The Onsager Equations

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In 1931, Onsager published a seminal mathematical description for the thermodynamics of irreversible processes.[1] In addition to showing that reciprocal relations, *i.e.* $R_{ij} = R_{ji}$, followed from assumptions of microscopic reversibility, he derived thermodynamic expressions for rates of entropy production and dissipation. Recently we have proposed an alternative approach and it is our present purpose to compare derivations. We first review Onsager's work with a vector-tensor notation and equation numbering mirroring his paper.

Onsager describes the rate of entropy generation in terms of internal energy fluxes, $\vec{\boldsymbol{J}}(\boldsymbol{r})$, within a system given an internal temperature profile, *T(r)*. This profile defines thermodynamic 'forces', $\vec{\boldsymbol{X}}(\boldsymbol{r})$,

$$\vec{\boldsymbol{X}}(r) = -\frac{\vec{\nabla} T(r)}{T(r)} = T\,\vec{\nabla}(1/T) \qquad 5.1$$

These are assumed to be linear sums of fluxes described by a tensor of given phenomenological constants ,

$$\vec{\boldsymbol{X}}(r) = \|\boldsymbol{R}\|\cdot\vec{\boldsymbol{J}}(r) \qquad 5.1$$

A quadratic local dissipative function is then introduced

$$2\,T(r)\phi(r) \equiv \vec{\boldsymbol{J}}(r)\cdot\vec{\boldsymbol{X}}(r) \equiv \vec{\boldsymbol{J}}(r)\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{J}}(r) \qquad 5.3\ \&\ 5.5$$

Dimensionally, $\vec{\boldsymbol{X}}(\boldsymbol{r})$ may be expressed in units of *meter* $^{-1}$, $\vec{\boldsymbol{J}}(\boldsymbol{r})$ in *watts/meter* ^{2}, and $T\,\phi(r)$ in *watts/meter* ^{3}.

On partial differentiation with respect to one component of $\vec{\boldsymbol{J}}(\boldsymbol{r})$ holding *T(r)* constant,

$$2T\frac{\partial\phi}{\partial J_k} = \vec{\boldsymbol{e}}_{\boldsymbol{k}}\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{J}} + \vec{\boldsymbol{J}}\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{e}}_{\boldsymbol{k}} = \sum_j (R_{kj}+R_{jk})J_j = 2X_k \qquad 5.4$$

The rates of entropy production by local heating and energy transport are, respectively,

$$\dot{S}(J) \equiv -\int dV\frac{\vec{\nabla}\cdot\vec{\boldsymbol{J}}}{T} \quad ; \quad \dot{S}^*(J_n) \equiv \int dV\,\vec{\nabla}\cdot\left(\frac{\vec{\boldsymbol{J}}}{T}\right) \qquad 5.7\ \&\ 5.8$$

Their total becomes

$$\dot{S}(J) + \dot{S}^*(J_n) \equiv \int dV\,\vec{\boldsymbol{J}}\cdot\vec{\nabla}(1/T) = 2\int dV\,\phi(r) \equiv 2\Phi(J,J) \qquad 5.9\ \&\ 5.10$$

Dimensionally, Φ may be expressed in *watts/kelvin.*

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[1] Lars Onsager, *Reciprocal Relations in Irreversible Processes. I*, Phys. Rev. **37**, p. 405 (1931) https://journals.aps.org/pr/pdf/10.1103/PhysRev.37.405

Varying the function $\dot{S}(J) + \dot{S}^{*}(J_n) - \Phi(J,J)$ while holding T*(r)* constant,

$$\left(\frac{\partial[\dot{S}(J) + \dot{S}^{*}(J_n) - \Phi(J,J)]}{\partial J_k}\right)_{T(r)} = \int dV \left(\nabla_k(1/T) - \frac{\partial \phi}{\partial J_k}\right) = 0$$

Thus, $\dot{S} + \dot{S}^{*} - \Phi$, is an extremum for variations of $\vec{\boldsymbol{J}}(\boldsymbol{r})$ with $T(r)$ fixed and a maximum if $\|\boldsymbol{R}\|$ is positive definite as, from *Eq. 5.4,*

$$2T\frac{\partial^2 \phi}{\partial J_k^2} = 2R_{kk} > 0$$

Onsager then argues:

