Thermoelectricity: Thomson vs. Onsager, with advice from Maxwell

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This paper deals with the long-standing conflict between interpretations of thermoelectricity based on the original reversible thermodynamics of W. Thomson and the later irreversible thermodynamics of L. Onsager. It is shown that, by a slight modification of the Maxwellian relaxation treated in a previous paper (J. Goddard and K. Kamrin. *Proc. Roy. Soc.* A 475.2226 (2019): 20190144), Onsager's symmetry is simply a reflection of the underlying symmetry of equilibrium thermodynamics. It is also shown that a modern interpretation of Thomson's thermodynamics, as given recently by the present author, reveals thermoelectricity to be the analog of a fluid-mechanical transport process with the limit of thermodynamic equilibrium corresponding to the convection-dominated regime of large Péclet number.

"Die ... Theorie ist so schön in sich abgeschlossen, dass die Möglichkeit irher vollständig Übereinstimmung mit den Thatsachen nicht geleugnet werden kann." L. Boltzmann (1887). Comment on Thomson's theory of thermoelectricity.[5]

I. INTRODUCTION

Classical thermodynamics involves two distinguished and idealized limits, namely, strictly reversible or conservative systems, and strictly irreversible or dissipative systems. Remarkably, these two extremes are joined at the hip mathematically since both involve thermodynamic potentials and may admit the associated variational principles. The classical treatments of thermoelectricity provide a perfect illustration, according to which we have, on the one hand, the landmark equilibrium-thermodynamic treatment of W. Thomson[1] (later Lord Kelvin) and, on the other, the diametrically opposed irreversible-thermodynamic treatment of L. Onsager[2]. What is most striking in this state of affairs is the apparent success of either treatment in describing the relation between various thermoelectric effects. The purpose of this brief article is to provide a plausible explanation, although time does not permit a detailed analyses of numerous and varied experiments.

II. HISTORY

In a previous work[3], hereinafter referred to as Ref. 1, the present author provides a review of Thomson's thermoelectricity recasting it into a modern equilibrium-thermodynamic form that provides a transparent interpretation of various thermoelectric quantities in terms of standard thermodynamic quantities. Table I summarizes the various effects and the related quantities

TABLE I. Thermoelectric effects

Effect	Relation
Volta	$\mathcal{V}^{\mathrm{AB}}(\theta) = -\mu_e^{\mathrm{AB}}(\theta)$
Seebeck	$\mathcal{S}^{\mathrm{AB}} = \partial_\theta \mathcal{V}^{\mathrm{AB}} = \eta_e^{\mathrm{AB}}(\theta)$
Peltier	$\dot{Q}^{\mathrm{AB}} = \Pi^{\mathrm{AB}} I = \theta \eta_e^{\mathrm{AB}}(\theta) I$
Thomson	$d\dot{Q} = \mathcal{T} I \, \mathrm{d}\theta = c_{pe} I \, \mathrm{d}\theta$

where θ denotes absolute temperature. Effects at the heterojunction AB between conductors A and B are given, respectively, in terms of the Volta potential $\mathcal{V}$, Seebeck coefficient $\mathcal{S}$, and Peltier heat $\dot{Q}$, with coefficient Π, where I denotes electrical current through effectively one-dimensional conductors and junctions. Last but not least is the Thomson effect, giving the external reversible increment of heat $d\dot{Q}$ released by electrical current flow through the incremental temperature change $\mathrm{d}\theta$ arising from a thermal gradient along a materially homogeneous conductor. As emphasized below, it is merely the convection of electronic enthalpy by electrical current.

Above as in the following we employ italic d to denote infinitesimal quantities, reserving the upright d to denote differentials of state variables. Also we employ superposed dots to denote temporal rates that are not necessarily rates of change of various quantities. Finally, we employ the thermodynamic notation of Gibbs employed in Ref. 1 and favored in much of the modern literature on continuum thermomechanics.

