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Book Review: *The Scientific Letters and Papers of James Clerk Maxwell*

The Scientific Letter and Papers of James Clerk Maxwell. P.M. Harman, ed. Vol. III[1], Cambridge University Press, Cambridge.

The final volume of this classic publication of Maxwell's personal documents deals with the last period of his short life, 1874–9. During this period Maxwell undertook the task of establishing and directing the Cavendish Laboratory as a requirement of the Chair to which he had been elected in 1871, and this must have absorbed much of his free time. In addition he had (perhaps unwisely) volunteered to edit the electrical papers of Henry Cavendish (1731–1810), a distinguished "gentleman" scientist, and an ancestor of the family who had endowed the Cavendish chair. Maxwell served as physical sciences editor of the ninth edition of the Encyclopedia Britannica, refereed liberally for the Transactions of the Royal Society, and played an active role in a number of other public scientific projects. It is not surprising that when his lifelong friend and biographer, Lewis Campbell, enquired about Maxwell's own investigations, he answered with a sad look, "I have had to give up so many things".

Nevertheless, one can only marvel at the stream of new ideas which he did put forward, many of them in thermodynamics and statistical mechanics. In fact one gains the distinct impression that had Maxwell lived longer, statistical physics would have been the major focus of his activities. This is confirmed by the publication in the year before his death, of important new ideas on rarefied gases, and on Boltzmann's equilibrium distribution.

Since the current publication is concerned only with previously unpublished material, a comprehensive guide to the documents reproduced is essential, and the Introduction to the present volume provides this competently and efficiently. But anyone who wishes to engage in a serious study

[1]Vol. 1 is reviewed in J. Stat. Phys. *67* 837–8 (1992), and Vol. 2 in J. Stat. Phys. *88* 1419–22 (1997).

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of this interesting material must have the two volumes of Maxwell's collected papers at hand.

Quite early on in the volume one comes across correspondence which throws further light on the Maxwell "equal area" construction to provide the horizontal portions of the isotherms in van-der Waals' equation. In 1873 van-der Waals published his thesis in Dutch, and Maxwell immediately recognized its importance. Easily overcoming the language problem Maxwell reviewed the thesis in *Nature* in 1874, and gave it more prominence in a lecture to the Chemical Society in 1875 in which he introduced his construction. Maxwell justified his construction by means of a Carnot Cycle, but the argument is technically invalid since the fluid passes through unstable thermodynamic states where it cannot exist.

We learn from a letter to P.G. Tait in December 1874 and an unpublished note, that Maxwell was aware of this problem. But he dismisses it as follows: "That the substance is essentially unstable from D to F is no objection to this reasoning. For by proper application of the very smallest forces, stability might be ensured without expenditure of a sensible amount of energy". Unfortunately, although this argument may sound plausible, it cannot be substantiated. Maxwell's superb intuition had not let him down. His result is correct, but nearly a century passed before it was established rigorously. There is a sentence in the draft of his lecture to the Chemical Society in the volume under review, which was not included in the final published version, which well summarizes his philosophy in matters of this kind: - "If the pioneers of science were forbidden to make any advances in unknown ground before they had established a complete system of communications with a secure base of operations, we might be spared many erroneous statements, but we should obtain few new suggestions". In his letter to Tait Maxwell regrets not having included the equal-area construction in his *Theory of Heat* – "That I did not do it in my book shows my invincible stupidity."

As Professor of Experimental Physics Maxwell was always alert to experimental results, and an unpublished note records his calculation of critical data for water by applying the equation of van-der Waals to the experimental data of Regnault.

During the period covered by the previous two volumes in this series Maxwell had put forward his formula for the probability distribution of the velocities of the molecules in a gas, when it has reached its state of thermodynamic equilibrium, as well as the formula for the equipartition of energy when different types of molecules are present. Boltzmann's derivation of these results in his seminal 1868 paper and his famous $\exp(-\epsilon/kT)$ relation which extended the treatment to the presence of an external field, clearly made a deep impression on Maxwell. But he seems to have been worried that the method applied only to a quasi-ideal gas, in which "it is expressly stipulated that the time during which a particle is encountering other particles is very small compared with the time during which there is no sensible action between it and other particles". He felt an urgent need to extend the treatment to material points "which may act on each other at all distances and according to any law which is consistent with the conservation of energy" as well as any external forces. It would then apply equally well to solids and liquids.

One of the last papers Maxwell published, entitled "On Boltzmann's Theorem on the Average Distribution of Energy in a System of Material Points" is devoted to this topic. The volume under review contains a draft of this paper which was read to the Cambridge Philosophical Society in May 1878 and published in a much more polished form in the Transactions about a year later. Maxwell accepted the ergodic hypothesis, used Hamiltonian dynamics, and averaged over all possible configurations consistent with a constant total energy to derive the required results for the equilibrium state.

It is clear that he had been thinking about the problem for some time, since a year previously he had published a lengthy review in "Nature" of H.W. Watson's "Kinetic Theory of Gases", a book which was devoted completely to this topic. Both the draft and final form of this review are published in this volume, which is particularly useful since the latter was omitted from Maxwell's Collected Scientific Papers.

Watson relied mainly on Boltzmann, but also used some unpublished ideas of Maxwell for his discussion of "thirteen propositions in which different cases are considered in the order of their complexity". Here are a couple of Maxwellian gems from this colorful review: "No part of mathematical science requires more careful handling than that which treats of probabilities and averages. Mathematicians, whose competence to deal with other questions is undoubted, have fallen into errors in treating of probabilities, and even the validity of certain methods of proof is still apparently an open question". "The clear way in which Mr. Watson has demonstrated these propositions leaves us no escape from the terrible generality of his results. Some of these, no doubt, are very satisfactory to us in our present state of opinion about the constitution of bodies, but there are others which are likely to startle us out of our complacency, and perhaps ultimately to drive us out of all the hypotheses in which we have hitherto found refuge into the state of thoroughly conscious ignorance which is the prelude to every real advance in knowledge".

Maxwell maintained his interest in thermodynamics as is evidenced by the significant number of communications on this topic. In 1873 Gibbs had published his proposed representation of the thermodynamic properties of a substance by means of a surface in the space of energy, entropy and volume. This would be particularly useful for representing equilibrium between solid, liquid and gaseous phases. Maxwell considered this idea of such importance that he constructed a model of a typical surface in plaster. A photograph of this surface is beautifully reproduced, as well as Maxwell's hand written diagrams of various lines on the surface which represent other thermodynamic parameters. These are taken from sketches which he sent to James Thomson (brother of William Thomson, Lord Kelvin) at Belfast.

He often used postcards as a vehicle of communication, but employed a code of his own which must be deciphered if they are to be understood properly. The cards all bear the signature dp/dT in accordance with the thermodynamic relation dp/dT = JCM. T refers to William Thomson, T' to P.G. Tait. One such postcard to P.G. Tait contains the following intriguing sentence: - "The three ΘΔ men, R, C and T are getting it hot and strong". ΘΔ means "Thermodynamics", R is Rankine, C is Clausius, and he is referring to his extensive review in "Nature" of Tait's book on thermodynamics in which he expresses strong criticism of certain ideas of each of those "three founders of theoretical thermodynamics".

This final volume of the series ends with a supplement containing additional documents located after the publication of the first two volumes. The publication of these three volumes by Prof. P.M. Harman with their enlightening explanatory notes will undoubtedly serve as a landmark for any future work on Maxwell.

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