1. Should the surface be adiabatically insulated, $\dot{S}^{*}(J_n)=0$ and therefore $\dot{S}(J) - \Phi(J,J)$ is a maximum.
2. For stationary flow, $\dot{S}(J)=0$ and $\dot{S}^{*}(J_n) - \Phi(J,J)$ is a maximum. Entropy production is also a maximum as $\dot{S}^{*}(J_n) = 2\Phi(J,J)$.
3. For a steady state, $\oint J_n d\Omega = 0$, $\dot{S}^{*}(J_n)$ is prescribed and therefore $\Phi(J,J)$ is a minimum.

These conclusions, those of maximum entropy production in particular, have proved exceptionally confusing. They suggest that this variational function equals an undefined constant of magnitude $\Phi(J,J)$. Others have also considered temperature variations, but their basic parameters remain these introduced by Onsager.[2] An analysis in the Appendix of generic variational functions of this form indicates the appropriate functions for entropy production and energy dissipation differ and that it is the latter which corresponds to the Onsager function.

Although not mentioned in Onsager's paper, it is helpful to introduce fluxes, $\vec{\boldsymbol{J}}_{\boldsymbol{S}}(\boldsymbol{r})$ and $\vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r})$, for the extensive functions of entropy and free energy as defined in the following equations:

$$\begin{aligned}
\int dV \frac{\vec{\nabla}\cdot\vec{\boldsymbol{J}}(r)}{T(r)} &= \int dV\, \vec{\nabla}\cdot\left(\frac{\vec{\boldsymbol{J}}}{T}\right) - \int dV\, \vec{\boldsymbol{J}}\cdot\vec{\nabla}(1/T) \\
&= \int dV\, \vec{\nabla}\cdot\left(\frac{\vec{\boldsymbol{J}}}{T}\right) - \int dV\, \vec{\nabla}\cdot\boldsymbol{J}_{\boldsymbol{S}}(r) \\
&= \int dV\, \vec{\nabla}\cdot\left(\frac{\vec{\boldsymbol{J}} - T\vec{\boldsymbol{J}}_{\boldsymbol{S}}}{T}\right) \\
&= \int dV\, \vec{\nabla}\cdot\left(\frac{\vec{\boldsymbol{J}}_{\boldsymbol{F}}(r)}{T}\right)
\end{aligned}$$

The rates at which entropy is produced and free energy dissipated then equal

$$\begin{aligned}
\langle\dot{S}\rangle &= \int dV\, \vec{\nabla}\cdot\vec{\boldsymbol{J}}_{\boldsymbol{S}}(r) = 2\int dV\, \phi(r) \\
-\langle\dot{F}\rangle &= -\int dV\, \vec{\nabla}\cdot\boldsymbol{J}_{\boldsymbol{F}}(r) = 2\int dV\, T(r)\phi(r)
\end{aligned}.$$

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

Our alternative formulation, specific to steady states, is expressed through three coupled differential functions, two vector, one scalar, $\vec{\boldsymbol{J}}_U(r)$, $\vec{\boldsymbol{J}}_{\boldsymbol{S}}(r)$ and $T(r)$, fluxes of internal energy and entropy, and temperature.[3] Solutions are based on the equivalence of volume and surface integrals for thermodynamic functions. They follow from three constraints:

1*. The Second Law of Thermodynamics:* This law, as expressed by Onsager, may be written as

$$\vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{S}}(r) \;=\; \vec{\boldsymbol{J}}_U(r) \cdot \vec{\boldsymbol{\nabla}}(1/T(r)) \tag{1}$$

It then follows that the rate of entropy production

$$\begin{aligned} \langle \dot{S} \rangle \;\equiv\; \iiint d\,V \vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{S}}(r) \;&=\; \iiint d\,V \vec{\boldsymbol{J}}_U(\boldsymbol{r}) \cdot \vec{\boldsymbol{\nabla}}(1/T(r)) \\ &=\; \oint\!\!\!\oint d\,\boldsymbol{\sigma} \cdot \frac{\vec{\boldsymbol{J}}_U(r)}{T(r)} \;-\; \iiint dV \frac{\vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_U(\boldsymbol{r})}{T(r)} \end{aligned} \tag{2}$$