As pointed out in Ref. 1, Thomson's analysis is based on a *tour de force* application of Carnot's principle, whereas the modern treatment offered in Ref. 1 and summarized in Table I makes evident the relation of various effects and associated coefficients to the thermodynamic functions h_e, the electronic enthalpy, μ_e, the electronic Gibbs free energy, and the entropy $\eta_e = -\partial_\theta \mu_e(\theta)$. For rigid conductors with uniform electrical charge density ρ_e all the above thermoelectric relations follow by standard thermodynamic formulae from Thomson's "specific heat of electricity" $\mathcal{T} = c_{pe}(\theta)$, as discussed in detail in Ref. 1. That review is concerned with mechanical effects and the specific Helmholtz free energy ψ of a conductor is allowed to depend on strain and specific electrical charge $q_e = \rho_e/\rho$, where ρ_e is electrical charge density, ρ is mass density of the conductor, and the subscript e stands for the partial derivative $\partial_e = \partial/\partial q_e$ of thermodynamic state functions with strain or stress and temperature θ held constant. In summary, we have

$$\psi_e = \varepsilon_e - \theta\eta_e = \varepsilon_e \;\&\; \mu_e = \psi_e + pv_e = h_e - \theta\eta_e + pv_e, \tag{1}$$

where $\varepsilon, v = 1/\rho, p$ denote, respectively, specific internal energy, specific volume, and isotropic pressure.

In addition to the above relations we recall that the the total electrochemical potential is given by

$$\phi_e = \mu_e + \Phi = \partial_e(g + \Phi q_e,) \tag{2}$$

where g is specific Gibbs free energy and Φ is the potential of an external electric field. Continuity of ϕ_e a heterojunction gives the jump in Φ in terms of that of μ^e represented by the Volta effect in Table I.

For purposes of the present discussion, it suffices to consider rigid conductors with partial electronic volume $v_e = 0$ so that $\varepsilon_e \equiv h_e$ and $\mu_e \equiv \psi_e$. Moveover, setting aside certain capacitance effects we may assume q_e to be constant and spatially uniform. Hence, as anticipated in Table I, we may assume ε_e, h_e and η_e to depend only on θ.

It should be noted that the above theoretical framework is in keeping with Thomson's analogy of thermoelectric currents to the flow of a massless incompressible fluid (well before the discovery of the electron by another Thomson[4] and the advent of modern theories of electronic conduction).

Following Thomson's express concerns as to the separability of reversible and irreversible thermodynamic effects, doubts were subsequently raised by others, notably by Boltzmann[5] whose admiration of Thomson's theory is summarized by the above epigrammatic quote. Thomson's treatment was later obscured and nearly swept away by the linear irreversible thermodynamics of Onsager[2], at least according to one group of eminent scientists. Ref. 1 cites certain tortured logic that occasionally surrounds the question.

Table II gives a brief history of the opposing treatments of the subject. As one exception in Table II, the calculation done by Boltzmann[5] led him to conclude that both reversible and irreversible heating are inevitable in a closed thermoelectric circuit, as already anticipated for electrically linear conductors by Thomson[1,6]. In particular, Thomson posits that the rate of heat exchange with the surroundings $\dot{Q}$ should depend on the thermoelectric current I as $\dot{Q} = aI + bI^2$, where the coefficients a, b are independent of I. The linear term in I represents reversible heat effects associated with thermodynamic equilibrium while the quadratic term represents dissipative (Joule) heating. Thus, the extremes identified in the present work correspond to $b \equiv 0$ (Thomson) or $a \equiv 0$ (Onsager). In that connection, we recall that Thomson stipulates that his equilibrium-thermodynamic relations should apply only for sufficiently small I, also noting that this could be achieved by insertion of a device to extract work from the thermoelectric circuit. Thus, the back-emf of the device would serve to diminish the current I allowing one to approach a quasi-static thermodynamic equilibrium.

