Thermal Dissipation V

Thermodynamic Variational Theorems

“In science if you know what you are doing you should not be doing it. ” — R. Hamming

This essay is the fifth in a series concerning thermal dissipation in nonlinear thermodynamic steady states.[1] Our focus is restricted to thermodynamic states which, by definition, are independent of the paths by which these states are reached. An implicit assumption is the existence of temperature, mathematically an integrating function rendering a differential energy equation complete or exact. External observables for finite systems with fully defined boundary parameters are thus presumed reproducible.

Variational calculus has long been among the most powerful tools in the scientist's arsenal for solving problems lacking analytical solutions. Ideally, one would like a methodology with which one might make an educated guess at a thermal profile within a system to calculate some property and then refine this guess until a convergent result emerges. In the thermodynamics of equilibrium systems, it is well-established that entropy is a maximum and dissipation a minimum (zero). Onsager's seminal 1931 paper first addressed variational properties of thermodynamic systems near equilibrium for rates of entropy generation and energy dissipation.[2] A recent review indicates scant subsequent progress despite intensive efforts.[3]

> *“Energy dissipation and entropy production extremal principles are ideas developed within non-equilibrium thermodynamics that attempt to predict the likely steady states and dynamical structures that a physical system might show. The search for extremum principles for non-equilibrium thermodynamics follows their successful use in other branches of physics. According to Kondepudi (2008), and to Grandy (2008), there is no general rule that provides an extremum principle that governs the evolution of a far-from-equilibrium system to a steady state. According to Glansdorff and Prigogine (1971), irreversible processes usually are not governed by global extremal principles because description of their evolution requires differential equations which are not self-adjoint, but local extremal principles can be used for local solutions. Lebon Jou and Casas-Vásquez (2008) state that "In non-equilibrium ... it is generally not possible to construct thermodynamic potentials depending on the whole set of variables". Šilhavý (1997) offers the opinion that "... the extremum principles of thermodynamics ... do not have any counterpart for [non-equilibrium] steady states (despite many claims in the literature)." It follows that any general extremal principle for a non-equilibrium problem will need to refer in some detail to the constraints that are specific for the structure of the system considered in the problem.”*

Given the results of a near century's attempts to understand nonlinear thermodynamics, one might well conclude no generic solutions exist, with perhaps one rather familiar exception, $W = I\,\Delta V$. This applies to the basic nonlinear tungsten light bulb as well as high-pressure gas discharge lamps, despite unsolvable turbulent and chaotic fluxes within the latter. Brief reflection reveals this to be a consequence of global charge conservation. Why then should one not expect an equivalent expression for dissipation of an energy flux between two thermal boundaries?

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[1] Notebook, TD-I to TD-IV, http://quondam.000webhostapp.com/files.html

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

[3] https://en.wikipedia.org/wiki/Extremal_principles_in_non-equilibrium_thermodynamics

Thus, with temerarious trepidation, we offer the following:

> ***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.*

The following proof is a brief excursion into vector calculus based on four elementary equations,

$$\nabla\cdot\boldsymbol{J_S}(r) = \boldsymbol{J}_U(r)\cdot\nabla\left(\frac{1}{T(r)}\right) \tag{1}$$

$$\boldsymbol{J}_U(r) = \boldsymbol{J_F}(r) + T(r)\boldsymbol{J_S}(r) \tag{2}$$

$$W = -\frac{dF}{dt} = -\iiint d\tau\,\nabla\cdot\boldsymbol{J_F}(r) = -\oiint d\boldsymbol{\sigma}\cdot\boldsymbol{J_F} \tag{3}$$

$$\frac{dU}{dt} = \iiint d\tau\,\nabla\cdot\boldsymbol{J}_U(r) = \oiint d\boldsymbol{\sigma}\cdot\boldsymbol{J}_U(r) = 0 \tag{4}$$

The first is the 2nd law of thermodynamics as formulated by Onsager.[2] It defines entropy flux as a local function of an energy flux and a temperature gradient and is dimensionally equivalent to *ds=dq/T.* The second defines a free energy flux function, $\boldsymbol{J_F}(r)$, and the third defines dissipation, *W*, as the rate of loss of free energy. The last equation is a global constraint defining the steady state as one of constant internal energy. This allows us to consider internal variations with constrained boundary values as opposed to the local constraint, $\nabla\cdot\boldsymbol{J}_U(r) = 0$, which suppresses such variations.

