Thermal Dissipation IV Differentials, Reciprocity and Thermoelectricity

"Everything should be as simple as it can be, but not simpler." -A. Einstein

This essay is the fourth in a series on thermal dissipation.¹ TD-I and TD-II were concerned primarily with fundamentals of steady-state dissipation, with derivations mainly in the latter. Steady-state systems are expected to relax towards equilibrium when external constraints are removed. To balance this relaxation, constant work or dissipation is required and appears as a loss of free energy supplied by external sources.

Theorem: The thermodynamic steady state is that configuration, compatible with boundary constraints, requiring the minimum amount of work from external sources to counter relaxation towards equilibrium.

Only in isothermal systems is this equivalent to a principle of minimal entropy production. TD-III focused on the application of this principle to simple systems with energy transport involving coupled radiative and non-radiative processes. As photons are bosons, any differential volume element may contain radiative fluxes traveling in multiple directions, while molecular or electron-based fluxes can not.

This discussion focuses on the interactions of coexisting dissipative processes in steady-state thermodynamic systems. The interference of thermal and electric fluxes has long been a topic of thermodynamic interest. Should couplings exist, we may anticipate dissipation shall be reduced below the sum total of individual components. Onsager was first to address this problem theoretically and, in 1931, offered proof of a Reciprocity Theorem.² His proof for linear dissipative systems was based on analogy with a detailed balance description of microscopic reversibility in mechanical systems. Classical thermodynamic reasoning had been phenomenological and the need to invoke microscopic statistical arguments broke with this tradition.

At a most fundamental level, thermodynamics presumes the existence of thermodynamic states.³ By definition these possess path-independent properties. The thermodynamic properties of a water sample are independent of its history. Path-independence implies the existence of an exact differential and temperature, should it exist, is the integrating factor required for exactness.⁴ In elementary thermodynamic texts, this appears in the definition of entropy, $\delta S = \delta q/T$.

The following discussion shall be over well-furrowed ground, but restricted to cases with non-divergent flux functionals, thereby allowing reduction of volume integrals to explicit functions of surface fluxes and potentials and, in principle, susceptible to physical measurement.

^{1 &}lt;u>http://quondam.000webhostapp.com/Notebook.html</u>

² L. Onsager, Reciprocal Relations in Irreversible Processes. I., Phys. Rev. 37, 405–426 (1931)

³ https://en.wikipedia.org/wiki/Thermodynamic_state

^{4 &}lt;u>https://en.wikipedia.org/wiki/Integrating_factor</u>

In TD-II we examined the expression

$$\boldsymbol{J}_{\boldsymbol{U}}(r) + \boldsymbol{J}_{\boldsymbol{X}}(r) = \boldsymbol{J}_{\boldsymbol{F}}(r) + T(r)\boldsymbol{J}_{\boldsymbol{S}}(r)$$
(1)

 $J_U(r)$ is the flux of thermal energy. It typically includes those energies contributing to a system's heat capacity. $J_X(r)$ is the energy flux associated with coexisting dissipative processes. For an electric flux, noting that current flux is non-divergent,

$$\boldsymbol{J}_{X}(r) = \boldsymbol{J}_{V}(r) \cdot \boldsymbol{\nabla} V(r) = \boldsymbol{\nabla} \cdot \left[\boldsymbol{J}_{V}(r) V(r) \right]$$
(2)

The parameters on the left side of Eq. 1 are physical and expressible in mechanical terms. The parameters on the right are thermodynamic, temperature and fluxes of free energy and entropy. The local steady-state constraint is

$$\nabla \cdot (\boldsymbol{J}_{U}(\boldsymbol{r}) + \boldsymbol{J}_{X}(\boldsymbol{r})) = 0$$
(3)

As shown in TD-II, it then follows that⁵

$$\nabla \cdot \left(\frac{\boldsymbol{J}_F(r) - \boldsymbol{J}_X(r)}{T(r)} \right) = 0$$
(4)

The volume integral of this non-divergent function is readily transformed to a surface integral. For a two-terminal cell, with entering fluxes at terminal 1 assigned positive signs and exiting fluxes at terminal 2 negative ones, the resulting expression for free energy dissipation may be written as

$$D = (J_{FI} - J_{F2}) = \frac{(J_{FI} - J_{XI})}{T_1} (T_1 - T_2) + (J_{XI} - J_{X2})$$

= $J_T \Delta T + J_V \Delta V$ (5)

where

$$J_T \equiv \frac{J_{FI} - J_{XI}}{T_1}$$
, $\Delta T \equiv T_1 - T_2$, $\Delta V \equiv V_1 - V_2$ (6)

No assumptions of linearity, homogeneity or geometry have been made.⁶ *Equation 5* is the sum of two terms, the first the Carnot dissipation for a thermal flux between thermal reservoirs, the second the dissipation of an electric circuit.

