Thermal Dissipation II

The impetus for these notes lies in the marked absence of any serious discussion of thermodynamics in theories of 'greenhouse' effects. This seems quite remarkable, for the core problem involves energy transport in thermal gradients, the very genesis of thermodynamics. Our original notion was to develop a theoretical formulation for 'climate sensitivity' but, working from an axiomatic base, it became apparent that far more fundamental considerations of nonlinear, dissipative thermodynamics were inextricably entwined. To maintain focus on our initial goal, this discussion is offered as a derivation for sensitivity, while more general implications are discussed in appended notes.

Our basic thesis is that solar energy absorbed by the earth's surface returns to space only after its maximum possible dissipation within the troposphere, *i.e.* only when it can no longer perform any work therein. This is the antithesis of a non-dissipative, Stefan-Boltzmann radiative description for a thermally transparent atmosphere and, while apparently draconian, its consequences are far more benign than current consensus estimates.

We restrict our attention to steady-state processes. Salient features of such states are constant rates for the creation of entropy and the loss of free energy. The latter equals the rate of dissipation for irreversible systems. Thermodynamic formulae for such systems entail sums of bilinear products of extensive vector fluxes and intensive scalar potentials. For non-divergent flux functionals, volume integrals rigorously reduce to surface integrals, *i.e.* functions depending only on values for potential and flux over a bounding surface. This holds true in three dimensions as well as nonlinear systems far from equilibrium.

As an introductory example, consider thermodynamic dissipation due to electric currents interacting with potential gradients.

$$\begin{array}{lll} \vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r}) = \vec{\boldsymbol{J}}_{\boldsymbol{Q}}(\boldsymbol{r})\Phi(\boldsymbol{r}) & (\boldsymbol{a}) \\ \nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{Q}}(\boldsymbol{r}) = 0 & (\boldsymbol{b}) \end{array} \qquad (1)$$

The local free energy flux density, $\boldsymbol{J_F}$, is the product of a non-divergent current density, $\boldsymbol{J_Q}$, and a local potential, $\boldsymbol{\Phi}$. The rate of free energy dissipation follows from the divergence theorem,

$$\dot{\boldsymbol{F}} = \iiint \boldsymbol{d}\tau\nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r}) = \iiint \boldsymbol{d}\tau\ \vec{\boldsymbol{J}}_{\boldsymbol{Q}}(\boldsymbol{r})\cdot\nabla\Phi = \oiint \boldsymbol{d}\vec{\sigma}\cdot\vec{\boldsymbol{J}}_{\boldsymbol{Q}}(\boldsymbol{r})\ \Phi(\boldsymbol{r}) \qquad (2)$$

Should the surface have but two iso-potential regions through which current enters and exits, a familiar result follows,

$$\dot{\boldsymbol{F}} = \boldsymbol{J}_1\Phi_1 + \boldsymbol{J}_2\Phi_2 = -|\boldsymbol{J}|(\Phi_1-\Phi_2) \qquad (3)$$

with the standard conventions that entering flux, $\boldsymbol{J_1}$, is negative, exiting flux, $\boldsymbol{J_2}$, is positive and $\boldsymbol{\Phi_1} > \boldsymbol{\Phi_2}$. This result is incomplete for the implicit assumption of an isothermal system does not permit calculation of the rate at which entropy is increasing.[1]

Expressions for the thermal dissipation due to energy fluxes in thermal gradients follow from these postulates:

$$\begin{aligned} &\nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{S}}(\boldsymbol{r}) \;=\; \vec{\boldsymbol{J}}_U(\boldsymbol{r})\cdot\nabla\left(\frac{1}{\boldsymbol{T}(\boldsymbol{r})}\right) && (\boldsymbol{a}) \\ &\vec{\boldsymbol{J}}_U(\boldsymbol{r}) \;=\; \vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r}) \;+\; \boldsymbol{T}(\boldsymbol{r})\vec{\boldsymbol{J}}_{\boldsymbol{S}}(\boldsymbol{r}) && (\boldsymbol{b}) \\ &\nabla\cdot\vec{\boldsymbol{J}}_U(\boldsymbol{r}) \;=\; 0 && (\boldsymbol{c}) \end{aligned} \qquad (4)$$

