally, increasing. He would return to this, and his alert on unstable motion, in a paper to the Royal Society of Edinburgh in 1874.





Figure 2: Peter Guthrie Tait, age 32 (left), courtesy of Scottish National Portrait Gallery, and James Clerk Maxwell, age 30 (right), courtesy of Master and Fellows of Trinity College Cambridge.

Almost immediately after introducing this 'being' to Tait in 1867, Maxwell referred to its role, in severe summary, at the end of a letter on 16 January 1868 to Thomson [49]. Already in 1852 Thomson had pointed out that in natural processes there was a dissipation of energy, which was not recoverable in forwards moving time. Maxwell set out the scenario. 'I believe that if any body consists of finite molecules either solid or fluid knocking about, then this body when of uniform temperature consists of molecules going at different velocities. See my Dynamical Theory of Gases & the Laws of Collision.' There was no mention of diaphragm, hole or sliding door, but the starting point was a system in thermodynamic equilibrium. He continued: 'Now let an intelligent but finite and energy conserving being be appointed pointsman to the flying molecules and when he sees a swift one let him turn it to the place of the swift and when he sees a slow one let him turn it to go among the slow. Then without expenditure of work he will have made one part of the body hotter & the other colder. Hence energy need not always be dizzy pated as in the present wasteful world.' Paraphrasing, the recovery of a prior thermodynamic state in forwards moving time could be done by a sufficiently well apprised being ready to act on molecules individually.

4.3.2 A merging of views and a glance forward

In 1874, Thomson [50] returned to a discussion of dissipation of energy supported by the kinetic theory of gases. His starting point was the evidence that a thermally insulated bar of metal, hot at one end and cold at the other, would eventually assume a uniform temperature by conduction of heat. A spontaneous recovery to the original temperature distribution, with the potential of availability for useful work, is never observed. To illustrate this, he chose the simpler system of a gas consisting of a large number of identical molecules in a leak-proof, thermally insulated vessel. Thomson described a thought experiment in which a large number of Maxwell Demons could control the difference in temperature between two halves of the vessel.

He put them in charge of contiguous areas whose total flat area divided the volume into two equal parts. He expanded on Maxwell's specification of 'turning' molecules to the places of the swift or the slow by allowing the comparatively massive demons to 'bat' the moving molecules accordingly. For the special case of initially uniform temperature throughout the sample, the demons, whilst remaining in their positions, could make their combined area a boundary between hot and cold halves of the volume. They could do this by controlling, in concert, the allowed passages across the boundary of molecules selected according to their energy. If the demons were then made simultaneously inactive, subsequent intermolecular collisions throughout the whole volume of the gas would produce there an equilibrium temperature in a finite time.

He then considered what would happen if at that point, with the demons still inactive, the *velocities* of all molecules were suddenly reversed. In the same time as before, but now negative going, laws of physics would produce, by 'abstract dynamics', a complete re-tracing in reverse of its path by every molecule and the recovery the temperature difference engineered by the demons – which subsequent intermolecular collisions would eventually remove.

Thomson's preference was for 'physical dynamics', in which the motion of molecules would be conditioned by their interactions with the bulk of the sample whether on their 'outward' or 'return' paths. Recovery of the target temperature difference in the time available could be ruled out. A statistical thread in the argument became necessary, providing a bridge to a proposed feature of equilibrium distributions which he now considered in forwards going time. Short-



lived non-equilibrium states could happen and persist for a while, more easily the smaller the number of molecules in the sample, before a return to the equilibrium state would happen. Extending the line of reasoning, the larger the fluctuation, the less likely it is to occur, leading naturally to the need for application of the rules of probability theory. Supported by a few numerical estimates from it, Thomson felt justified in aligning his conclusions with his theory of the dissipation of energy. A reinstatement of the original temperature difference across an isolated metal bar, once it had changed irreversibly to uniform temperature throughout, was not possible unless the isolation was relaxed, permitting input from an 'agency of external sources of heat or cold'.