Couplings arises when we introduce functional relationships between fluxes and potentials, the simplest being linearity, *i.e.*

$$J_{T} = a_{11}\Delta T + a_{12}\Delta V$$

$$J_{V} = a_{21}\Delta T + a_{22}\Delta V$$
(7)

with coefficients independent of ΔT and ΔV . Their combined dissipation becomes (Eq. 5)

$$D(\Delta T, \Delta V) = a_{11}(\Delta T)^{2} + (a_{12} + a_{21})\Delta T \Delta V + a_{22}(\Delta V)^{2}$$
(8)

In principle, dissipation measurements in which both ΔT and ΔV are specified will provide values for a_{11} , a_{22} and $a_{12} + a_{21}$. As dissipation must be positive, a_{11} and a_{22} are positive and equivalent to thermal and electrical conductivities. The central term will be negative should coupling reduce dissipation.

⁵ Thermal Dissipation II, Note C.

⁶ It is an implicit assumption that each bounding surface region is of uniform temperature and electric potential.

Let us now consider the two cases for which either J_T or J_V is zero. Equation 5 indicates these will have the same dissipation as cases for which $\Delta T=0$ and $\Delta V=0$.

Case
$$J_T = 0$$
:

$$\Delta T = -(a_{12}/a_{11})\Delta V$$

$$J_V = \frac{a_{11}a_{22} - a_{12}a_{21}}{a_{11}}\Delta V$$

$$D(\Delta T, \Delta V) = J_V \Delta V = \left(\frac{a_{11}a_{22} - a_{12}a_{21}}{a_{11}}\right)(\Delta V)^2$$
(9)

$$Case J_{V} = 0:$$

$$\Delta V = -(a_{21}/a_{22})\Delta T$$

$$J_{T} = \frac{a_{11}a_{22} - a_{12}a_{21}}{a_{22}}\Delta T$$

$$D(\Delta T, \Delta V) = J_{T}\Delta T = \left(\frac{a_{11}a_{22} - a_{12}a_{21}}{a_{22}}\right)(\Delta T)^{2}$$
(10)

Our dissipation theorem states that all internal parameters, *e.g.* potential and flux distributions, will adopt configurations minimizing total dissipation while satisfying boundary constraints. Suppose a_{12} and a_{21} are such parameters. Should $D(\Delta T, \Delta V)$ in Eqs. 8-10 be stationary with respect to variations of a_{12} and a_{21} ,

$$\delta(a_{12} + a_{21}) = \delta a_{12} + \delta a_{21} = 0$$

$$\delta(a_{12}a_{21}) = a_{12}\delta a_{21} + a_{21}\delta a_{12} = 0$$
(11)

We conclude $a_{12} = a_{21}$, the condition of reciprocity, and *Equations 9* and *10* show dissipation is, as expected, reduced by these terms.

Alternatively, suppose all extensive differentials scale proportionally, perhaps with surface area. Differentiation of Eq. 5 yields δD , by definition exact, which may then be partitioned into two exact differentials each equal to δW .

$$\delta D - \Delta T \delta J_T - \Delta V \delta J_V = \delta W = J_T \delta T + J_V \delta V \tag{12}$$

As δW is exact, we can assert that⁷

$$\left(\frac{\partial J_T}{\partial V}\right)_T = \left(\frac{\partial J_V}{\partial T}\right)_V \tag{13}$$

again giving us $a_{12} = a_{21}$ when linearity is assumed *(Eq. 7)*. It may be noted that Eq. 13, is not restricted to an assumption of linearity.