Equation 4a is Onsager's expression for local entropy creation by energy fluxes in thermal gradients.[2] *Equation 4b* defines the Helmholtz free energy flux and *Equation 4c* defines a local steady state constraint.[3]

From the *divergence theorem*, the rate of entropy production is, *cf. Eq. 2,*

$$\dot{\boldsymbol{S}} \;=\; \iiint \boldsymbol{d}\tau\,\nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{S}}(\boldsymbol{r}) \;=\; \iiint \boldsymbol{d}\tau\;\; \vec{\boldsymbol{J}}_U(\boldsymbol{r})\cdot\nabla(1/\boldsymbol{T}) \;=\; \oiint \boldsymbol{d}\vec{\sigma}\cdot(\vec{\boldsymbol{J}}_U(\boldsymbol{r})/\boldsymbol{T}) \qquad (5)$$

For a steady-state flux between two isothermal surfaces, $(\boldsymbol{T_1} > \boldsymbol{T_2})$, we obtain the Clausius result

$$\dot{\boldsymbol{S}} \;=\; (\boldsymbol{J}_{\boldsymbol{U1}}/\boldsymbol{T}_1 + \boldsymbol{J}_{\boldsymbol{U2}}/\boldsymbol{T}_2) \;=\; |\boldsymbol{J}_U|(1/\boldsymbol{T}_2 \;-\; 1/\boldsymbol{T}_1) \qquad (6)$$

observing the conventions of sign for *Eq. 3*.

A similar approach lets us find the rate of free energy dissipation,

$$\dot{\boldsymbol{F}} \;=\; \iiint \boldsymbol{d}\tau\,\nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r}) \;=\; \oiint \boldsymbol{d}\vec{\sigma}\cdot\vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r}) \qquad (7)$$

Dividing *Eq. 4b* by *T(r)* and then taking its divergence gives, noting *Eq. 4c*,

$$\nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_U(\boldsymbol{r})}{\boldsymbol{T}(\boldsymbol{r})}\right) \;=\; \nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_{\boldsymbol{F}}(\boldsymbol{r})}{\boldsymbol{T}(\boldsymbol{r})}\right) \;+\; \nabla\cdot\vec{\boldsymbol{J}}_{\boldsymbol{S}}(\boldsymbol{r}) \;=\; \vec{\boldsymbol{J}}_U(\boldsymbol{r})\cdot\nabla\left(\frac{1}{\boldsymbol{T}(\boldsymbol{r})}\right) \qquad (8)$$

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[1] *Note C* examines the case in which dissipation involves both thermal and electric fluxes.

[2] Lars Onsager, *Equation 5.9*, (Phys. Rev. *37*, 405, 1931). More general expressions have been used with additional terms for material fluxes (S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics", Dover, 1984).* For the troposphere, no steady-state material fluxes transit the system, although such fluxes exist as internal degrees of freedom for energy storage and transport.

[3] In Note D, we consider a global steady-state constraint for discussion of fluctuations.

Comparison with *Eq. 4a* yields the important result characterizing steady-state dissipation,

$$\nabla\cdot\left(\frac{\vec{J}_F(r)}{T(r)}\right) = 0 \tag{9}$$

hence,

$$0 = \iiint d\tau\,\nabla\cdot(\vec{J}_F(r)/T) = \oiint d\vec{\sigma}\cdot(\vec{J}_F(r)/T(r)) \tag{10}$$