Equivalently, *Eq. 1* may written as

$$\vec{\boldsymbol{\nabla}} \cdot \left(\frac{\vec{\boldsymbol{J}}_U(r) - T(r)\vec{\boldsymbol{J}}_{\boldsymbol{S}}(r)}{T(r)} \right) \;=\; \frac{\vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_U(r)}{T(r)} \;=\; \vec{\boldsymbol{\nabla}} \cdot \left(\frac{\vec{\boldsymbol{J}}_{\boldsymbol{F}}(r)}{T(r)} \right) \tag{3}$$

or

$$\vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{F}}(r) \;=\; \vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_U(r) \;+\; \frac{\vec{\boldsymbol{J}}_{\boldsymbol{F}}(r) \cdot \vec{\boldsymbol{\nabla}} T(r)}{T(r)} \tag{4}$$

where we have defined a free energy flux as $\vec{\boldsymbol{J}}_{\boldsymbol{F}}(r) \equiv \vec{\boldsymbol{J}}_U(r) - T(r)\vec{\boldsymbol{J}}_{\boldsymbol{S}}(r)$

The rate of free energy dissipation is

$$\begin{aligned} -\langle \dot{F} \rangle \;&=\; \iiint d\,V\, \vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{F}}(r) \;=\; \iiint d\,V\, \vec{\boldsymbol{\nabla}} \cdot \boldsymbol{J}_U(r) \;+\; \iiint dV\, \vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) \cdot \vec{\boldsymbol{\nabla}} T(r) \\ &=\; \oint\!\!\!\oint d\,\vec{\boldsymbol{\sigma}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{F}}(r) \;=\; \oint\!\!\!\oint d\,\vec{\boldsymbol{\sigma}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{D}}(r)\, T(r) \end{aligned} \tag{5}$$

with $\vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) \equiv \vec{\boldsymbol{J}}_{\boldsymbol{F}}(r)/T(r)$.

2. *The First Law of Thermodynamics:* Our second constraint considers the conservation of energy. From *Eq. 2,* assuming a local constraint, $\vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_U(r) = 0$,

$$\langle \dot{S} \rangle \;=\; \iiint d\,V \vec{\boldsymbol{J}}_U \cdot \vec{\boldsymbol{\nabla}}(1/T(r)) \;=\; \oint\!\!\!\oint d\,\vec{\boldsymbol{\sigma}} \cdot (\vec{\boldsymbol{J}}_U(r)/T(r)) \tag{6}$$

From *Eq.* 5, with a less restrictive global constraint, $\iiint dV\, \vec{\boldsymbol{\nabla}} \cdot \vec{\boldsymbol{J}}_U(r) \;=\; \oint\!\!\!\oint d\,\vec{\boldsymbol{\sigma}} \cdot \vec{\boldsymbol{J}}_U(r) \;=0$

$$-\langle \dot{F} \rangle \;= \iiint dV\, \vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) \cdot \vec{\boldsymbol{\nabla}} T(r) \;=\; \oint\!\!\!\oint d\,\vec{\boldsymbol{\sigma}} \cdot \vec{\boldsymbol{J}}_{\boldsymbol{D}}(r)\, T(r) \tag{7}$$

In both instances, the volume integral of the product of a vector function and the gradient of a scalar function equals the surface integral of the product of the pair of functions.

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[3] https://quondam.000webhostapp.com/Thermal_Dissipation_V.pdf

3. *The Thermodynamic State:* The essence of the thermodynamic state lies in the assumption that extensive thermodynamic functions are described by exact differential equations. Such equations have path-independent solutions. Consider an experiment in which we apply prescribed temperatures to a set of contacts on a system and measure the resulting energy fluxes. Should we repeat this experiment, we would hope to get the same results no matter the order of application.[4] Should this prove the case, these properties must depend only on surface parameters. In classical thermodynamics, temperature is defined as an integrating function rendering the product *T dS* an exact differential. Qualitatively, information about the path by which a thermodynamic state has been reached is subsumed as entropy.