In his own Theory of Heat [5], Maxwell chose the scenario in his summary to Tait, leading to yet another paraphrase of his standpoint, claiming the second law of thermodynamics to be 'undoubtedly true as long as we can deal with bodies only in mass, and have no power of perceiving or handling the separate molecules of which they are made up.' Around this time, in correspondence with others, Maxwell would point to the constraint on the perfect reversibility of classical dynamics posed by the irreversibility of natural processes [51]. This was one facet of a larger issue which in time also had to be faced when the bridge between classical and statistical mechanics was being built. There the probabilistic arguments [52] can be traced back to those presented by Maxwell in his kinetic theory of gases. The imagery associated with the concept of Maxwell's Demon has been used in many areas of science, extending from biology and psychology to computing and information theory, and to the history of science [53].

5 Conclusion

Maxwell's note to Tait 'Concerning Demons', in 1875 [54] was in the form of a catechism, beginning 'Who gave them this name? Thomson.' In his Lecture in London at the Royal Institution in February 1879 [55], Thomson saw fit to juxtapose again energy dissipation and energy distribution changes that could be wrought whenever required by Maxwell's Demon. However, holding to the theme of the Lecture, he changed the order of the key events from that chosen in his 1874 paper – this time dissipation preceded intervention by the demon.

Quoting from the report of the Lecture: 'Clerk Maxwell's 'demon' is a creature of imagination having certain perfectly well-defined powers of action, purely mechanical in their character, invented to help us to understand the 'Dissipation of Energy' in nature. ... By operating selectively on individual atoms he can reverse the natural dissipation of energy ... [a dissipation which] follows in nature from the fortuitous concourse of atoms.' The Lecture was illustrated by a number of experiments, allowing Thomson to remind the audience that 'The conception of the 'sorting demon' is purely mechanical, and is of great value in purely physical science.'

Combined with his 1874 paper Thomson thus effectively completed his elaboration on the annotation he had made on Maxwell's letter to Tait 12 years before [42]. In doing so, he had rounded off, perhaps inadvertently, an important stage in the development of thermodynamics. Maxwell's contribution to it might have at first appeared maverick-like but it now sat more easily – providing clarification – within classical whilst also indicating the way to statistical thermodynamics.

In November of the same year, James Clerk Maxwell died from stomach cancer.

Appendix. Transcript [3] of words on postcard of Fig. 1

T 2 dp/dt

The el. m. f.^{ce} of a thermoelectric circuit belongs to the whole circuit not to either junction alone. See water pipe analogy ProcRSE 1851 (if the Secretaries have correctly reported the whole proceedings of the meeting).

The more we understand of the potential, pressure, &^c of electricity in metals the more perfect is the analogy. You are welcome to the thermo O^t copper zinc air I have done with it years ago till I come back to it again.

{On the card Thomson sketched a water pipe as a closed rectangular loop with corners rounded and with 'water' inside. The side on left was labelled 'cold' and the other on the right 'hot'. Inside the loop was written '25 years ago I did not know that $\iint \rho(x,y) dxdy$ is absurd'. Alongside, Thomson added 'if mean temp^{re} > 4°'. Below it he sketched a narrower loop representing two strips of metal, joined at the ends; the upper one 'copper' and the lower one 'iron.' The junctions were labelled 'cold' on left and 'hot' on right. Limit on mean temperature indicated by ' " " 289°'} Below was added 'The current is against hands of watch'.

Oil of turpentine (as dry as you can get) and melted paraffin may be substituted for the air. I am doing so not very successfully now, and did so many times and years back.

You said that Clausius made proportionality of current to external EMF in electrolysis which was what I objected to.

{In what little space was left in the left hand margin Thomson wrote (at right angles to the main text): 'I have no doubt of the diffusion theory of currents through electrolytes in infin. EMF'. Likewise in right hand margin: 'Can you come on Frid. or Sat. or if not, when?'}

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