To find the local dissipation function,

$$\begin{aligned}\iiint d\tau\;\; T(r)\nabla\cdot\left(\frac{\vec{J}_F(r)}{T(r)}\right) &= 0\\ &= \oiint d\vec{\sigma}\;\cdot\vec{J}_F(r) - \iiint d\tau\;\left(\frac{\vec{J}_F(r)}{T(r)}\right)\cdot\nabla T(r)\end{aligned} \tag{11}$$

and

$$\dot{F} = \oiint d\vec{\sigma}\cdot\vec{J}_F(r) = \iiint d\tau\,\vec{J}_F(r)\cdot\nabla\ln T(r) \tag{12}$$

From *Eqs. 7* and *10* for the two interface system,

$$\frac{J_{F1}}{T_1} + \frac{J_{F2}}{T_2} = 0 \tag{13}$$

$$\dot{F} = J_{F1} + J_{F2} = J_{F1}\left(1-\frac{T_2}{T_1}\right) \tag{14}$$

With $J_{F1}<0$ and $T1>T2$, the rate at which free energy dissipates reduces to a function dependent only on surface parameters. This result is analogous to *Eq. 3* for electric dissipation. Both expressions apply to dissipative transport processes and involve only external observables. The reduction of volume integrals to surface functions is a consequence of the divergence theorem and the identification of non-divergent internal flux functionals. For entropy the functional is $\vec{J}_U(r)$; for free energy, $\vec{J}_F(r)/T(r)$; for electric currents, $\vec{J}_Q(r)$.

When *Eq .14* is applied to each layer of a laminar configuration with the output free energy flux of one layer the input of the next, total dissipation depends only on the bounding temperatures and is independent of the intervening thermal profile. Note that *Eq.* 14 also describes the work obtained from a Carnot engine operating reversibly. Energies lost either by reversible or irreversible processes are losses of free energy and thermodynamically indistinguishable.

We define thermal sensitivity as the differential of dissipation with respect to surface temperature. For analysis, it is convenient to introduce positive parameters, $W=-\dot{F}$ and $J_1=-J_{F1}$ so that W

corresponds to watts dissipated and $\boldsymbol{J_1}$ is the free energy flux internal to the warmer interface.[4] From *Eq. 14*, with $\boldsymbol{\Delta T=T_1-T_2}$

$$\frac{\delta \boldsymbol{W}}{\delta \boldsymbol{T}_1} = \frac{\boldsymbol{W}}{\Delta \boldsymbol{T}}\left[\frac{\boldsymbol{d}\ln(\boldsymbol{J}_1)}{\boldsymbol{d}\ln(\Delta \boldsymbol{T})} + \frac{\boldsymbol{T}_2}{\boldsymbol{T}_1}\right] \qquad (15)$$

We have here assumed $\boldsymbol{T_2}$ to be constant, *i.e.* the cooler boundary is a fixed isotherm. Let α represent the logarithmic derivative.[5] Typical tropospheric parameters are dissipations of $240\ W/m^2$ and temperature differences of $70K$ $(T_1=280K,\ T_2=210K)$. For the $3.7\ W/m^2$ change in dissipation associated with CO_2 doubling, there follows a temperature change of $0.62K$ assuming linearity ($\alpha=1$), increasing in the 'worst' case $(\alpha=0)$ to $1.44K$. Plugging these values for dissipation and temperature into *Eq. 15* indicates upward internal flux densities of order $1\ kW/m^2$, twice values associated with radiation, convection apparently being responsible for the difference.

This note is intended to offer a rigorous description of thermal dissipation which follows from the postulates in *Eq. 4* for a nonlinear dissipative system. No phenomenological relation is assumed or implied between energy fluxes and thermal gradients other than a mean negative correlation to ensure steady-state stability. The presumption of a steady state, and thereby definition of a thermodynamic temperature, is itself of prime concern. Would our conclusions be modified if explicit consideration of non-divergent mass fluxes were incorporated? Experience suggests that electric dissipation in a gas-discharge tube follows the classical current-voltage formula despite large internal turbulent fluctuations, and one might then presume the same to hold for a Carnot cell. The expression derived for the thermal dissipation coefficient further presumes all incoming energy fully dissipates within the troposphere before escape. The basis for this abstraction is the principle that dissipated energy can not be re-dissipated and is unable to perform additional work within the system – not that it immediately vanishes as a consequence of dissipation.