Consider a general function of the form, $\langle \Psi \rangle = \iiint dV\, \vec{\boldsymbol{A}}(r) \cdot \vec{\boldsymbol{B}}(r)$ with variations in both $\delta\vec{\boldsymbol{A}}(r)$ and $\delta\vec{\boldsymbol{B}}(r)$.

$$\begin{aligned} \langle \delta\Psi \rangle &= \iiint dV\, [\delta\vec{\boldsymbol{A}}(r) \cdot \vec{\boldsymbol{B}}(r) + \vec{\boldsymbol{A}}(r) \cdot \delta\vec{\boldsymbol{B}}(r)] \\ &= \delta \iiint dV\, [\vec{\boldsymbol{A}}(r) \cdot \vec{\boldsymbol{B}}(r)] \\ &= \delta \langle \Psi \rangle \\ \langle \delta^2\Psi \rangle &= \iiint dV\, \delta\vec{\boldsymbol{A}}(r) \cdot \delta\vec{\boldsymbol{B}}(r) \end{aligned} \tag{8}$$

If $\langle \Psi \rangle$ is also equal to a surface integral of $\vec{\boldsymbol{A}}(r)$ and $\vec{\boldsymbol{B}}(r)$ as in *Eqs. 6* and *7* and $\vec{\boldsymbol{A}}(r)$ is constrained by boundary conditions, $\delta\vec{\boldsymbol{A}}(r) = 0$ on the surface, then a path-independent solution for $\vec{\boldsymbol{B}}(r)$ also requires $\delta\vec{\boldsymbol{B}}(r) = 0$ on the surface. Thus, $\langle \delta\Psi \rangle = 0$ and $\langle \Psi \rangle$ an extremum. The acuity of these extrema depends upon the internal correlation of flux and thermal gradients,

$$\begin{aligned} \langle \delta^2 \dot{S} \rangle &= -\iiint dV\, \frac{\delta\vec{\boldsymbol{J}}_U(r) \cdot \delta\vec{\nabla} T(r)}{T(r)^2} \\ \langle \delta^2 \dot{F} \rangle &= -\iiint dV\, \delta\vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) \cdot \delta\vec{\nabla} T(r) \end{aligned} \tag{9}$$

If, on average, a local positive thermal fluctuation is quenched by an energy outflux, both entropy production and dissipation will be minima. Otherwise, the system becomes unstable and will change until a steady state is reached compatible with the prescribed boundary parameters.

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[4] Physical systems exhibiting memory or hysteresis are not going to satisfy the thermodynamic requirements of path-independence.

Although both approaches share similar constraints, they are not equivalent in even the most trivial of cases. For discussion, we shall refer to an Onsager description as Case **I** and our latter as Case **II**. Consider a homogeneous, one-dimensional system with boundary temperatures T_1 and T_2. For Case **I**,

$$
\begin{aligned}
\phi(x) &= -\frac{J_0}{2T^2}\frac{\partial T}{\partial x} \\
\langle \dot{S} \rangle &= 2\int dx\,\phi(x) = -J_0\int dx\,\frac{1}{T^2}\frac{\partial T}{\partial x} = -J_0\int_{T_1}^{T_2} d(1/T) = J_0\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \\
\langle \dot{F} \rangle &= 2\int dx\,T\,\phi(x) = J_0\int dx\,\frac{1}{T}\frac{\partial T}{\partial x} = J_0\int_{T_1}^{T_2} d\ln(T) = -J_0\ln(T_1/T_2)
\end{aligned}
\tag{10}
$$