For clarity's sake, we proceed, perhaps gratuitously, step by step. First divide *Eq. 2* by *T(r)* and take its divergence:

$$\nabla\cdot(\boldsymbol{J}_U/T) = \nabla\cdot(\boldsymbol{J_F}/T) + \nabla\cdot\boldsymbol{J_S} \tag{5}$$

Expand the left-hand side and substitute *Eq.1* in the right-hand side:

$$\frac{\nabla\cdot\boldsymbol{J}_U}{T} + \boldsymbol{J}_U\cdot\nabla(1/T) = \nabla\cdot(\boldsymbol{J_F}/T) + \boldsymbol{J}_U\cdot\nabla(1/T) \tag{6}$$

Cancel the common terms on each side, multiply by *T(r)* and swap sides:

$$T\nabla\cdot(\boldsymbol{J_F}/T) = \nabla\cdot\boldsymbol{J}_U \tag{7}$$

Expand the left-hand side:

$$\nabla\cdot\boldsymbol{J_F} + T\,\boldsymbol{J_F}\cdot\nabla(1/T) = \nabla\cdot\boldsymbol{J_U} \qquad 8)$$

Define a new variable, $\boldsymbol{J_D}(r)$. Note it is dimensionally (only) equivalent to an entropy flux,

$$\boldsymbol{J_D}(r) \equiv \frac{\boldsymbol{J_F}(r)}{T(r)} \tag{9}$$

and that *Eq. 7* requires:

$$T\nabla\cdot\boldsymbol{J_D}(r) = \nabla\cdot\boldsymbol{J}_U(r) \tag{10}$$

Substitute $\boldsymbol{J_D}(r)$ into the second term on the left-hand side of *Eq. 8* and move it to the right-hand side:

$$\nabla\cdot\boldsymbol{J_F} = -T^2\boldsymbol{J_D}\cdot\nabla(1/T)+\nabla\cdot\boldsymbol{J_U} = \boldsymbol{J_D}\cdot\nabla T+\nabla\cdot\boldsymbol{J_U} \tag{11}$$

Finally, upon substitution of this result in *Eq. 3*, together with *Eq. 4,* we obtain the general expression for steady-state dissipation:

$$\begin{aligned} W &= -\iiint d\tau\, \boldsymbol{J_D}(r)\cdot\nabla T(r) - \iiint d\tau\nabla\cdot\boldsymbol{J_U}(r) \\ &= -\iiint d\tau\,\boldsymbol{J_D}(r)\cdot\nabla T(r) \end{aligned} \tag{12}$$

We seek solutions to *Eq. 12* for $\boldsymbol{J_D}(r)$ and $T(r)$ with $T(r)$ constrained to match externally defined boundary values. Assume approximate functions differing from the true solutions by $\boldsymbol{\delta J_D(r)}$ and $\delta T(r)$. Thus,

$$W = \langle W\rangle + \langle\delta W\rangle + \langle\delta^2 W\rangle \tag{13}$$

where

$$\begin{aligned} \langle W\rangle &= -\iiint d\tau\, \boldsymbol{J_D}(r)\cdot\nabla T(r) \\ \\ \langle\delta W\rangle &= -\iiint d\tau\left(\delta\boldsymbol{J_D}(r)\cdot\nabla T(r)+\boldsymbol{J_D}(r)\cdot\nabla\delta T(r)\right) \\ &= -\delta\iiint d\tau\, \boldsymbol{J_D}(r)\cdot\nabla T(r) \\ &= \delta\langle W\rangle \\ \\ \langle\delta^2 W\rangle &= -\iiint d\tau\left(\delta\boldsymbol{J_D}(r)\cdot\delta\nabla T(r)\right) \end{aligned} \tag{14}$$

Dissipation will be a stationary function for variations of $T(r)$ and $\boldsymbol{J_D}(r)$ with $\langle\delta W\rangle = 0$. Whether a maximum or minimum depends on the sign of $\langle\delta^2 W\rangle$. Should the direction of a 'hot' local flux vector perturbation globally correlate with a flow towards cooler temperatures, dissipation will be a minimum and the steady state stable. Should hot spots grow, the system becomes dynamically unstable.

Substitution of Eq. 9 in Eq. 3 yields the surface integrals

$$\begin{aligned} \langle W\rangle &= -\oint\!\!\!\oint d\boldsymbol{\sigma}\cdot(T\boldsymbol{J_D}) \\ \langle\delta W\rangle &= -\oint\!\!\!\oint d\boldsymbol{\sigma}\cdot(T\delta\boldsymbol{J_D}) \end{aligned} \tag{15}$$

as $T(r)$ is fixed on the surface. We expect this sufficient to also determine the thermodynamic state of the system and consequently fix the corresponding distribution of surface fluxes.[4] Then $\langle\delta W\rangle = 0$ and dissipation will be an extremum with respect to internal energy flux variations.

