William Thomson and Thermoelectricity

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Abstract

Among the many pathbreaking scientific works of Lord Kelvin's early years, one of the more impressive is his treatment of thermoelectricity. After laying the theoretical foundations for the first and second laws of thermodynamics in the 1840s, he obviously recognized that the conversions of electrical and mechanical energy are governed by the same thermodynamic principles.

Taking up the analysis of thermoelecticity in the period 1851-54, when modern continuum-thermodynamics did not yet exist, Thomson's *tour de force* application of Carnot's principle to thermoelectric circuits led to his recognition of electronic heat capacity, to his discovery of what is today known as the Thomson effect, and to his prediction of the effect of mechanical stress on thermoelectric potentials.

Thomson's theory is based on equilibrium thermodyanmics and he himself harbored doubts about its applicability to real thermoelectric circuits owing to irreversibilities such as resistance to electric currents. His theory was further thrown into doubt by Boltzmann's 1877 calculations for a real thermoelectric circuit indicating that irreversible effects cannot be neglected. This seems partly to have inspired Onsager's 1931 linear theory of dissipation. This theory was immediately seized upon by numerous influential scientists since the associated "Onsager symmetry" was found experimentally to describe the coupling between various thermoelectric effects. Following Onsager, the theory of thermoelectricity has been thrown into what might be described as a state of limbo, with scientific opinion hovering between Thomson's equilibrium-thermodynamic "heaven" and Onsager's irreversible-thermodynamic "inferno".

In this talk, I propose to review the main results from some relative recent publications[1, 2, 3], casting Thomson's equilibrium theory into a modern form, hopefully more transparent, citing proponents of Thomson and Onsager while noting the amusing incoherence of some renowned scientists who have adopted Onsager's theory, and, finally, mentioning a possible connection of Onsager's dissipational symmetry to the symmetries of equilibrium thermodynamics arising from Maxwellian symmetry of cross derivatives.

As one "take-away" from the present work, it is worth recalling Thomson's insightful *Ansatz* for the rate of heat liberation or absorption $\dot{Q}$ in a thermoelectric circuit as function of electrical current I embodied in the special form of a more general relation

$$\dot{Q} = aI + bI^2$$

where a and b are material constants. The linear term captures the reversibility of equilibrium thermodynamics while the quadratic term arises from irreversibility. It is curious that Boltzmann and others, including perhaps Thomson himself, did not envisage the possibility of inserting an electrical device into a thermoelectric circuit so as to approach a thermostatic state with extraction of useful work. The question of symmetry is still open and may be only partly addressed by a recent publication[3].

Literature Cited

[1] J. Goddard. On the thermoelectricity of W. Thomson: Towards a theory of thermoelastic conductors. *J. Elasticity*, 104(1-2):267–280, 2011.

[2] J. Goddard and K. Kamrin. Dissipation potentials from elastic collapse. *Proc. Roy. Soc. A*, 475(2226):20190144, 2019.

[3] JD Goddard. Thermoelectricity: Thomson vs Onsager, with advice from Maxwell. *Physics of Fluids*, 33(12), 2021.