TABLE II. Brief historical summary of opposing views

Reversible	Irreversible
W. Thomson (1851-54)[1,6]	...
...	L. Boltzmann (1887)[5]
G.N. Lewis (1918)[7]	...
P.W. Bridgman (1918-29)[8]	...
E.H. Hall (1918-20)[9]	...
...	L. Onsager (1931)[2]
...	H. Callen (1948)[10]
....	J.F. Nye (1957)[11]
N.F. Mott (1958)[12]	...
...	A. Sommerfeld (1964)[13]
...	C. Kittel (1986)[14]
...	(Many others)
This Author (2011)[3]	...

With the above as background, the present work is aimed at reconciliation of the two extreme models of the thermodynamics by means a recent work that connects the two otherwise distinct types of potentials involved.

III. POTENTIALS AND RELAXATION

A simple equilibrium-thermodynamic systems with finite degrees of freedom is described by the temperature θ and an n-dimensional vector space of configurational variables $\mathbf{x} = \{x^1, x^2, \dots, x^n\}$, and we can identify dual space of generalized specific forces $\mathbf{f}(\theta, \mathbf{x}) = \{f_1, f_2, \dots, f_n\}$ (force per unit mass) such that the incremental work done on the system is given by

$$dw = \mathbf{f}\cdot \mathrm{d}\mathbf{x} = \; f_i\,\mathrm{d}x^i, \text{ with } f_i = \partial_{x^i}\psi(\theta, \mathbf{x}),\ i = 1, \dots, n. \tag{3}$$

where $\partial_z = \partial\,/\partial z$ and sums from 1 to n are taken over repeated indices, here and below, and where ψ denotes specific Helmholtz free energy. We recall that there exists a Legendre dual

$$\varphi(\theta, \mathbf{f}) = \mathbf{f}\cdot\mathbf{x} - \psi \text{ with } x^i = \partial_{f_i}\varphi \tag{4}$$

.

For the other extreme of interest here, strictly dissipative systems (i.e. generalized Onsager-symmetric systems devoid of gyroscopic or powerless force-velocity pairs[15–17]), we encounter a parallel structure with generalized velocities $\mathbf{v} = \{v^1, v^2, \dots\}$, for example, $v^i = \dot{x}^i$, replacing $\mathbf{x}$, such that

$$f_i = \partial_{v^i}\tilde{\psi}(\theta, \mathbf{v}), \text{ and } v^i = \partial_{f_i}\tilde{\varphi}(\theta, \mathbf{f}), \tag{5}$$

The tildes identify the dissipation potentials of Edelen[15–17] which serve to define non-linear Onsager symmetry, exemplified by

$$\partial_{v^i} f_j = \partial_{v^j} f_i, \text{ for } i, j = 1, ..., n \tag{6}$$

In the notation of Onsager $\{\mathbf{v}, \mathbf{f}\}$ is denoted by the "flux-force" pair $\{\mathbf{J}, \mathbf{X}\}$, where the fluxes are abstract rates, not generally given as the time rate of change of configurational variables, and the same interpretation of $\mathbf{v}$ can be made for purposes of the present formulation. We recall the well-known fact that the Onsager symmetry in (6) breaks down in the presence of gyroscopic effects of the kind associated with magnetic fields.

A. Thermoelectric relaxation

In an effort to clarify the origins of dissipation potentials, Goddard and Kamrin[18] have recently proposed a generalization of Maxwellian relaxation on small time scales τ, which leads in the the present context to the *relaxation approximation*:

$$\tilde{\psi}(\theta, \mathbf{v}) = \tau^{-1}\psi(\theta, \tau\mathbf{v}), \text{ and } \tilde{\varphi}(\theta, \mathbf{f}) = \tau^{-1}\varphi(\theta, \mathbf{f}), \tag{7}$$

where τ denotes a relaxation or "elastic-collapse" time, for which relevant estimate is given below. We note that this time constant is related to that defining the retarded motions of Coleman and Noll[19] and that terms $O(\tau)$ represent the onset of dissipation.