While the original focus of this research sought a clearer formulation of “greenhouse” thermodynamics, it has evolved into considerations of far more fundamental issues. That the Carnot Equation is the basic expression for thermal dissipation, the equivalent of the current-voltage product for electric dissipation, is not widely recognized. Nor that it is a consequence of Onsager's expression for entropy creation in a steady state, requiring no reference to hypothetical devices. Fluctuation analysis indicates that steady-state stability implies a minimum dissipation condition, but not so for entropy creation. Qualitatively this follows from distinctions in the behavior of internal energy and free energy fluxes when thermal gradients can no longer be treated as linear perturbations.

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12/29/2015

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[4] The immediate relevance of *Eq. 14* to the troposphere may not be apparent as it implies thermal reservoirs at each interface transparent to all energy fluxes. In *Note B*, we show that, should the cooler interface only transmit dissipated energy, *Eq. 14* still applies with $\boldsymbol{J_1}$ including both flux entering the system and the internal reflux forced by a blocking interface.

[5] Note A indicates how 'feedback' effects may be incorporated into α.

Note A:
The terms forcings and feedbacks, as currently used, are implied in the dissipation formula

$$\boldsymbol{W} \; = \; \boldsymbol{J}(\boldsymbol{T}, \boldsymbol{q}_i(\boldsymbol{T})) \;\; \Phi(\boldsymbol{T}) \qquad \text{(A1)}$$

where $\boldsymbol{q}_i$ represents a set of arbitrary parameters which may or may not be temperature dependent. Consider a perturbation changing their values while holding the temperature profile fixed:

$$\delta \boldsymbol{W} \; = \; \boldsymbol{W} * \left(\frac{\partial \ln(\boldsymbol{J})}{\partial \boldsymbol{q_i}} \right)_{\boldsymbol{T}} \delta \, \boldsymbol{q}_i \qquad \text{(A2)}$$

and *δW,* is the forcing associated with $\boldsymbol{q}_i$ (summation over ***i*** is implied.)

Feedbacks reflect the temperature dependence of ***J*** when all parameters except the temperature profile are held fixed:

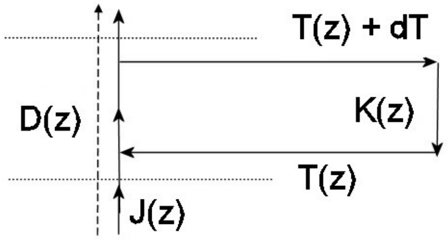
$$\frac{\boldsymbol{d} \ln(\boldsymbol{J})}{\boldsymbol{d} \ln(\Delta \boldsymbol{T})} \; = \; \left(\frac{\partial \ln(\boldsymbol{J})}{\partial \ln(\Delta \boldsymbol{T})} \right)_{q_i} \; + \; \left(\frac{\partial \ln(\boldsymbol{J})}{\partial \boldsymbol{q}_i} \right)_{\boldsymbol{T}} \; \frac{\boldsymbol{d} \, \boldsymbol{q}_i}{\boldsymbol{d} \ln(\Delta \boldsymbol{T})} \qquad \text{(A3)}$$

The first term on the right-hand side defines zero feedback. As $\Delta T \rightarrow 0$, this term approaches unity, *i.e.* linear dissipation , and nonlinear deviations are assigned to parameters in the second or feedback term. Suppose $\boldsymbol{q}_i$ describes water content in the atmosphere. The first factor of the feedback term is negative, water being a greenhouse gas. The second factor is positive, as water content increases with surface temperature, with a net net negative contribution.