⁷ https://en.wikipedia.org/wiki/Exact_differential

There are several thermoelectric coefficients which are defined as partial derivatives in the linear limit.⁸ The Seebeck coefficient, S(volts/deg), measures the change in open-circuit potential due to thermal gradients. From Eq. 10,

$$S(volts/deg) = -\left(\frac{\partial V}{\partial T}\right)_{J_{\nu}=0} = a_{21}/a_{22}$$
(14)

The Peltier coefficient, $\Pi(volts)$, measures the change of thermal energy flux due to a change of electric current given isothermal boundary conditions,

$$\Pi(volts) = T\left(\frac{\partial J_T}{\partial J_V}\right)_{\Delta T=0} = T\left(\frac{\partial J_T}{\partial V}\right)_{\Delta T=0} \left(\frac{\partial V}{\partial J_V}\right)_{\Delta T=0} = T\frac{a_{12}}{a_{22}}$$
(15)

The Thomson coefficient is defined as

$$K \equiv \frac{d\Pi}{dT} - S \tag{16}$$

When reciprocity is assumed, Thomson's thermoelectric relations follow:

$$K = T \frac{dS}{dT} \quad ; \quad \Pi = TS \tag{17}$$

The generality of Eq. 5 implies a correspondence principle for diverse physical phenomena. Should we wish to examine the coupling of thermal and mass fluxes, the latter being a non-divergent function, we need only let

$$D = J_T \Delta T + J_M \Delta (P/\rho)$$
(18)

and arrive at similar results with ΔV replaced by $\Delta (P/\rho)$, the pressure/density ratio difference for two bounding reservoirs.⁹

Onsager's 1931 analysis of the linear dissipative region around equilibrium remains the only generally accepted description for non-equilibrium thermodynamics. It is based on the rate of local entropy formation,

$$\frac{ds}{dt} = \nabla \cdot \boldsymbol{J}_{s} = \boldsymbol{J}_{U} \cdot \nabla (1/T)$$
(19)

as a first-order perturbation of an equilibrium system and establishes extremal principles for both steady and non-steady states.¹⁰ The choice between extremals based on dissipation *vs.* entropy formation considerations depends on one's definition for the steady state. A micro-canonical constraint, $\nabla \cdot J_{II} = 0$, has no fluctuations and consequently no extremals. The global canonical constraint

$$\iiint d \,\tau \, \nabla \cdot \boldsymbol{J}_{U}(r) = 0 \tag{20}$$

^{8 &}lt;u>https://en.wikipedia.org/wiki/Thermoelectric_effect</u>

⁹ Should P/ρ be proportional to T and $\Delta(P/\rho)$ and ΔT therefore not independently variable, Eq. 18 is reduced to a single term. Ideal gases have null thermal conductivities and viscosities and are inherently nondissipative.

¹⁰ Parenthetically, it should be noted that, if instead of Eq. 4, we had used $\nabla \cdot J_s(r) = \nabla \cdot (J_u(r)/T(r))$ to calculate the integrated rate of entropy formation, we would have found $\dot{S} = D/T_2$, with *D* given by *Eq. 5*, and reached the same conclusions.

leads to dissipative extremals whereas

$$\iiint d \tau \left(\frac{\nabla J_U(r)}{T(r)} \right) = 0$$
(21)

leads to extremals for entropy formation. Our analysis is based upon Eq. 20. Despite nearly a century of effort, no significant progress has been made in the search for extremal behavior beyond the linear regime.¹¹

"Until recently, prospects for useful extremal principles in this area have seemed clouded. C. Nicolis (1999) concludes that one model of atmospheric dynamics has an attractor which is not a regime of maximum or minimum dissipation; she says this seems to rule out the existence of a global organizing principle, and comments that this is to some extent disappointing; she also points to the difficulty of finding a thermodynamically consistent form of entropy production. Another top expert offers an extensive discussion of the possibilities for principles of extrema of entropy production and of dissipation of energy: Chapter 12 of Grandy (2008) is very cautious, and finds difficulty in defining the 'rate of internal entropy production' in many cases, and finds that sometimes for the prediction of the course of a process, an extremum of the quantity called the rate of dissipation of energy may be more useful than that of the rate of entropy production; this quantity appeared in Onsager's 1931 origination of this subject. Other writers have also felt that prospects for general global extremal principles are clouded. Such writers include Glansdorff and Prigogine (1971), Lebon, Jou and Casas-Vásquez (2008), and Šilhavý (1997). "

While there is certainly a correlation between the expressions we have derived and Onsager's results, they are by no means identical. Our description applies to externally observable properties of thermodynamic steady-state systems, properties which are independent of the paths by which these states are reached. Onsager's analysis is based on the rate of entropy formation within internal volume elements. In a magnetic field, however, some forces are velocity-dependent, time-reversal symmetry no longer holds and reciprocity is presumed broken. For our two-terminal system with insulating sides, transverse electric fluxes induced by an applied magnetic field will charge these sides until the resulting electric field neutralizes this flux as a steady state is reached and we anticipate reciprocity to persist.