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[4] The assumption that temperature, by definition, renders thermodynamic states path-independent implies a determination of boundary fluxes. This does not exclude the possibility for the existence of a finite number of steady states compatible with the same boundary potentials, each a local dissipative minimum, *e.g.* neon lamps at potentials intermediate to ignition and extinction potentials.

Given the historical interest in variational solutions for entropy generation, we examine this function in similar fashion. Based on the second law *(Eq. 1)*,

$$\frac{dS}{dt} = \langle \dot{S} \rangle = \iiint d\tau \boldsymbol{\nabla}\cdot\boldsymbol{J_S}(r) = \iiint d\tau \boldsymbol{J_U}\cdot\boldsymbol{\nabla}(1/T) \tag{16}$$

Partial integration of the right-hand side gives

$$\begin{aligned}\langle \dot{S} \rangle &= \iiint d\tau \boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{J}_U}{T}\right) - \iiint d\tau \frac{\boldsymbol{\nabla}\cdot\boldsymbol{J}_U}{T} \\ &= \oiint d\boldsymbol{\sigma}\cdot\left(\frac{\boldsymbol{J}_U}{T}\right) - \iiint d\tau \frac{\boldsymbol{\nabla}\cdot\boldsymbol{J}_U}{T}\end{aligned} \tag{17}$$

In contrast to *Eq. 12,* the second integral is not our fixed internal energy constraint, save in an isothermal limit, and extremal behavior for entropy generation is not a general steady-state property.

To continue discussion, suppose that the surface of our undefined volume contains only two isothermal areas or ports through which flux may pass, with $T_1 > T_2$. No explicit geometry, such as rectilinearity, is implied. We now also adopt the local steady-state constraint, $\boldsymbol{\nabla}\cdot\boldsymbol{J_U}(r) = 0$. Let J_1 and J_2 be the total flux through each port, with a positive sign indicating outward flow and conversely.[5] For a steady state, $J_{U1} + J_{U2} = 0$ and

$$\langle \dot{S} \rangle = -J_{U1}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{18}$$

Similarly, for dissipation

$$\langle W \rangle = -\oiint d\boldsymbol{\sigma}\cdot(T\boldsymbol{J_D}) = -(T_1 J_{D1} + T_2 J_{D2}) = -(J_{F1} + J_{F2}) \tag{19}$$

From the definition of $\boldsymbol{J_D}$ in *Eq. 9*

$$J_{D1} + J_{D2} = \frac{J_{F1}}{T_1} + \frac{J_{F2}}{T_2} \tag{20}$$

and elimination of J_{F2} between these last two equations gives

$$\langle W \rangle = -J_{F1}\left(1 - \frac{T_2}{T_1}\right) \tag{21}$$

If the ports are thermal reservoirs, $J_{F1} = J_{U1}$ and $\langle W \rangle = -T_2 \langle \dot{S} \rangle$. *Equations 18* and *21* are the familiar equations of Clausius and Carnot. Although it plays a fundamental role in nonlinear thermodynamics, the Carnot equation is not to be found in current theoretical discussions of dissipation. That the maximum rate of work obtainable from a steady-state process might correspond to a free energy dissipation rate should not seem too surprising, however, and one might suspect that our analysis encompasses more than a rephrasing of “conventional wisdom.”

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[5] Input fluxes for port 1, *i.e.* J_{F1} and J_{U1}, will be negative in these equations.

Examples

A calculation in TD-III demonstrated the variational use of the Carnot equation for handling a problem involving coupled radiative and convective fluxes for a two-port model.[6] Here we briefly sketch the methodology. Formally, assume two coexisting energy fluxes satisfying the differential equations

$$\begin{aligned} (D^2-1)J_r(\zeta) &= 2\varphi'(T(\zeta)) \\ J_c(\zeta) &= -\psi'(T(\zeta)) \end{aligned} \tag{22}$$