For **II**, from *Eqs. 6* and *7*,

$$
\begin{aligned}
\langle \dot{S} \rangle &= \iiint dV\,\vec{\boldsymbol{J}}_{\boldsymbol{U}}\cdot\vec{\nabla}(1/T) = \oiint d\vec{\boldsymbol{\sigma}}\cdot(\vec{\boldsymbol{J}}_{\boldsymbol{U}}(r)/T(r)) = J_{UI}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \\
0 &= \iiint dV\,\vec{\nabla}\cdot\vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) = \oiint d\boldsymbol{\sigma}\cdot\vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) = \frac{J_{FI}}{T_1}+\frac{J_{F2}}{T_2} \\
-\langle \dot{F} \rangle &= J_{FI}+J_{F2} = J_{FI}\left(1-\frac{T_2}{T_1}\right) = J_{UI}\left(1-\frac{T_2}{T_1}\right)
\end{aligned}
\tag{11}
$$

Entropy production proves identical for both cases, whereas, **I** allows a dissipation in excess of the incoming energy flux. For **II,** dissipation is given by Carnot's equation and is always less than the incoming flux.[5]

Case **I** is formulated in terms of a local description of entropy production in terms of energy flux and temperature. Existence requirements for a scalar temperature are not mentioned. Case **II** focuses on the dissipation of free energy and the conversion of volume integrals (local) to surface integrals (global).

Case **I** presumes a linear local relationship between flux and gradients with constant coefficients independent of position, $\|\boldsymbol{R}\|$. Case **II** makes no assumptions as to either such a relationship or its homogeneity.

Case **I** describes dissipation in terms of a non-divergent internal flux $\vec{\boldsymbol{J}}(r)$, whereas **II** introduces a non-divergent function $\vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) = \vec{\boldsymbol{J}}_{\boldsymbol{F}}(r)/T(r)$ and fluxes of entropy and free-energy.

Case **I** is not restricted to steady-states and suggests possibilities for describing the evolution of thermodynamic systems. Imagine we can internally observe a system as it transits from steady-state A to steady-state B following a change in external forces. If we then undo this change we expect the system to return to state A, but will its return path be the same? A *Principle of Maximum Entropy Production* has frequently been discussed, based on Case **I**, to little effect.[6] Case **II** denies a possibility on the basis of path-invariance to describe non-steady states.

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[5] It may be noted that the two formulae for dissipation are identical to first-order in ΔT.

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

Finally, we note that thermodynamic reciprocity, the title subject of Onsager's paper, is implicit in functions described by path-independent or exact differential equations. Formally, thermodynamic functions are described as sums of products of an extensive function with a conjugate intensive function, *e.g.* J_i and X_i ,

$$F = \sum_i J_i X_i \tag{12}$$

Consider a differentiation of this function and collection of all extensive differentials on one side,

$$\begin{aligned} \delta F &= \sum_i (\delta J_i X_i + J_i \delta X_i) \\ \delta F - \sum_i (\delta J_i X_i) &= \sum_i J_i \delta X_i \end{aligned} \tag{13}$$

Should all extensive differentials proportionally scale, each side is itself an exact differential and

$$\frac{\partial J_i}{\partial X_j} = \frac{\partial J_j}{\partial X_i} \tag{14}$$

This is no more than an extension of Maxwell's equations for equilibria to non-linear, dissipative steady states. One may infer that principles of microscopic reversibility and macroscopic path-independence are not unrelated.

At equilibrium, it is generally accepted that entropy is maximum and the rates of entropy production and dissipation, both positive functions, have minimum values of zero. For steady states, of which equilibrium is a member, a *Principle of the Least Dissipation of Energy* (Lord Raleigh) is also now commonly accepted. For entropy production the situation is less clear. Onsager has concluded that the rate of steady-state entropy production is a maximum (*Eq. 6.4).* His defined functions are equivalent to those analyzed in the Appendix,

$$\dot{S}(J) + \dot{S}^*(J_n) = \int dV\, \Phi_1(X, Y) \;\; ; \;\; 2\,\Phi(J, J) = \int dV\, \Phi_2(X, Y) \tag{15}$$

and his variational function is also equivalent for $\gamma = 2$,

$$\delta\,[\dot{S}(J) + \dot{S}^*(J) - \Phi(J, J)] = 0 = \delta \int dV\, [2\,\Phi_1 - \Phi_2] \tag{16}$$

Arguments regarding maximum entropy production are predicated on the condition that this variational function is a stationary maximum for variations of both *S* and Φ , whereas this is only true for the latter. For the former, the appropriate variational function derived in the Appendix is[7]

$$\delta \int dV\, [\Phi_1 - 2\,\Phi_2] = 0 = \delta\,[\dot{S}(J) + \dot{S}^*(J) - 4\,\Phi(J, J)] \tag{17}$$

and leads to a stationary state of minimum entropy production. In 1945, Prigogine proposed a *Theorem of Minimum Entropy Production* for steady states.[8,9] While the notion that transitions between steady states should occur as quickly as possible is attractive, there appears no theoretical justification for such an assertion beyond Onsager's arguments.

