ARTICLES

COMMENTS ON THE BENOFY AND QUAY THEORY OF THERMOMAGNETIC EFFECTS

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ABSTRACT

The claim by Benofy and Quay that Fourier's inequality ($J_q \cdot \nabla T \leq 0$) contains a further thermodynamic principle beyond that contained in the Second Law of Thermodynamics is investigated. It is shown that the inequality is not in contradiction with the usual assumptions of linear irreversible thermodynamics, and when properly interpreted, the inequality is not violated as is claimed. It is not necessary to postulate a 'change in material coefficients' for thermo-electrical phenomena.

INTRODUCTION

Benofy and Quay (henceforth abbreviated BQ)[1] claim that Fourier's inequality $J_q \cdot \nabla T \leq 0$, where J_q is the heat current vector and T the temperature, contains a further thermodynamical principle beyond that contained in the Second Law of Thermodynamics. BQ explicitly state that their treatment refers to conductive heat only in an early part of their paper[2], and in this respect there may well be (within the classical, non-statistical continuum scheme) some validity in their arguments. However, later in their paper there is a tendency to treat this form of heat as the only form of thermal energy flux.

It is (as will be shown) this failure to recognize other forms of thermal energy flow that has led BQ to misunderstand such works as Callen's Linear Irreversible Thermodynamics (LIT) formulation of magnetothermoelectric effects[3]. They seem to have misunderstood that while Callen's equations predict non-zero isothermal heat currents, such currents are due to 'heat of transport' and not conductive heat, and therefore do not violate Fourier's inequality, which refers to conduction alone. By 'heat of transport' is meant the thermal energy transported by a current of particles as discussed following equation (2) below and also in Callen's article[5]. This misunderstanding is evident in their objection to Callen's equations requiring that heat should flow in the absence of a temperature gradient due to the 'mutual interference of heat flow and electric current flow in a system'[3,5]. Furthermore, BQ seem to imply that the LIT 'coupling' of various forces and fluxes are the root of the problem regarding violations of the Fourier inequality.

"But, unlike previous workers in this area, we do not 'couple' the equations themselves by adding any term depending on electric field to Fourier's equation or one depending on thermal gradient to Ohm's Law. For, it is such 'couplings' that generate theoretical violations of Fourier's inequality. Rather, we add one further equation, long known in its rudimentary form, which 'couples' the two gradients in such a way as to give the full set of empirically observable relations while maintaining Fourier's Principle intact."

THE INTERPRETATION OF LIT AND THE CONNECTION TO THE BQ THEORY

It must be understood that in LIT heat processes involve both conduction by a 'medium' and transport by particle currents. In the case of the treatment of magnetothermoelectric effects by Callen and BQ, the medium is a flat, uniform (metallic) conductor. Taking the simplest possible case, consider the LIT expression for a one-dimensional flow of heat and an electric current[6,7] in an electrical conductor given by the equations:

$$\mathbf{J}_q^{\text{tot}} = -L_{qq} \nabla T/T^2 - L_{qe} \nabla E/T, \quad (1)$$

$$\mathbf{J}_e = -L_{ee} \nabla E/T - L_{eq} \nabla T/T^2, \quad (2)$$

where we have neglected (as with Callen) the concentration of the electrons and only consider the electrical potential term E, the temperature T and their respective gradients as components of the force. The L's are the temperature-dependent coupling coefficients. $\mathbf{J}_e$ represents the electrical current flow vector and $\mathbf{J}_q^{tot}$ the thermal energy flow vector, where we have written $\mathbf{J}_q^{tot}$ as a sum with contributions from the thermal (non-conductive thermal transport energy flow due to electrons, i.e. heat of transport) $\mathbf{J}_q^{trans}$ and a Fourier-like conductive heat flow term $\mathbf{J}_q^c$ defined respectively by the equations:

$$\mathbf{J}_q^{\text{trans}} = -L_{qe}\nabla E/T \quad (3)$$

and

$$\mathbf{J}_q^c = -L_{qq}\nabla T/T^2.$$

It can be shown[8] that

$$-L_{qe}\nabla E/T = \varepsilon T K_e \nabla E, \quad (4)$$

and in the absence of a thermal gradient, $\mathbf{J}_e = -K_e\nabla E$, so that

$$\mathbf{J}_q^{\text{tot}}|_{\nabla T=0} = \mathbf{J}_q^{\text{trans}} = \varepsilon T\mathbf{J}, \quad (5)$$

where εT is neither more nor less than the thermal energy per unit current (K_e is the electrical conductivity) per unit area.