Note B:

The two-interface model described by *Eq. 14* assumed thermal reservoirs as boundaries fully transparent to energy fluxes. We now consider a cooler interface transparent only to dissipated energy. All incoming free energy must internally circulate until dissipated. To reach a steady state, temperature gradients must increase until dissipation balances the rate at which free energy is entering the system. In the adjacent sketch, the upward flux stream, ***J(z)***, is enhanced by a local reflux, ***K(z),*** and the incremental dissipation is

$$\delta \boldsymbol{D}(z) = -\frac{\boldsymbol{J}(z)+\boldsymbol{K}(z)}{\boldsymbol{T}(z)}\,\delta \boldsymbol{T} \qquad \text{(B1)}$$



with ***J(z)*** decreasing as dissipation increases.

$$\boldsymbol{J}(z) = \boldsymbol{J}(\boldsymbol{T}_1)-\boldsymbol{D}(z) \qquad \text{(B2)}$$

Thus

$$\boldsymbol{T}(z)\frac{\boldsymbol{dD}(z)}{\boldsymbol{dT}(z)} - \boldsymbol{D}(z) = -(\boldsymbol{J}(\boldsymbol{T}_1)+\boldsymbol{K}(z)) \qquad \text{(B3)}$$

or

$$\frac{\boldsymbol{d}}{\boldsymbol{dT}(z)}\left(\frac{\boldsymbol{D}(z)}{\boldsymbol{T}(z)}\right) = -\frac{\boldsymbol{J}(\boldsymbol{T}_1)+\boldsymbol{K}(z)}{\boldsymbol{T}(z)^2} \qquad \text{(B4)}$$

Upon integration,

$$\left[\frac{\boldsymbol{D}(z)}{\boldsymbol{T}(z)}-\frac{\boldsymbol{J}(\boldsymbol{T}_1)}{\boldsymbol{T}(z)}\right]_{\boldsymbol{T}_1}^{\boldsymbol{T}_2} = \int_{\boldsymbol{T}_2}^{\boldsymbol{T}_1}\frac{\boldsymbol{K}(z)}{\boldsymbol{T}(z)^2}\,\boldsymbol{dT} = \frac{\boldsymbol{J}(\boldsymbol{T}_1)}{\boldsymbol{T}_1} \qquad \text{(B5)}$$

When all incoming energy, $\boldsymbol{J}(\boldsymbol{T}_1)$, is dissipated, $\boldsymbol{D}(\boldsymbol{T}_2) = \boldsymbol{J}(\boldsymbol{T}_1)$. Net flux conservation requires

$$\boldsymbol{J}(z)+\boldsymbol{D}(z)-\boldsymbol{K}(z)=\boldsymbol{J}(\boldsymbol{T}_1)-\boldsymbol{K}(z) = \boldsymbol{constant} \qquad \text{(B6)}$$

Hence ***K(z)*** must also be constant and total dissipation is thus

$$\boldsymbol{D}(\boldsymbol{T}_2) = \frac{\boldsymbol{K}}{\boldsymbol{T}_2}(\boldsymbol{T}_1-\boldsymbol{T}_2) \qquad \text{(B7)}$$

This result becomes identical to *Eq. 14* when **K** is identified as $-\boldsymbol{J}_{F2}$ in *Eq. 13*, *i.e.* the free energy flux exiting a cell bounded by two thermal reservoirs is reflected back into the cell, with only dissipated energy escaping.

Note C:

This essay began with a discussion of electric dissipation in terms of thermodynamic fluxes and potentials. Electric dissipation involves local heating of volume elements and, to reach a steady state, this energy is removed from the system by a thermal energy flux, $\boldsymbol{J_U(r)}$.