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[7] Both variational functions follow from the ratio of *1st* order variations of Φ_1 and Φ_2 at their intersection.

[8] I. Prigogine, *Modération et transformations irréversibles des systèmes ouverts*. Bulletin de la Classe des Sciences., Académie Royale de Belgique. **31**: 600–606 (1945).

[9] S.R. de Groot & P.M. Mazur, *Non-Equilibrium Thermodynamics,* Dover (1984), pp. 46-48.

All previous variational methodologies have been based on the Rayleigh dissipation function, $\sum \boldsymbol{J}_i(r) \cdot \boldsymbol{X}_i(r)$, a sum of products of linearly conjugate 'fluxes' and 'forces' . Case **II** differs in two fundamental respects. It differentiates between fluxes of internal energy, J_U, and fluxes of free energy, J_F. While the former are relevant for entropy production, only the latter are subject to dissipation. This is basically why *Eqs.10* imply an impossible Case **I** steady-state dissipation rate greater than the input flux. Secondly, Case **II** is independent of assumptions of a homogeneous linearity in local flux-force relationships, *i.e.* $\|\boldsymbol{R}\|$. In practice, one is free to choose a 'model' local relationship and an arbitrary thermal profile of adjustable coefficients and integrate to calculate a total dissipation. One may then vary these coefficients in search of a dissipation minimum.

The objective of variational analysis is to provide a methodology for solving otherwise intractable problems. As a hypothetical, nontrivial example we explored the interaction of radiative and 'convective' energy fluxes in a one-dimensional system between 300K and 200K.[10] The former fluxes are $\vec{\nabla} T^4$ functions, the latter $\vec{\nabla} T$ functions, each characterized by a distance scale chosen to make these fluxes of comparable magnitude.[11] With boundary temperatures fixed, minimum global dissipation implies a minimum total energy flux. The latter is the sum of three fluxes, radiation, convection and a hybrid term resulting from their coupling.[12] As these fluxes of energy flow from hot to cold, their ratios change while their sum remains constant. The problem thus reduces to finding that profile for which the total energy flux is a minimum and independent of position. For the variational profile, $T(\zeta) = T(0) + [T(l) - T(0)] \cdot [\xi + \xi(1-\xi)(a + b\xi + c\xi^2 + d\xi^4)]$,

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

Table 1: Polynomial coefficients minimizing *rms* variations of J_{tot} .

Initially, a linear profile was assumed and flux deviations are horrendous although the calculated dissipation appears good to four significant figures when compared with a convergent limit. Adding a quadratic term reduces deviations an order of magnitude, a cubic term another order, *etc.* It should be noted that these parameters have been chosen to minimize flux variations and dissipation approaches a minimum value in a convergent limit.[13]

As an alternative to this profile, we also examined the single parameter exponential function, $T^n(\zeta) = T^n(0) + [T^n(l) - T^n(0)]\, \xi$, exact for undissipated radiation when $n=4$ and for convection when $n=1$. A minimum was found with $n=2.49$, $J_{tot}=14.3709$ and $rms=0.257\%$. Although for a profile of quite different functional form, these values are virtually identical to five significant figures with those for a two parameter polynomial function.

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[10] http://quondam.000webhostapp.com/Thermal_Dissipation_III.pdf

[11] In a 'real' problem these scales might be expected to depend on density and temperature.

[12] The hybrid term is most significant when the cell length is commensurate with the radiation absorption distance.

[13] No constraint equalizing the fluxes at each boundary was made and is presumably responsible for the non-monotonic variation of J_{tot} far from this limit.