Equations (1) and (2) are first order local equations. If there is conversion, i.e. dissipation where the electrical potential work is dissipated as heat to the lattice, then local heating would cause a near instantaneous temperature change in the lattice so that the resulting temperature gradient would cause heat to flow by a lattice conductive mechanism as given in (1). There is no reason why (1) would preclude the possibility of conductive heat and thermal energy of transport from moving in opposite directions.

With the assumption of 'local equilibrium' in LIT as a basic postulate[9], we can interpret T in (5) as the local temperature and $\varepsilon=\varepsilon(T)$ as a locally defined Seebeck coefficient which will of course depend not only on the temperature but also on the nature of the medium[10].

Subtracting the effects of Joulean heating (by, for instance immersing the conductor in a constant temperature bath) there can be no net conduction of heat along the direction of electron flow in the isothermal situation, in accordance with the Fourier principle. However, electrons will flow along the conductor and carry thermal energy in the direction of their flow. Since the system is characterized by a constant temperature, there will only be transfer of thermal energy by transport and no conduction.

The LIT formulation therefore does not contradict the ideas presented by BQ provided both refer to conductive heat, whereas the 'rational thermodynamics' school of Truesdale and others are not compatible with the BQ assertions regarding conductive heat[11].

It is only when BQ regard their $\mathbf{q}$ vector as constituting the total heat current that misunderstandings with the LIT theory become apparent, since one of the BQ assumptions is that[12] $\mathbf{q}=0$ entails $\nabla T=0$. Equation (1) does not support this view if the BQ $\mathbf{q}$ is identified with $\mathbf{J}_q^{tot}$. There is no other way in which it is possible for LIT to violate the Fourier inequality unless this identity is made. BQ have not shown why any violations should occur, although they insist that the LIT coupling coefficients cause violations to the Fourier inequality.

BQ introduced the idea of the 'change of material coefficients'[13] as an alternate way of viewing coupled phenomena[13] to circumvent the purported difficulties inherent in other approaches. Such a viewpoint may in part be traced to the influence of Campbell[14,15] in his experimental description of thermomagnetic effects in which the actual form of the kinetic equations does not change; the result of the interaction of a magnetic (and possibly other fields) simply serves to modify the kinetic coefficient pertinent to the flow. For instance, if the resistance R_e is said to be defined for a conductor according to the phenomenological equation:

$$\mathbf{J}_e = (1/R_e)\Delta E, \quad (6)$$

where ΔE is a fixed potential difference across the uniform conductor for current flow $\mathbf{J}_e$ (see reference *16 for BQ interpretation of magneto-resistance*), for large enough fixed ΔE (i.e. a voltage source across the conductor) the current through the conductor will vary as the applied magnetic field (or other field) gradient varies due to the presence of the Lorentz and lattice forces on the moving electrons due to the magnetic field gradient; what has occurred is that a seat of e.m.f. has been created within the conductor which modifies the flow of electrons, so that from (6), Campbell concludes that a 'change' of resistance has occurred. If there exists an active Seebeck field in the conductor due to a temperature gradient instead of a magnetic filed, a similar situation as for the magnetic case would ensue, i.e. the current will vary (for fixed ΔE) as the temperature gradient varies.

However, it may be argued that definition (6) only applies to isothermal conductors with no other interactions apart from the external field ΔE. If an active e.m.f. seat is induced within the conductor (e.g. by say the Seebeck field due to a temperature gradient) then it would tend to oppose or assist the field due to an external seat of e.m.f. Hence a different steady state current would flow through the conductor for the same voltage difference ΔE if these fields were present compared to the case when they are not. The 'actual' resistance of the material does not in fact change if we properly account for the induced e.m.f.

We now give an example which will also provide the proper coupling relationship between the electric field and temperature field, other than the one provided by BQ[17], which cannot be correct, as will be shown.

For the Seebeck effect, for example, the non-uniform temperature distribution will complicate the measurement of resistance because of the induced e.m.f. This can be allowed for, however, by defining the passive resistance of a conductor with a non-uniform temperature distribution maintained at T_1 and T_2 at the ends by

$$R_e = \overline{R(T_1)} + \int_{T_1}^{T_2} R(T)\cdot l'\,\mathrm{d}T \tag{7}$$

with $l' = \partial l/\partial T$. Here, $R(T)$ is the resistance per unit length, and $\overline{R(T_1)}$ the resistance of the conductor at temperature T_1 and l the length parameter of the conductor. The change of resistance may be determined by isothermal measurements of the resistance at different temperatures.