For a 'gray' gas model, J_r represents the net flux of bidirectional radiative energy with $\varphi(T(\zeta))$ a T^4 Stefan-Boltzmann function. J_c is a flux wholly determined by the gradient of some function of local temperature. The formal solution for the total flux, $J_{tot}(\zeta) = J_r(\zeta) + J_c(\zeta)$, is

$$J_{tot}(\zeta) = (1+D^2)(-2\varphi' - \psi' + \psi''') + \epsilon(D^4 J_{tot}) \tag{23}$$

and a steady-state solution requires finding a function, $T(\zeta)$, for which $J_{tot}(\zeta)$ is constant. We adopt a polynomial trial function, *i.e.*

$$T(\zeta) = T(0) + [T(l)-T(0)]\cdot[\xi + \xi(1-\xi)(a+b\xi+c\xi^2+d\xi^4)] \qquad (\xi=\zeta/l), \tag{24}$$

and seek that set of coefficients minimizing *rms* deviations of $J_{tot}(\zeta)$ from a mean value with fixed boundary temperatures *T(0)* and *T(l)*. As dissipation equals $J_{tot}(1-T(l)/T(0))$, J_{tot} will also be a variational minimum.

The following Table summarizes results for a particular set of modeling parameters.

J_{tot}	*rms%*	*a*	*b*	*c*	*d*
14.37734	17.481%				
14.36359	2.230%	-0.28600			
14.37070	0.185%	-0.24980	-0.09680		
14.37062	0.014%	-0.25350	-0.07460	-0.02476	
14.37061	0.011%	-0.25354	-0.07483	-0.02469	0.00039

Immediately apparent is the insensitivity of J_{tot} to the approximate thermal profile, a characteristic of an extremal. As the thermal profile is modified with additional terms, this value decreases slightly, as if approaching a minimum.[7] Adding nonlinear corrections to the thermal profile greatly reduces the

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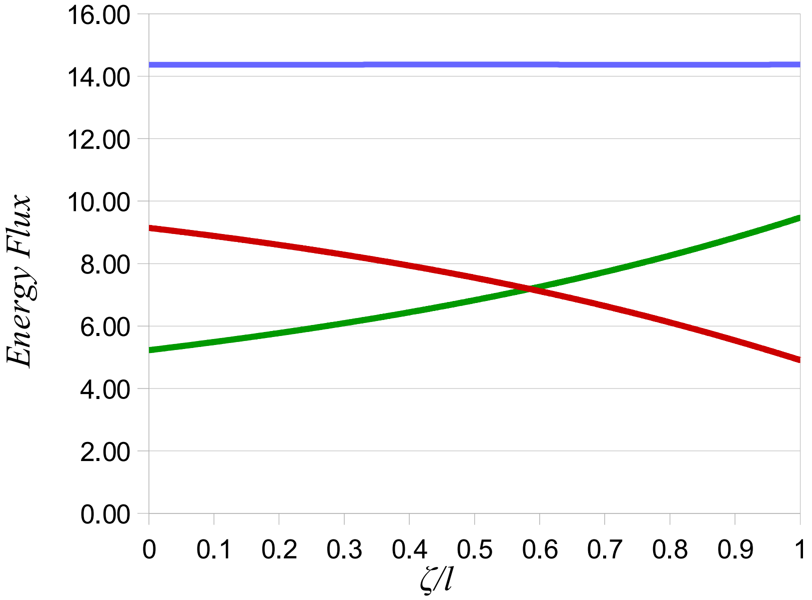
[6] For this model, a dimensionless coordinate ζ expresses the physical coordinate x in terms of the gray-gas absorption distance λ, with l then a measure of the cell's size, $l = \int_0^l d\zeta = \int_0^L \frac{dx}{\lambda(x)}$. In this calculation, *l=100*. The two functions in Eq. 22 are defined as $\varphi'=4\sigma T^3 T'$ with σ the Stefan-Boltzmann constant and $\psi' = \kappa(x)(dT/dx)=\gamma(\zeta)T'$. The dimensionless parameter γ is the ratio of the distances characterizing convective and radiative dissipation, $\gamma = \kappa/\lambda$. For the calculation described, $\gamma=7$ and independent of ζ, a ratio for which both fluxes are roughly equal.

[7] Why the value found using a single adjustable parameter is less than the final value is not evident, although boundary values for J_{tot} are not equal as required by *Eq. 4* and only become so in the convergent limit.

deviations of $J_{tot}(\zeta)$, allowing us to calculate the contributions of the three terms in *Eq. 23*, which we label J_R , J_C and J_{RC} , corresponding to radiative, convective and hybrid fluxes. Numerically the last is negative, but 4-6 orders of magnitude less than the others. This term becomes significant, however, with cell lengths less than the effective gray-gas absorption depth. Having found $T(\zeta)$, we may calculate the profiles for the several flux components from *Eqs. 22,* and these are plotted below.