It is clear that the transformation (7) preserves forces and gives a "displacement" $\tau\mathbf{v}$ occurring on time-scale τ.

To a large extent, the present connection of irreversible forces and fluxes to thermodynamic equilibrium may serve to allay some albeit not all of the well-known critiques of "Onsagerism"[20,21].

B. Clapeyron energy

With $\mathcal{E} = \mathbf{f}\cdot\mathbf{x}$ as analog of *Clapeyron* elastic energy, the relaxation approximation for the rate of dissipation is given by

$$\mathcal{D} = \tau^{-1}\mathcal{E}(\tau\mathbf{v}) = \mathbf{v}\cdot\mathbf{f}(\tau\mathbf{v}) = \tau^{-1}\mathbf{f}\cdot\mathbf{x}(\mathbf{f}), \tag{8}$$

It is worthwhile noting the generally important result that convex equilibrium-thermodynamic potentials can be derived from convex Clapeyron energies by Edelen's transformation[17] between dissipation rate and dissipation potential, namely

$$\varphi(\mathbf{f}) = \int_0^1 \varepsilon(\xi\mathbf{f})\frac{\mathrm{d}\xi}{\xi} = \mathbf{f}\cdot\int_0^1 \mathbf{x}(\xi\mathbf{f})\,\mathrm{d}\xi, \tag{9}$$

and an identical relation for the dual potential $\psi(\mathbf{x})$ with roles of $\mathbf{f}$ and $\mathbf{x}$ reversed and ε given as function of $\mathbf{x}$.

For the linear response treated below, the Clayperon energy reduces to a quadratic form, such that it is equal to twice the stored energy, as has been considered in detail by Fosdick and Truskinovsky[22]. Hence, the rate of dissipation assumes the Onsager quadratic form $\mathcal{D} = \mathbf{f}\cdot\mathbf{L}\mathbf{f}$ which, as pointed out elsewhere[17] is twice the dissipation potential $\tilde{\varphi}$.

C. Multimodal forms

As another important general matter that has direct bearing on the present application, it is necessary to extend the above treatment of uniform relaxation given by Goddard and Kamrin[18] to relaxation on commensurate but distinct time scales for the various modes of relaxation. With a primary view to local linear forms, these modes may be associated with the eigenvectors and eigenvalues λ_i of the local Hessian $\mathbf{H}$ with components H^{ij} and diagonalization given by

$$H^{ij} = \partial_{f_i}\partial_{f_j}\varphi(\theta, \mathbf{f}), \text{ with } \mathbf{H} = \mathbf{P}\mathbf{\Lambda}\mathbf{P}^{\mathrm{T}}, \tag{10}$$

where the diagonal form $\mathbf{\Lambda} = \text{diag} = \{\lambda_1, \ldots, \lambda_n\}$ is given by a standard orthogonal matrix $\mathbf{P}$. Given a second diagonal matrix $\mathbf{R} = \{r_1, \ldots, r_n\}$ of inverse ratios of relaxation times we obtain the linear symmetric form $\hat{\mathbf{H}}$

$$\mathbf{L} = \hat{\mathbf{H}} = \tau^{-1}\hat{\mathbf{R}}\mathbf{H}, \text{ with } \hat{\mathbf{R}} = \mathbf{P}\mathbf{R}\mathbf{P}^{\mathrm{T}}, \tag{11}$$

The symmetric matrices $\mathbf{H}$ and $\hat{\mathbf{R}}$ are readily shown to commute yielding symmetry of $\hat{\mathbf{H}}$, and Onsager's linear theory is of course obtained by evaluation of the local Hessian $\mathbf{H}(\mathbf{f})$ at $\mathbf{f} = \mathbf{0}$.