While the basic concepts of classical thermodynamics assign a quantitative significance to temperature, entropy and free energy, their reductionist interpretation is lacking – save for one particular steady state, equilibrium. The Boltzmann Equation provides a molecular interpretation for this state in terms of a distribution over energy levels, but this exclusive state is one of maximum entropy and uniform temperature. That the factor kT appears in descriptions of non-equilibrium phenomena is simply because first-order perturbation theory invokes distributions of an unperturbed state. The ratio of populations for any two energy levels suffices to define a temperature, but it is only for equilibrium that all thermometers agree. Classical thermodynamics assumes temperature to be an integrating factor rendering physical properties of a thermodynamic state path-independent, given a small set of boundary parameters. Reductionist interpretations for the differences between fluxes of energy and free energy in dissipative systems are presently not available. A principle of *local thermodynamic equilibrium* is often postulated. But, while differences of parameters such as density and temperature within a microscopic region may be thereby reduced, gradients and corresponding fluxes of mass and energy are not.

A yet more serious challenge remains understanding the kinetics of transitions between steady states. Time was introduced by Onsager through definitions of entropy production *(Eqs. 5.7 and 5.8),* but all phenomenological properties are encompassed in the time-independent $\|\boldsymbol{R}\|$ matrix. The electrical analog of a Case **I** thermodynamic system is a complex network of microscopic ohmic resistances. Globally the network is still going to exhibit frequency-independent ohmic dissipation, whether I^2R or E^2/R. For a non-ohmic Case **II** system, dissipation remains IE. For an electrical network, it is reactive elements of capacitance and inductance that shape the temporal dependence of transitions between steady states. Their thermodynamic analogs correspond to local accumulations of energy in terms of heat (scalar fluctuations of temperature) or rotational energy fluxes (convective eddies). Such elements have yet to be parametrized within the framework of classical thermodynamics.

Finally, we note that the stability of a steady-state is determined by the *2nd* derivative of a local correlation function such as $\langle \delta \vec{\boldsymbol{J}}_{\boldsymbol{D}}(r) \cdot \delta \vec{\nabla} T(r) \rangle$ *(Eqs. 9).* One might anticipate that transitions in and out of steady-states should favor paths of least resistance or minimal curvature. Linear dissipation theory (Kubo) is based on time-dependent correlation functions such as $\langle \delta \vec{\boldsymbol{J}}_{\boldsymbol{D}}(t) \cdot \delta \vec{\nabla} T(t+\tau) \rangle$ and these would seem a logical path to describing time-dependent thermodynamic phenomena. Minimum dissipation implies that steady states are those requiring the least work to sustain. To be proved, however, is that nature also seeks the easiest path from A to B. Does time define this path?

APPENDIX

Consider two functions defined by two other functions *X(r)* and *Y(r),*

$$\begin{aligned} \Phi_1(X,Y) &= Y \cdot F(X) \\ \Phi_2(X,Y) &= X \cdot G(Y) \end{aligned} \tag{A1}$$

which intersect for functions $X_0(r)$ and $Y_0(r)$,[14]

$$X_0 G(Y_0) = Y_0 F(X_0) \tag{A2}$$

Let γ be the ratio of the first-order variations of Φ_2 and Φ_1 at their intersection. As a second condition at this intersection,[15]

$$\gamma \delta \Phi_1(X,Y) - \delta \Phi_2(X,Y) = 0 \tag{A3}$$

Differentiating,

$$\delta X \left[\gamma \, Y \frac{\partial F(X)}{\partial X} - G(Y) \right] + \delta Y \left[\gamma \, F(X) - X \frac{\partial G(Y)}{\partial Y} \right] = 0 \tag{A4}$$

and at the intersection,

$$Y_0 \delta X \left[\gamma \left(\frac{\partial F(X)}{\partial X} \right)_{X=X_0} - \frac{F(X_0)}{X_0} \right] + X_0 \delta Y \left[\gamma \frac{G(Y_0)}{Y_0} - \left(\frac{\partial G(Y)}{\partial Y} \right)_{Y=Y_0} \right] = 0 \tag{A5}$$