For a more complete description of electric dissipation, consider an expression similar to *Eq. 4b*,

$$\vec{\boldsymbol{J}}_U(\boldsymbol{r}) + \vec{\boldsymbol{J}}_X(\boldsymbol{r}) = \vec{\boldsymbol{J}}_F(\boldsymbol{r}) + \boldsymbol{T}(\boldsymbol{r})\vec{\boldsymbol{J}}_S(\boldsymbol{r}) \tag{C1}$$

to which an additional flux, $\boldsymbol{J_X(r)}$ has been added, representing a generalized non-thermal energy flux such as an electric current (c.f. *Eq. 1),* an attenuating laser beam, etc. The steady-state condition, *Eq. 4c,* is replaced with

$$\nabla\cdot\vec{\boldsymbol{J}}_U(\boldsymbol{r}) + \nabla\cdot\vec{\boldsymbol{J}}_X(\boldsymbol{r}) = 0 \tag{C2}$$

While both fluxes are now divergent, their sum is not.

Following Onsager, the entropy changes associated with a volume element resolve into internal and external terms:

$$-\nabla\cdot\vec{\boldsymbol{J}}_{S_{int}}(\boldsymbol{r}) = \frac{1}{\boldsymbol{T}}\nabla\cdot(\vec{\boldsymbol{J}}_U(\boldsymbol{r}) + \vec{\boldsymbol{J}}_X(\boldsymbol{r})) = 0 \tag{C3}$$

$$\nabla\cdot\vec{\boldsymbol{J}}_{S_{ext}}(\boldsymbol{r}) = \nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_U(\boldsymbol{r})}{\boldsymbol{T}}\right) = \nabla\cdot\vec{\boldsymbol{J}}_S(\boldsymbol{r}) \tag{C4}$$

The former vanishes in a steady state by virtue of *Eq. C2* leaving only the external contribution to their sum. Taking the divergence of *Eq. C1* after dividing by $\boldsymbol{T}$ and rearranging terms,

$$\nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_F(\boldsymbol{r})-\vec{\boldsymbol{J}}_X(\boldsymbol{r})}{\boldsymbol{T}(\boldsymbol{r})}\right) = \nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_U(\boldsymbol{r})}{\boldsymbol{T}(\boldsymbol{r})}\right) - \nabla\cdot\vec{\boldsymbol{J}}_S(\boldsymbol{r}) \tag{C5}$$

and, equivalent to *Eq. 9,*

$$\nabla\cdot\left(\frac{\vec{\boldsymbol{J}}_F(\boldsymbol{r})-\vec{\boldsymbol{J}}_X(\boldsymbol{r})}{\boldsymbol{T}(\boldsymbol{r})}\right) = 0 \tag{C6}$$

If internal temperature gradients are neglected or, less restrictively, if all flux-bearing surface regions share a common temperature , *Eqs. 1-3* follow from *Eq. 1A* when $\boldsymbol{J_X=J_Q\Phi}$.

For a two surface system, steady rates of entropy gain and free energy loss are:

$$\dot{\boldsymbol{S}} = (\boldsymbol{J}_{U1}/\boldsymbol{T}_1 + \boldsymbol{J}_{U2}/\boldsymbol{T}_2) \tag{C7}$$

$$\dot{\boldsymbol{F}} = \boldsymbol{J}_{F1} + \boldsymbol{J}_{F2} = (\boldsymbol{J}_{F1} - \boldsymbol{J}_{X1})\left(1 - \frac{\boldsymbol{T}_2}{\boldsymbol{T}_1}\right) + (\boldsymbol{J}_{X1} + \boldsymbol{J}_{X2}) \tag{C8}$$

Consider a 100W heater in a bath thermostatted at 300K,

$$\begin{aligned} \boldsymbol{J}_{U1} &= 0 \\ \boldsymbol{J}_{F1} &= \boldsymbol{J}_{X1} = -100 \\ \boldsymbol{J}_{X2} &= 0 \\ \boldsymbol{J}_{U2} &= -(\boldsymbol{J}_{U1} + \boldsymbol{J}_{X1} + \boldsymbol{J}_{X2}) = 100 \end{aligned} \tag{C9}$$

$\boldsymbol{J}_{U1}$ is zero as there is no influx of thermal energy and $\boldsymbol{J}_{X2}$ may be set to zero as only the electric potential difference, $\boldsymbol{\Phi}_1 - \boldsymbol{\Phi}_2$, is involved. The rate of entropy creation is thus 100/300 W/K and the rate of free energy dissipation is simply 100W. In the general case, the total dissipation is the sum of values calculated separately for each process, *using the temperature profile with both processes active*.