IV. ONSAGER'S THEORY

As the key result of this section, the above considerations imply that we may obtain a generalization of Onsager's strictly dissipative model from Thomson's strictly conservative model by the transformation $\{\mathbf{x}, \mathbf{f}(\mathbf{x})\} \to \{\tau\hat{\mathbf{R}}\mathbf{v}, \mathbf{f}(\tau\hat{\mathbf{R}}\mathbf{v}\}$. In the case of the linearized response arising for small $|\tau\mathbf{v}|$ note that the relation (11) is the analog and generalization of Maxwell's expression for viscosity as product of relaxation time and elasticity[18,23]. (cf. the "pseudolinear" forms for non-linear response given elsewhere[17] (and Errata).)

Should the above ideas prove correct, they might serve generally to establish the equivalence of Onsager's celebrated "microscopic reversibility" to macroscopic thermodynamic reversibility.

At any rate, we require convexity of the function $\varphi(\mathbf{f})$, except possibly for certain "soft-mode" instabilities such as those occurring at phase transitions, so that its Hessian is positive-definite and invertible, leading to similar results for Onsager resistance as inverse of $\mathbf{L}$.

As regards the linear theory, it is worth noting the oft-quoted paper of Miller (1960) which claims to offer experimental tests of Onsager symmetry for various dissipative transport phenomena. In the case of thermoelectricity[24] (Section III,Eq. (18)), Miller makes unabashed use of Thomson's relations for the ratio of off-diagonal terms (L_{12}/L_{21}) to establish the putative Onsager symmetry and then rejects the validity of Thomson's analysis, as is the case with several prominent researchers cited in Table 1 and pointed out elsewhere[17]. It is clear that the relaxation times representing irreversibility must drop out of this ratio, so that Onsager symmetry is nothing more than *Thomson symmetry*, a matter revisited below.

V. CIRCUITS

In the case of a simple thermoelectric circuit we may provisionally regard $\tau|\mathbf{v}|$ as the analog of Maxwell's dielectric displacement which could be realized in principle by interruption of the circuit with a capacitor or storage battery, which would also serve to store thermoelectrostatic energy.

It is clear that the thermal driving forces arise from temperature gradients in the surrounding, and one drawback of Thomson's theory is that it requires reversible external heat exchange everywhere on the boundary of a conductor, requiring a very special environmental temperature gradient and, in effect, a continuum of Carnot engines on which his analysis is based[3]. We consider below a somewhat less idealized and also less complicated set-up involving internal heat transfers which allows us to treat the case of a thermally insulated thermoelectric circuit with external heating only at discrete points. With the insertion of a voltage source into the thermoelectric circuit we obtain a simple Carnot heat engine or heat pump depending on $\Theta = \theta_{\mathrm{H}} - \theta_{\mathrm{L}}$ and on the emf V of the voltage source, as depicted below in Fig. 1.

A. Dissipative transport phenomena

Assuming Fourier's and Ohm's law for heat flux $\mathbf{q}$ and electrical flux $\mathbf{j}_e$, the steady-state energy balance, given as Eq. (2) in Ref. 1, reduces for a rigid conductor to

$$\begin{gathered}\boldsymbol{v_e}\cdot\nabla\theta = \alpha_e\left(\nabla^2\theta + \frac{j_e^2}{\sigma k}\right) + \beta, \text{ with } \alpha_e = k/\rho_e c_{pe}, \\ \beta = J/c_{pe}\rho_e, \text{ and } j_e = |\mathbf{j}_e|,\end{gathered} \tag{12}$$

where k, σ, $\boldsymbol{v}_e = \mathbf{j}_e/\rho_e$, and J denote, respectively, the thermal and electrical conductivities, the effective velocity of the electrical current, and the influx of external heat which depends in general on spatial position. Moreover, the barycentric velocity of the conductive medium has been taken as zero, neglecting the contribution from electrical current. There nevertheless remains the convective term in (12), representing the Thomson effect, while the source terms on the right-hand side represents Joule and external heating and the heat conduction term is diffusive .