The heat dissipated in an isothermal passive resistor is given by the total work done by the field and is given per unit length by the term $-\mathrm{d}E/\mathrm{d}x\cdot J_e$ which may be termed the isothermal Joulean dissipation. For a resistance of unit length, we may write:

$$\text{Joulean dissipation} = \mathbf{J}_e^2 R_e = -\mathrm{d}E/\mathrm{d}x\cdot\mathbf{J}_e. \tag{8}$$

On the other hand, the total heat dissipated in unit length of a conductor[18] in the steady state in the presence of both an electrical and thermal gradient may be written as (neglecting the Fourier conduction component):

Total heat dissipated =

$$-T\mathbf{J}_e\cdot\frac{\mathrm{d}\varepsilon}{\mathrm{d}x} + \mathbf{J}_e^2/K_e = -T\mathbf{J}_e\cdot\frac{\mathrm{d}\varepsilon}{\mathrm{d}x} - \mathbf{J}_e\cdot\frac{\mathrm{d}E}{\mathrm{d}x} - E\frac{\mathrm{d}T}{\mathrm{d}x}\cdot\mathbf{J}_e \tag{9}$$

where

$$\mathbf{J}_e^2/K_e = \mathbf{J}_e^2 R_e = -\mathbf{J}_e\cdot\mathrm{d}E/\mathrm{d}x - \varepsilon\cdot\mathrm{d}T/\mathrm{d}x\cdot\mathbf{J}_e. \tag{10}$$

Thus, in the presence of a thermal gradient, the Joulean dissipation $\mathbf{J}_e^2 R_e$ is composed of two terms, the isothermal Joulean dissipation $-\mathbf{J}_e\cdot\mathrm{d}E/\mathrm{d}x$ and a correction term linear in the temperature gradient which may be called the 'Seebeck' heat $-\varepsilon\cdot\mathrm{d}T/\mathrm{d}x\cdot\mathbf{J}_e$.

We may simulate a unit length of the conductor by the circuit element depicted in figure 1 where R_e is the intrinsic resistance, V_1 the Seebeck active e.m.f., and $\mathrm{d}E/\mathrm{d}x$ is the actual e.m.f. across the segment whose surfaces are at a and b.

Then Kirchoff's voltage law gives for the above system:

$$\mathrm{d}E/\mathrm{d}x = -\mathbf{J}_e R_e + V_1, \tag{11}$$

where V_1 is $-\varepsilon\ \mathrm{d}T/\mathrm{d}x$, the Seebeck active e.m.f. field. Thus from (11)

$$\mathbf{J}_e^2 R_e = \mathbf{J}_e^2/K_e = -\mathrm{d}E/\mathrm{d}x\cdot\mathbf{J}_e - \varepsilon\,\mathrm{d}T/\mathrm{d}x\,\mathbf{J}_e \tag{12}$$

as before in (10).

If $\mathbf{J}_e \to 0$, (i.e. the Joulean heat is made to vanish) then the actual work done $-\mathrm{d}E/\mathrm{d}x\cdot\mathbf{J}_e$ in a unit length is numerically equal to the Seebeck heat loss[14]. The terms ϕ and $\nabla\phi$ used by BQ[1] are equivalent to our E and $\mathrm{d}E/\mathrm{d}x$ (in one dimension).

When $\mathbf{J}_e^2 R_e \to 0$, then (12) yields

$$\mathrm{d}E/\mathrm{d}x|_{\mathbf{J}_e=0} = -\varepsilon\nabla T. \tag{13}$$

This relation defines the Seebeck coefficient ε (ref. 20). BQ write instead

$$\nabla\phi = \tau\nabla T, \tag{14}$$

where τ is the Thomson coefficient.

Equation (14) is supposed to represent the link between the electrical potential and temperature