Note D:

Variational thermodynamic expressions for systems outside the linear region near equilibrium remain an unresolved topic of fundamental interest. Intuitively, when parameters for a steady-state are modified, one anticipates the transition to a new steady state will occur as quickly as constraints allow and that the new state will require the minimum input energy needed to sustain it. Onsager showed such behavior did characterize near-equilibrium behavior, but further extension has been elusive.

To simplify discussion, we introduce the thermo-dissipation flux defined as

$$\vec{J}_D(r) \equiv \frac{\vec{J}_F(r)}{T(r)} \tag{D1}$$

From *Eqs. 4a* and *4b* it then follows that

$$T(r)\vec{\nabla}\cdot\vec{J}_D(r) = \vec{\nabla}\cdot\vec{J}_U(r) \tag{D2}$$

The steady-state constraint, *Eq. 4c*, is too restrictive for variational considerations as it does not permit local flux and thermal fluctuations. Rather, we adopt the less restrictive integral constraint

$$\iiint d\tau\, \vec{\nabla}\cdot\vec{J}_U(r) = \iiint d\tau\, T(r)\vec{\nabla}\cdot\vec{J}_D(r) = 0 \tag{D3}$$

Dissipation may then be expressed as

$$\begin{aligned} W &= -\oiint d\vec{\sigma}\cdot\vec{J}_F(r) = -\iiint d\tau\, \vec{\nabla}\cdot\vec{J}_F(r) = -\iiint d\tau\, \vec{\nabla}\cdot\left(\vec{J}_D(r)T(r)\right) \\ &= -\iiint d\tau\, \vec{J}_D(r)\cdot\vec{\nabla}T(r) \end{aligned} \tag{D4}$$

Introducing variations for both ***J_D(r)*** and ***T(r)***,

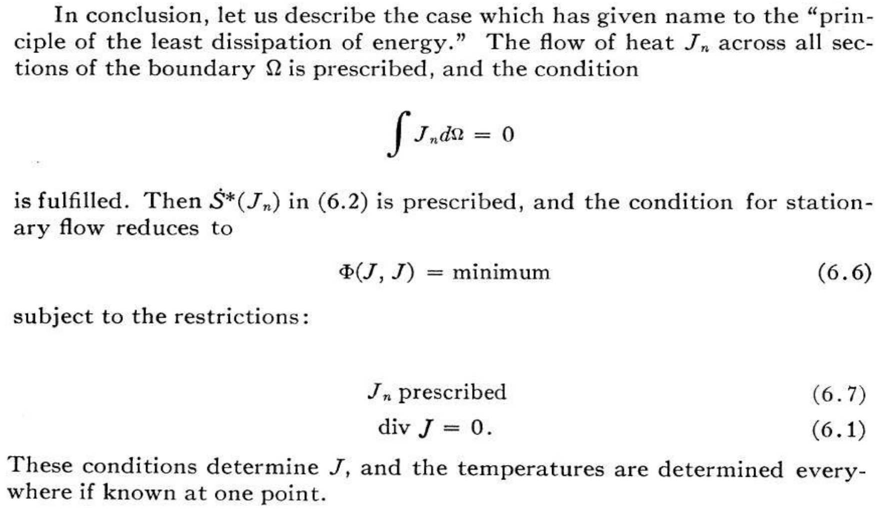
$$\begin{aligned} W &= -\iiint d\tau\, \left(\left(\vec{J}_D(r)+\delta\vec{J}_D(r)\right)\cdot\nabla\left(T(r)+\delta T(r)\right)\right) \\ &= \langle W\rangle + \langle\delta W\rangle + \langle\delta^2 W\rangle \end{aligned} \tag{D5}$$