We note that (12) is the rough analog of the fluid-mechanical Brinkman equation for heat transport with viscous dissipation[25] (pp. 276 ff.). Hence, one can identify the corresponding Péclet and Brinkman numbers Pe and Br. When the equation is cast into a non-dimensional form based on a characteristic length, velocity, and effective thermal diffusivity α_e, the latter is replaced by 1/Pe. This may suggest a treatment of dissipative effects as a singular perturbation on the non-dissipative limit.

It now becomes evident that the Thomson's equilibrium limit corresponds to the convection-dominated regime of large Pe such that, with irreversible internal heat conduction neglected, the resulting equation for external heat transfer contains both a "reversible" linear term and a quadratic "irreversible" term in $\mathbf{j}_e$. This confirms and generalizes Thomson's *Ansatz* for one-dimensional conduction.

As final and crucial remarks in this subsection, note that the preceding analysis provides a relaxation time-scale $\tau = \ell^2/\alpha_e$, where ℓ is a characteristic linear dimension of the thermoelectric conductor. One may also identify a second "*RC* " time constant

$$\tau_e = C/\sigma\ell, \text{ with } \tau_e/\tau = C\alpha_e/\sigma\ell^3, \tag{13}$$

where C is a constant with units of capacitance, which like ℓ depends on the details of the thermoelectric system. Note that C/τ_e may be identified with the ratio $I(V)/V$ or $I/V(I)$, respectively, for linear voltage-controlled current source or current-controlled voltage source. To illustrate the foregoing considerations, we reinterpret the formulae for the local dissipation in a conductor given by Miller[24].

B. Onsager's conduction

Guided by the form for dissipation employed by Miller[24] and references therein, we assume a local thermoelectric (Clapeyron) energy density in a conductor as

$$\rho_\varepsilon = \mathbf{Q}\cdot\nabla\ln\theta + \mathbf{Q}_e\cdot\nabla\Phi, \tag{14}$$

where $\mathbf{Q}$ and $\mathbf{Q}_e$ denote the respective quasi-static thermal and electrical displacements, which are assumed to represent uncoupled equilibrium modes. Thus, as dependence on the nominal thermal and electrical forces $\nabla\theta$ and $\nabla\Phi$ we assume

$$\mathbf{Q}(\nabla\theta) = \rho_e c_{pe}\nabla\theta, \text{ and } \mathbf{Q}_e(\nabla\Phi) = C\nabla\Phi \tag{15}$$

The first is compatible with the equilibrium thermodynamic relation $dQ = \theta\, \mathrm{d}\eta = \rho_e c_{pe}\, \mathrm{d}\theta$ and the second

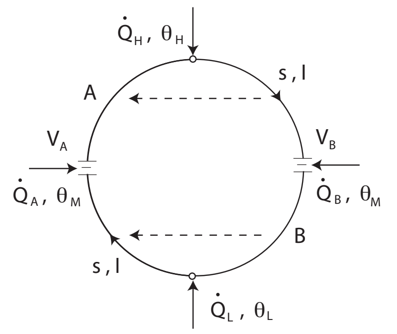

FIG. 1. Carnot circuit with $V = V_{\rm A} + V_{\rm B}$, $\dot{Q}_{\rm M} = \dot{Q}_{\rm A} + \dot{Q}_{\rm B}$

involves a necessary capacitance effect either real, e.g. associated with surface charge, or fictitious, consistent with our treatment of electrical flux as an incompressible flow. From the time constants in (13) we then obtain Onsager's form for local dissipation density as

$$\begin{aligned}\rho_D &= \tau^{-1}\mathbf{Q}\cdot\nabla\ln\theta + \tau_e^{-1}\mathbf{Q}_e\cdot\nabla\Phi \\ &= \frac{1}{\ell^2}\left(k\frac{|\nabla\theta|^2}{\theta} + \sigma|\nabla\Phi|^2\right),\end{aligned} \tag{16}$$

employed by Miller[24] and assumed in (12). The characteristic length ℓ can be interpreted as the square root of mean cross sectional area of the conductor.

