A Query Relating to Irreversible Thermodynamics.

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Abstract.
Relatively recent work highlighting the quaternion formulation of Maxwell's electromagnetic equations has provoked a re-emergence of the work of Bridgman dating back to the 1920's and this, in turn, raises interesting thoughts concerning the basis of present-day irreversible thermodynamics. Here several questions are considered briefly to, hopefully, provoke further thought and discussion. .

The Query.

Few can doubt the success of traditional irreversible thermodynamics[1], as based on the pioneering work of Onsager[2], in explaining a large number of observed physical processes. However, a query has always existed over the assumption of microscopic reversibility. This assumption is basic to the ensuing theory but, as pointed out by Bridgman[3], does not necessarily apply in all genuine physical cases which might need to be examined. It is interesting, therefore, to realise that, as long ago as the 1920's, several thermoelectric and thermomagnetic processes normally felt to be within the preserve of irreversible thermodynamics had had explanations proffered via classical thermodynamics by Bridgman[3] himself, but all this was achieved prior to the appearance of Onsager's elegant treatment and so, possibly because of this, has been overshadowed if not forgotten.

Recently, Jack[4] has re-examined the seemingly forgotten quaternion formulation of Maxwell's electromagnetic equations and then proceeded to consider, with some success, several processes normally thought to be the preserve of traditional irreversible thermodynamics. His initial analysis is seen to lead to the following set of four modified Maxwell electromagnetic equations

$$\nabla \times \boldsymbol{B} = \frac{1}{c}\frac{\partial \boldsymbol{E}}{\partial t} + \nabla T, \qquad \nabla \times \boldsymbol{E} = -\frac{1}{c}\frac{\partial \boldsymbol{B}}{\partial t},$$

$$\nabla.\boldsymbol{E} = +\frac{1}{c}\frac{\partial T}{\partial t}, \qquad \nabla.\boldsymbol{B} = 0,$$

where the 'new' scalar T field is given by

$$T = -\frac{1}{c}\frac{\partial \phi}{\partial t} + \nabla.\boldsymbol{A}$$

with ϕ and $\boldsymbol{A}$ being the scalar and vector potentials as usual. All other variables retain their normally accepted meanings within electromagnetic theory.

Interestingly, the examples of effects Jack[4] then chose to consider were, understandably, also within the realms of thermoelectric and thermomagnetic phenomena. In this, he seemed to follow Bridgman's lead as referred to above. Bridgman introduces a second electro-motive force and refers to the two emf's as a 'driving' emf and a 'working' emf. Jack speculates on whether or not his two emf's correspond to these but, considering his linking up of the scalar T field, which appears in the quaternion formulation of Maxwell's equations, with heat, one wonders if the second emf Jack introduces should be referred to as a tmf or thermo-motive force such as Bridgman introduces when discussing the Ettinghausen effect without assuming that effect to be essentially irreversible. Bridgman assumes the temperature difference between the sides of the plate in the Ettinghausen effect does not result in a thermal conduction current but is a temperature difference maintained permanently with no thermal flow; that is, the plate is the seat of a 'thermo-motive' force which may be viewed as analogous to the electro-motive force of a battery. This would seem to indicate it sensible for Jack's so-called second emf to be aligned with Bridgman's notion of a thermo-motive force. Hence, Jack linking the scalar T field with heat appears to be a viable thought. Also, it is after this identification that he is able to discuss the Seebeck and Thomson effects which are normally regarded as being within the realm of irreversible thermodynamics.

Bridgman investigates four specific effects in chapter seven of his book: the Hall effect, the Ettinghausen effect, the Nernst effect and the Righi-Leduc effect. In some ways, especially concerning the present context, the main point of interest to emerge from Bridgman's discussion as far as these effects are concerned is the fact that, assuming the Ettinghausen effect to be essentially irreversible, leads to an incorrect conclusion. He himself proceeds to discuss the effect afresh, introducing some new ideas such as the notion of a thermo-motive force, and succeeds in deducing correct expressions to describe the said effect. As he himself points out, all this work was seemingly made redundant after the emergence of Onsager's elegant theory for a basic interpretation of irreversible thermodynamic effects. However, the question of the range of applicability of the idea of microscopic reversibility is still present, if only in the background. Therefore, the emergence of this work by Jack which reintroduces the scientific community to a quaternion formulation of Maxwell's electromagnetic equations and, with it, the identification of a scalar field in addition to the vector electric and magnetic fields might be felt to herald the need for a reinvestigation of some well-established views on irreversible thermodynamics, given that this reintroduced formulation allows the explanation of several effects, previously deemed to be explainable only within the domain of irreversible thermodynamics, without recourse to the techniques of that branch of physics.

Obviously, the subject of irreversible thermodynamics is applicable to many areas other than those concerned with thermo-electric and thermo-magnetic phenomena. However, the very fact that effects in these two areas may be investigated successfully without recourse to the methods of traditional irreversible thermodynamics, together with the thought that the assumption of microscopic reversibility might not hold in all circumstances, does raise the query of whether the whole basis of irreversible thermodynamics as presently understood might usefully be examined afresh?

References.

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2. Onsager, L., 1931, Phys. Rev. **37**, 405-426; **38**, 2265-2279
3. Bridgman, P. W., 1961, *The Thermodynamics of Electrical Phenomena in Metals,* Dover Publications Inc., New York
4. Jack, P. M., 2003, *Physical Space as a Quaternion Structure,*1 *Maxwell Equations. A Brief Note,* https://doi.org/10.48550/arXiv.math-ph/0307038