yields

$$\begin{aligned} \langle W\rangle &= -\iiint d\tau\, \vec{J}_D(r)\cdot\vec{\nabla}T(r) = -\oiint d\vec{\sigma}\cdot\vec{J}_D(r)T(r) \\ \langle\delta W\rangle &= -\iiint d\tau\, \left(\delta\vec{J}_D(r)\cdot\vec{\nabla}T(r) + \vec{J}_D(r)\cdot\vec{\nabla}\delta T(r)\right) \\ &= -\delta\oiint d\vec{\sigma}\cdot\vec{J}_D\vec{T}(r) = \delta\langle W\rangle \\ \langle\delta^2 W\rangle &= -\iiint d\tau\, \left(\delta\vec{J}_D(r)\cdot\delta\vec{\nabla}T(r)\right) \end{aligned} \tag{D6}$$

The first-order variation is a secular perturbation depending only on boundary changes and vanishes when these are prescribed. The second-order variation reflects the correlation of internal flux and thermal gradient fluctuations. A positive variation, and consequently a dissipation minimum, characterizes the thermodynamic steady state. Consider a small region within the integral which experiences a random increase in temperature. Thermal gradients will be directed into this region. A correlated outward flux makes a positive contribution to the second variation and, should this behavior dominate, a macroscopic dissipation minimum follows. Conversely, a negative contribution indicates instability, with energy flux drawn towards the 'hot spot' feeding its growth.[6]

Onsager's description of minimal dissipation is [2]:



In conclusion, let us describe the case which has given name to the "principle of the least dissipation of energy." The flow of heat J_n across all sections of the boundary Ω is prescribed, and the condition

$$\int J_n d\Omega = 0$$

is fulfilled. Then $\dot{S}^*(J_n)$ in (6.2) is prescribed, and the condition for stationary flow reduces to

$$\Phi(J, J) = \text{minimum} \qquad (6.6)$$

subject to the restrictions:

$$J_n \text{ prescribed} \qquad (6.7)$$

$$\text{div } J = 0. \qquad (6.1)$$

These conditions determine J, and the temperatures are determined everywhere if known at one point.

To relate our results to Onsager's, from *Eqs. 4,*

$$\vec{\nabla}\cdot\vec{J}_U = 0 = \vec{\nabla}\cdot\vec{J}_F + T\,\vec{J}_U\cdot\vec{\nabla}(1/T) + \vec{J}_S\cdot\vec{\nabla}T \qquad \text{(D6)}$$

In the linear region near equilibrium, only the last term is quadratic in ∇T. When this term is dropped,

$$\dot{F} = \oiint d\vec{\sigma}\cdot\vec{J}_F(r) = \iiint d\tau\,\vec{J}_U(r)\cdot\nabla\ln T(r) \qquad \text{(D7)}$$

differing from *Eq. 12* by replacement of $J_F(r)$ with $J_U(r)$. Neglect of the thermal gradient term increases dissipation, qualitatively because it permits dissipated energy to be continually re-dissipated and eventually exceed the energy being input to the system!

It should be noted that this analysis is wholly secular. In real systems, after an abrupt change in boundary conditions, fluxes show a lagging temporal response. For slow changes, one might expect the system to follow a dissipation minimum from one steady state to the next. Fast nonsecular relaxation mechanisms dependent on rates of change fall beyond the scope of this note.

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[6] It may be noted that, for the rate of entropy generation be an extremal, similar analysis requires the steady-state condition to be $\iiint d\tau\,\vec{\nabla}\cdot\vec{J}_U(r)/T = 0$, a condition only generally satisfied by an isothermal approximation.