Red=J_r *, Green =* J_c*, Blue =* J_{tot}

The radiative component falls with decreasing temperature, a consequence of its T^4 dependence, and the convective component increases correspondingly.

As an alternative,we also examined a single-parameter power-law function for $T(\zeta)$,

$$T^n(\zeta) \;=\; T^n(0) + [T^n(l) - T^n(0)]\,(\zeta/l) \tag{25}$$

For $n=4$, this becomes a Stefan-Boltzmann function, for $n=1$, a linear function. Given the previous parameters, varying n to minimize deviations of $J_{tot}(\zeta)$ yields $n=2.244$, *rms%=0.257%* and $J_{tot} = 14.3709$, in quite satisfactory agreement with the polynomial results.

In TD-IV, we found that the Onsager reciprocal relations characterizing linear dissipative systems could be derived from the extremal properties of steady-state dissipation. Briefly, dissipation with both thermal and electric fluxes flowing between two terminals is

$$W \;=\; J_T \Delta T \;+\; J_V \Delta V \tag{26}$$

with $J_T = J_{FI}/T_1$ the thermal flux and J_V the electric current for given boundary temperature and potential differentials. In the linear dissipation approximation,

$$\begin{pmatrix} J_T \\ J_V \end{pmatrix} \;=\; \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} \Delta T \\ \Delta V \end{pmatrix} \tag{27}$$

The a_{ij} are constant coefficients and

$$W(\Delta T, \Delta V) \;=\; a_{11}(\Delta T)^2 + (a_{12}+a_{21})\Delta T \Delta V + a_{22}(\Delta V)^2 \tag{28}$$

Suppose the contacts permit only a flow of thermal energy, i.*e.* $J_V = 0$. The thermal gradient will induce a potential difference and the dissipation will be given by

$$W(\Delta T, \Delta V) \;=\; J_T \Delta T \;=\; \left(\frac{a_{11}a_{22} - a_{12}a_{21}}{a_{22}}\right)(\Delta T)^2 \tag{29}$$

If a_{12} and a_{21} are considered internal variational parameters and *Eqs. 28* and *29* are extrema,

$$\begin{aligned} \delta(a_{12} + a_{21}) \;&=\; \delta a_{12} + \delta a_{21} \;=\; 0 \\ \delta(a_{12}a_{21}) &= a_{12}\delta a_{21} + a_{21}\delta a_{12} \;=\; 0 \end{aligned} \tag{30}$$

Thus $a_{12} = a_{21}$. Dissipation is reduced by thermo-electric coupling, in accord with a minimum dissipation theorem for internal degrees of freedom.

To this point, we have only considered systems bounded by thermal reservoirs which are essentially sources for free energy and sinks for incoming energies. As an alternative, suppose we have a boundary which is only a sink for dissipated energy, reflecting free energy back into a two-port system where it is forced to circulate until eventually dissipated. Free energy flux entering from the other interface will accumulate and thermal gradients will increase until a steady state is reached satisfying the Carnot equation,

$$W \;=\; (J_{F1}/T_1)\Delta T \tag{31}$$

The system's dissipative sensitivity may be defined as $\delta W/\delta T_1$ and thus equals

$$\frac{\delta W}{\delta T_1} \;=\; \frac{W}{\Delta T}\left(\frac{\partial \ln(J_{F1})}{\partial \ln(\Delta T)} + \frac{T_2}{T_1}\right) \tag{32}$$

To the extent that this limiting behavior is relevant to tropospheric thermodynamics, its variational properties imply that internal degrees of freedom will always minimize thermal gradients. Current uncertainties focus on the presumption that small magnitudes for the log-log partial derivative lead to large values for δT_1.

Summary

The intent of this essay has been to explore the utility of variational theorems for solving nonlinear, steady-state thermodynamic problems. We have restricted attention to a classical or macroscopic thermodynamic analysis and not attempted statistical mechanical interpretations as is commonly the expectation. The latter have primarily, if not exclusively, attempted unsuccessfully to extend Onsager's approach for linear dissipation. Gyarmati has analyzed a variety of thermodynamic theorems for both dissipation and entropy generation in exhaustive detail for the linear regime and, although dated, his treatise remains a fair representation of the current state for this field.[8]