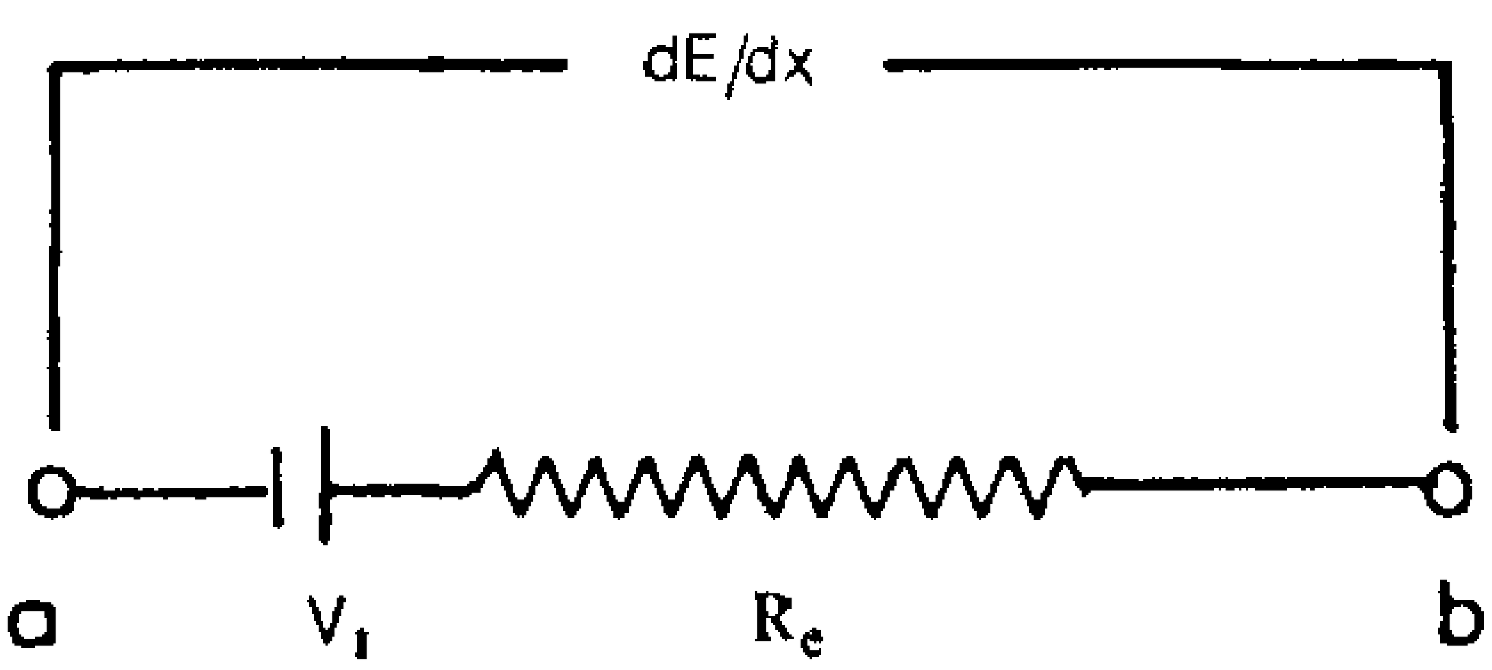

Figure 1.

gradient, "long known in its rudimentary form"[21]. The only reference to any such relationship is in one of Bridgman's theoretical constructs. If they were influenced by this construct, then it appears that they have misconstrued Bridgman's expression[22]

$$(\text{e.m.f.})\, w = \sigma (\mathrm{d}T/\mathrm{d}x), \tag{15}$$

where σ is the Thomson coefficient in Bridgman's notation. The BQ e.m.f. $\nabla\phi$ refers not to the 'conventional' potential difference but rather to Bridgman's hypothetical 'working' e.m.f. denoted (e.m.f.)w which is not a directly observable quantity but is defined in terms of the rate at which heat is absorbed when current flows[23].

In any case, it is not correct to use (14) as a link between the electrical potential and the temperature gradient.

CONCLUSIONS

It is conceivable that the 'change in material coefficients' may feature in a higher order expansion of flux expressions than is used in LIT (which is a first order expansion) but it would not be appropriate to equate these changes with the first order approximations characteristic of such theories as Onsager's LIT. BQ, however, neglected the importance of thermal transport and convective heat, and required the "change in material coefficients" as a device to compensate for this neglect. However, since conductive heat transfer does not involve the same mechanism as the other forms of thermal exchange, it follows that the BQ theory is incomplete if not flawed. We have shown that LIT is a consistent theory to first order and yields the correct convergence in the restricted treatment of thermo-electric effects above. The BQ hypothesis regarding the Fourier inequality for the conductive part of the heat current still remains a very interesting and original conjecture.

It must be stressed that the above derivations are based on 'per unit length', of material. It will be shown in future communications that a more detailed analysis of the above implies further generalizations of the Kelvin relations for thermocouples and that Onsager-like reciprocity may be derived from the conjecture on Fourier heat conduction within the LIT framework which couples forces and fluxes linearly with no reference whatsoever to the Onsager hypothesis of detailed balance, microscopic reversibility and the regression of fluctuations. Finally, a certain degree of scepticism is warranted in regard to the Bridgman equation and its experimental verifiability.

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