In TD-III, we discussed a hypothetical Carnot cell containing a metallic barrier at some intermediate position. With this barrier unconnected and bounding temperatures of 100K and 10K, we measure a 100W energy flux. Dissipation is 90W, entropy formation 9 W/K. We note that the barrier temperature, which is position dependent, happens to be 50K. We then connect the barrier to a 50K external reservoir, in effect creating a three-terminal cell with two tandem Carnot cells, $100K \rightarrow 50K$ and $50K \rightarrow 10K$. No net energy enters the cell, the rate of entropy formation remains unchanged, but dissipation has increased to 130W! The resolution of this seeming paradox is basically a difference between internal energy and free energy fluxes, $J_U = J_F + TJ_S$. From a thermodynamic perspective, 50W of dissipated energy is being exchanged for 50W of free energy. From a statistical mechanical perspective one might suppose that a distribution is being re-normalized to Boltzmann behavior, but a formulation thereof is not self-evident. This result is independent of material-specific properties of the contents of the cell and belies the notion of local thermodynamic equilibrium.

Rarely mentioned is the definition for temperature in non-equilibrium systems. For equilibria, temperature appears as a constant integrating factor making $\delta S = \delta q/T$ an exact differential. *Equation 19* is an equivalent expression for dissipative systems. The possibility of a thermodynamic description requires the existence of an integrating factor T(r) and an exact differential with path-

¹¹ https://en.wikipedia.org/wiki/Non-equilibrium_thermodynamics

independent properties. A necessary and sufficient condition for this factor to exist is discussed in Margenau and Murphy.¹² Geometrically, adjacent isotherms should never touch or intersect.

In any arbitrary neighborhood of an arbitrarily given initial point there is a state that cannot be arbitrarily approximated by adiabatic changes of state. ¹³

Our discussion has been exclusively within the framework of *Classical Thermodynamics*, the phenomenology of dissipative or heat producing processes. The relationship between classical and *Statistical Thermodynamics* or statistical mechanics is a curious one. The latter is based on the Boltzmann distribution which applies only to a state of maximum entropy, yet today it is a common presumption that classical relationships should be derivable from statistical considerations. The *raison d'être* for thermodynamics is the path-independence of thermodynamic functions. A necessary and sufficient condition for this behavior is description by an exact differential equation with the requisite integrating factor then defining temperature.

Our focus has been on a two-terminal system with interacting thermal and electrical fluxes, although we note that additional degrees of freedom with more I/O ports may lead to differing results. We have chosen free energy dissipation as the thermodynamic variable of interest rather than entropy formation for extremal reasons. Within the linear region near equilibrium, both are equivalent as regards dissipation, for the difference between energy and free energy fluxes, increases quadratically with perturbation.

Reciprocity, by definition a relationship of linear coefficients, was found with two phenomenological methodologies, the stationary nature of a macroscopic dissipation function and the exactness of the subset of extensive terms within the exact differential for a dissipation function. The latter implies the additional restriction that a thermodynamic system be divisible into equivalent thermodynamic sub-systems and is thus not applicable to a solitary black box.

The mathematics of path-invariant integrals, exact differentials and reciprocal partial derivatives has long been understood and it seems a bit odd to assert that one needs statistical mechanics to understand thermodynamic reciprocity near equilibrium. The more challenging task would be derivation of conditions for macroscopic path-independence from microscopic time-dependent considerations.

"A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts." - A. Einstein

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¹² H. Margenau and G.M. Murphy, The Mathematics of Physics and Chemistry, §2.18.

^{13 &}lt;u>http://www.neo-classical-physics.info/thermodynamics.html</u>, C. Carathéodory, "Examination of the foundations of thermodynamics," Math. Ann. 67 (1909), 355-386.