There is the *ab initio* assumption that a thermodynamic system may be described by a local bilinear sum of products of physical fluxes and thermodynamic "forces". In Onsager's notation,

$$2T\phi(r) = \sum \boldsymbol{J}_i(\boldsymbol{r})\cdot\boldsymbol{X}_i(\boldsymbol{r}) \tag{33}$$

which he describes as the rate of "dissipation" of free energy (his quotes).[9] In the linear dissipation approximation,

$$\boldsymbol{X}_i(\boldsymbol{r}) = \sum R_{ij}\boldsymbol{J}_j(\boldsymbol{r}) \tag{34}$$

with constant material coefficients R_{ij} . The local rate of entropy generation then becomes

$$\nabla\cdot\boldsymbol{J}_S(\boldsymbol{r}) = 2\phi(r) = \sum_{i,j} R_{ij}\boldsymbol{J}_i(\boldsymbol{r})\cdot\boldsymbol{J}_j(\boldsymbol{r}) \tag{35}$$

For thermal dissipation, $\boldsymbol{J}=\boldsymbol{J}_U$ and $\boldsymbol{X} = -\nabla\cdot\ln(T)$. The local dissipation contribution is

$$\delta W = -\boldsymbol{J}_U\cdot\nabla\ln T\ \delta\tau \tag{36}$$

Whereas in our analysis,

$$\delta W = -\boldsymbol{J}_F\cdot\nabla\ln T\ \delta\tau \tag{37}$$

In the two-port case with $T_1 > T_2$, these become, respectively,

$$\begin{aligned}\langle W\rangle &= -J_{UI}\ln(T_1/T_2)\\ \langle W\rangle &= -J_{FI}\left(1-\frac{T_2}{T_1}\right)\end{aligned} \tag{38}$$

As T_2 approaches T_1 these expressions become identical but, in the limit of a large ratio, dissipation in the first case may exceed the energy entering the system. In the latter case, dissipation is limited to the free energy entering the system which can not exceed J_U. Even in the linear case with $\boldsymbol{J}_i(\boldsymbol{r})$ directly proportional to $\boldsymbol{X}_i(\boldsymbol{r})$, the dissipation function approach is only useful when the distinction between fluxes of energy and free energy can be neglected, *i.e.* $\delta T \ll T$.

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[8] Gyarmati, I. (1970). Non-equilibrium Thermodynamics, Springer, Berlin; translated, by E. Gyarmati and W.F. Heinz.

[9] This sum is often referred to as the Rayleigh-Onsager dissipation function.

This distinction undermines any statistical mechanical attempt to extend thermodynamics beyond linear perturbations of equilibria based on Boltzmann statistics. In TD-III, we examined dissipation and entropy generation for several 'trivial' two-port models. Initially, as energy enters from the warmer interface, energy and free energy are identical. As it flows towards the cooler interface, the former remains unchanged, whereas the latter decreases due to thermal dissipation. But, it is only the remaining free energy at any point which can be dissipated. Although the total energy flux is constant, its ability to do work is being steadily reduced. By definition, flux exiting a thermal reservoir is assumed to show a Boltzmann distribution among its microscopic degrees of freedom. As dissipation progresses, however, this distribution must be changing in a manner which reduces the work it can do. Energy originally in higher levels is presumably being reallocated to lower levels until absorbed by a boundary reservoir which then renormalizes its distribution. That the Carnot equation is not material specific, suggests there may exist an alternative distribution function describing free energy dissipation.

It should also be noted that the correspondence of dissipation and entropy generation found for the two-port system is limited. In TD-III, we considered a tandem model of two Carnot cells with boundary temperatures T_1 , T_2 and T_3 . If only T_1 and T_3 are connected to thermal reservoirs, we have a two-terminal cell for which dissipation and entropy generation are given *Eqs. 18* and *21*. We observe the temperature of the floating interface, T_2 , and connect it to a third reservoir at that temperature. No net energy flows into this third contact, although we have decoupled the model into two distinct cells and find that dissipation has increased while entropy generation remains unchanged. The intervening boundary has, in effect, adiabatically re-normalized the energy distribution without altering the system's rate of entropy production.

Finally, we note that our discussion has been restricted to steady-state dissipation. One of the historic goals has been the search for a methodology describing the temporal evolution of a thermodynamic system, given the *a priori* assumption that a scalar temperature function does exist. Fundamentally, the existence of such a function follows from the presumption of path-independent thermodynamic states with temperature being an appropriate integration factor. The concomitant appearance of an extensive entropy function incorporates 'missing' trajectory information. Reconciliation of notions of predictable future paths with past independent paths would seem a proper preliminary for discussing time-dependent thermodynamic evolution beyond the limits of first-order equilibrium perturbation theories.

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