C. A generalized Carnot circuit

Consider now an idealized circuit with one-dimensional conductors so that (12) reduces to

$$v_e\frac{\mathrm{d}\theta}{\mathrm{d}s} = \alpha_e\left(\frac{\mathrm{d}^2\theta}{\mathrm{d}s^2} + \frac{j_e^2}{\sigma k}\right) + \beta(s), \tag{17}$$

from which it is evident from that the reversible purely convective limit without external heat transfer ($\alpha_e = 0 = \beta$) implies either a uniform temperature or a zero electric current. However, we may imagine an idealized circuit involving external heat exchange only at discrete locations on the circuit. We shall treat these as heat inputs which take on negative values for heat rejection.

Thus, consider the circuit with total length ℓ illustrated in Fig. 1 and having symmetrically disposed branches A and B that represent the two thermoelectric conductors A and B, with distance s along the circuit reckoned clockwise, such that $s = 0 \mod \ell$ at junction AB where $\theta = \theta_{\rm H}$ and $s = \ell/2 \mod \ell$ at junction BA where $\theta = \theta_{\rm L}$. We assume that one or both branches of the circuit are interrupted by an external voltage or current source, with $V = V_{\rm A}+V_{\rm B}$, $\dot{Q}_{\rm M} = \dot{Q}_{\rm A}+\dot{Q}_{\rm B}$, and combined external power input or output VI. Also indicated is a heat effect with entropy change at the sources anticipated by Gibbs[26] (Section VII) and which involves on external heat exchanges indicated on the figure. This also covers the case of the Peltier refrigerator as heat pump, with $\theta_{\rm M}$ representing the ambient temperature at which heat is rejected. It is understood that $\theta_{\rm H} \geq \theta_{\rm M} \geq \theta_{\rm L}$.

Then we have two equations of the form Eq. (17) with superscripts A & B affixed to θ and β accordingly as $s \lessgtr \ell/2$ and with discontinuities at discrete points of external heat exchange. Now, we assume a continuous reversible heat transfer between points at the same temperature on the separate branches A & B, as suggested by the dashed arrows in the figure. Adding the two balance equations gives an elementary differential equation for $\theta^A + \theta^B$ in terms of $\beta^A + \beta^B$ which is satisfied by taking $\theta^B(s) = \theta^A(s-\ell/2)$ and $\beta^B(s) = -\beta^A(s-\ell/2)$, with $\mathrm{d}(\theta^A(s) + \theta^B(s))/\mathrm{d}s = 0$, i.e. such θ' and β are odd functions of $s - \ell/2 \mod \ell$. Note that the definition of β in (12) implies that the rate of heat exchange depends on the ratio of Thomson coefficients c_{pe}^A/c_{pe}^B.

Note that the global energy and entropy balances are

$$\begin{aligned}&\dot{Q}_{\rm H} + \dot{Q}_{\rm L} + \dot{Q}_{\rm M} + VI = 0, \\ &\text{and } \dot{S}_{\rm H} + \dot{S}_{\rm L} + \dot{S}_{\rm M} = 0, \text{ with } \dot{S}_i = \frac{\dot{Q}_i}{\theta_i},\end{aligned} \tag{18}$$

where I is the electrical current around the circuit. Hence, if each of the terms $\dot{Q}_i/\theta_i$ takes on the Peltier form $\Delta\eta_e(\theta_i)I$ then we obtain the change of η_e taken around the circuit equal to zero as required by equilibrium thermodynamics.

The above device can be restricted to the form of a heat engine or pump by placing the voltage sources next to a heterojunction at the same temperature and taking $\dot{Q}_{\rm M} = 0$ In practice, such a device might be realized approximately by contiguous linear wires in contact through an electrically insulating but thermally conductive lamella or sheath. In the absence of a coherent solid material for this application an alternative such as radiant or convective heat transport across an evacuated or fluid-filled gap comes to mind.