For constrained variations with $\delta X = 0$, stationary solutions require

$$\left(\frac{\partial G(Y)}{\partial Y} \right)_{Y=Y_0} = \gamma \frac{G(Y_0)}{Y_0} \tag{A6}$$

Differentiating once more

$$\left(\frac{\partial^2 G(Y)}{\partial Y^2} \right)_{Y=Y_0} = \gamma(\gamma-1) \frac{G(Y_0)}{Y_0^2} \tag{A7}$$

Constrained variations with $\delta Y = 0$ will be stationary when

$$\left(\frac{\partial F(X)}{\partial X} \right)_{X=X_0} = (1/\gamma) \frac{F(X_0)}{X_0} \tag{A8}$$

and

$$\left(\frac{\partial^2 F(X)}{\partial X^2} \right)_{X=X_0} = \frac{(1-\gamma)}{\gamma^2} \frac{F(X_0)}{X_0^2} \tag{A9}$$

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[14] Subsequently *X* and *Y* shall be associated *w*ith temperature and flux and Φ_1 and Φ_2 with entropy production and dissipation.

[15] *Eq. A2* is separable in *X* and *Y* at the intersection, decoupling their first-order variations but with independent γ values for δX and δY variations.

To apply this theorem to *Equations 5.9-5.10,*

$$\int dV\ \vec{\boldsymbol{J}}\cdot\vec{\nabla}\,(1/T) \;=\; \int dV\ \frac{\vec{\boldsymbol{J}}\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{J}}}{T} \tag{A10}$$

let

$$X \;=\; 1/T \quad ; \quad Y \;=\; |J| \tag{A11}$$

and,

$$\begin{aligned} F(X) \;&=\; \vec{\boldsymbol{e}}_{\boldsymbol{J}}\cdot\nabla\,(1/T) \;=\; -(1/T^2)\,\vec{\boldsymbol{e}}_{\boldsymbol{J}}\cdot\vec{\nabla}\,T \\ G(Y) \;&=\; \vec{\boldsymbol{J}}\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{J}} \;=\; |J|^2\,(\vec{\boldsymbol{e}}_{\boldsymbol{J}}\cdot\|\boldsymbol{R}\|\cdot\vec{\boldsymbol{e}}_{\boldsymbol{J}}) \end{aligned} \tag{A12}$$

For variations with $\delta X = 0$,

$$\frac{\partial G}{\partial |J|} \;=\; 2\,\frac{G}{|J|} \tag{A13}$$

Thus $\gamma = 2$ and *G(Y₀)* is a minimum. As the matrix $\|\boldsymbol{R}\|$ is positive definite, $G(Y_0)>0$, and dissipation also a minimum.

For variations with $\delta Y = 0$, let

$$T(x) \;=\; T_0 + \left(\frac{\partial T}{\partial x_J}\right)_{T=T_0} x_J \tag{A14}$$

with x_J a local displacement in the direction of flux flow. Then

$$F(X) \;=\; -(1/T^2)\left(\frac{\partial T}{\partial x_J}\right)_{T=T_0} \;=\; -\left(\frac{\partial T}{\partial x_J}\right)_{X=X_0} X^2 \tag{A15}$$

Thus

$$\left(\frac{\partial F(X)}{\partial X}\right)_{X=X_0} \;=\; (1/\gamma)\frac{F(X_0)}{X_0} \;=\; -2\left(\frac{\partial T}{\partial x_J}\right)_{X=X_0} X_0 \;=\; -(1/\gamma)\left(\frac{\partial T}{\partial x_J}\right)_{X=X_0} X_0 \tag{A16}$$

and $\gamma = 1/2$. Both *$F(X_0)$* and its second derivative are positive, and *$F(X_0)$* is therefore a minimum.

Entropy production is given by

$$\langle \dot{S} \rangle \;=\; \int dV\ \vec{\boldsymbol{J}}\cdot\vec{\nabla}\,(1/T) \;=\; \int dV\ Y\,F(X) \tag{A17}$$

and a minimum should $|J|$ be constant along lines of flux, *i.e.* $\vec{\nabla}\cdot\vec{\boldsymbol{J}}(r) = 0$.