D. Application to the Carnot circuit

For a rudimentary lumped-parameter description of the overall thermodynamics of the simple circuit illustrated in Fig. 1, we choose as forces and displacements

$$\begin{aligned}&\mathbf{f} = \{X_{\rm H}, X_{\rm M}, V\}, \mathbf{x} = \{S_{\rm H}, S_{\rm M}, Q_e\}, \\ &\text{with } S_{\rm i} = Q_{\rm i}/\theta_{\rm i}, X_{\rm H} = \theta_{\rm H} - \theta_{\rm M}, X_{\rm M} = \theta_{\rm M} - \theta_{\rm L} \\ &V + \mathcal{V}(\theta_{\rm H}) - \mathcal{V}(\theta_{\rm L}) = 0,\end{aligned} \tag{19}$$

where $\mathcal{V} = \mathcal{V}^{\rm AB}$, and Q & Q_e denote quasi-static transfers of heat and electrical charge. The Clapeyron energy (8) becomes

$$\begin{aligned}\mathcal{E} &= X_{\rm H}S_{\rm H} + X_{\rm M}S_{\rm M} + VQ_e \\ &= Q_{\rm H}\left(1 - \frac{\theta_{\rm M}}{\theta_{\rm H}}\right) + Q_{\rm M}\left(1 - \frac{\theta_{\rm L}}{\theta_{\rm M}}\right) + VQ_e,\end{aligned} \tag{20}$$

involving evident Carnot work. For simplicity, we consider the special case of the Carnot engine considered above, with $\theta_{\mathrm{M}} = \theta_{\mathrm{L}}$.

In view of the Peltier effect (20) reduces to the form

$$\mathcal{E} = \eta^{\mathrm{AB}}(\theta_{\mathrm{H}})(\theta_{\mathrm{A}} - \theta_{\mathrm{L}}) + VQ_e \tag{21}$$

Under linearization and assumptions like those employed for (16), one obtains a similar form:

$$\mathcal{D} = \frac{1}{\ell^2}\left(k(\theta_{\mathrm{H}}-\theta_{\mathrm{L}})^2 + \sigma V^2\right), \tag{22}$$

with dissipation due solely to conduction without consideration of dissipation in the heterojunction. Moreover, there is now a coupling described by the last equation of (19), which under linearization gives $V \propto (\theta_{\mathrm{H}}-\theta_{\mathrm{L}})$ serving to describe the control of one quantity by the other, depending on whether the device works as heat engine or heat pump.

VI. CONCLUSIONS

The main conclusions are stated above in the Abstract. As future work and testing ground for the present hypotheiss, there is an array of other thermoelectrochemical transport processes such as those studied by Miller[24] that are worthy of investigation. The extension to Edelen's non-linear Onsager symmetry[15] would be both interesting and challenging. While the present paper focuses on the application to thermoelectricity in metals it can be extended to semi-conductors and electrolytic systems involving multiple charge carriers[3]. Finally, there is an interesting question of the relation of breakdown of symmetry in magneto-thermoelectricity to the underlying equilibrium thermodynamics.

ACKNOWLEDGMENTS

In this commemorative article, I join colleagues the world over in the appreciation of the life of Robert Byron Bird, a most remarkable scholar, scientist, and engineer. Further to the sentiments expressed in a previous tribute[27] (in the Acknowledgement), I add the observation that those who have attempted to teach the rudiments of transport phenomena owe an enduring debt to him and the coauthors of their renowned textbook[25], known affectionately to many as "BSL" or "Birdfoot". As universally recognized by the academic community, this treatise revolutionized not only the teaching of a difficult subject but also its very comprehension by teachers and by authors of derivative textbooks.

With lingering sadness for his passing, I regret all the more that there will be no chance in this life for us to discuss with Bob this tribute to his legacy.

An expression of gratitude is due Professor Lev Truskinovsky, host for my visits at the École supérieure de physique et de chimie industrielles de la ville de Paris, for alerting me to the notion of Clapeyron energy.

DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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