Thermal Dissipation I

By way of introduction I am a physical chemist, now two decades into retirement. Several years ago, I grew curious about the science underlying headlines of pending catastrophe due to increasing atmospheric carbon dioxide levels. From the Internet, I learned of a field long on hypothesis and rhetoric, but lacking the analytical rigor of chemistry and physics. The venerable equations of Navier-Stokes and Schwarzschild appeared to be the only tools in the arsenal of this science – the former dealing with isothermal viscous phenomena and the latter with radiative fluxes in defined thermal profiles. The dormant chemist within asked, "Isn't this basically a problem of energy transport in thermal gradients? Where's the Thermodynamics?"

Thermodynamics began when Clausius asked what happens when a given amount of heat moves from one thermal reservoir to another. It remains taught today from 'gedanken' experiments with Carnot engines, perpetual motion machines, *etc.* In mature physical sciences, historical description has evolved to axiomatic generalization, *e.g.* Lagrangian mechanics. Carathéodory attempted this in 1909, but his efforts remain, at most, a footnote in thermodynamic texts.¹

Extensive thermodynamic parameters for equilibrium systems are conventionally expressed in units per volume. Non-equilibrium systems are better described in terms of vector fluxes and scalar potentials.² Vector thermodynamics allows simple solutions for apparently intractable problems by reducing volume integrals to surface integrals when non-divergent fluxes can be defined.

These notes began as a mathematical search for a thermodynamic "thermal coefficient of dissipation". As analysis progressed, however, it became evident that a much larger field was involved — nonlinear thermodynamic systems far from equilibrium, and more descriptive comments would not be unwelcome. Therefore, these notes are offered in two documents, this, a subjective description of this writer's interpretation of the second, rigorous mathematical derivations for thermal dissipation.

Temperature seems a simple intuitive concept. Its physical definition is not. It can not be expressed in MKS units. Mathematically, temperature can be axiomatically defined as a scalar potential or integration factor which renders the path integral of a function, *i.e.* entropy, between two points independent of the chosen path. Entropy then becomes a state function, characterized by an exact differential.^{3,4} For a mechanical system traveling from point A to point B, time reversal returns one to point A, but in a thermodynamic system required information is missing. Baranger depicts this loss as an increase of entropy when a complex system passes from a mechanistic regime, through the mists of chaos, to a thermodynamic regime.⁵ The product of temperature and entropy is expressible in MKS units. The axiomatic definition of temperature in terms of invariant path integrals raises several questions. Is there an inconsistency with using temperature to calculate future or past trajectories of a system? What if points A and/or B are themselves moving targets and do not correspond to steady-states?

¹ L. Pogliani and M. N. Berberan-Santos, "Constantin Carathéodory and the axiomatic thermodynamics", J. Math. Chem. 28, 313 (2000)

² S. R. de Groot and P. Mazur, "Non-Equilibrium Thermodynamics", Dover Publications, 1984.

³ C. Carathéodory, Math. Ann. 67, 355 (1909).

⁴ M. W. Zemansky, "Kelvin and Carathéodory-A Reconciliation", Am. J. Phys. 33, 914 (1966).

⁵ Michel Baranger, "Chaos, Complexity, and Entropy" http://necsi.edu/projects/baranger/cce.pdf

We confine our attention to steady-states with spatially dependent temperatures defined by a timeindependent scalar potential. Steady-state behavior is by no means universal. While we expect the luminosity of an incandescent bulb to depend only on an applied potential and not the path by which this value is reached, this is not so for the simple neon bulb or, more generally, systems with regions of differential negative resistance, *e.g.* superheated or supercooled states. We shall employ a fluxpotential description of thermodynamics and define dissipation to be the rate at which free energy is consumed. Dissipation is commonly associated with the conversion of other forms of energy to heat, but the notion that heat itself dissipates as it flows from hot to cold is less widely appreciated.

The dissipation coefficient of interest is the rate at which a steady-state system dissipates thermal energy as a function of the surface temperatures at which this energy enters and leaves the system with units $W/m^2/K$. This is, in many respects, equivalent to the reciprocal of the "climate sensitivity" parameter discussed in climate science literature. Our thermodynamic description for tropospheric dissipation is quite simple. As energy enters the system, dissipation creates thermal gradients. As more and more enters, these gradients grow until the rate at which energy enters matches the rate at which it dissipates and a steady-state is achieved. In this limit, only dissipated energy escapes, and undissipated energy is continually recycled until drained of its ability to act further within the system.

Before tackling this subject, however, it may be insightful to take a look at the more familiar process of electric dissipation as a vector thermodynamics problem. The local free energy flux density in a volume element is given by the product of the current density and electric potential for this element and a vector calculus theorem tells us that the total rate at which free energy changes is given by a volume integral of the divergence of the free energy flux. If we further assume the current to be conservative, *i.e.* non-divergent, the volume integral reduces to an integral involving only surface fluxes and potentials. Electric dissipation thus becomes a state function and can be determined without specifying the internal paths traced by electric currents or potential gradients, or even the physical nature of charge carriers within.

Onsager, in 1931, used a flux-potential description as the basis of a theory for irreversible thermodynamics.⁶ His local expression for the divergence of entropy flux, J_s , as the scalar product of an extensive flux of internal energy, J_U , and the gradient of an intensive scalar potential forms the axiomatic cornerstone of our methodology.⁷

$$\nabla \cdot \vec{J}_{s}(r) = \vec{J}_{u}(r) \cdot \nabla \left(\frac{1}{T(r)}\right)$$

This expression presumes no phenomenological relationship between local flux density and potential, although Onsager did introduce linearity for derivation of his reciprocity theorem, thereby restricting results to regions near equilibrium. If we take the internal energy flux to be locally conservative, ⁸

$$\nabla \cdot \vec{J}_{U}(r) = 0$$

⁶ Lars Onsager, "Reciprocal Relations in Irreversible Processes. I", Phys. Rev. 37, p. 405 (1931)

⁷ A more general expression for the rate of entropy creation involves material fluxes and pressure or concentration gradients.² We here consider only closed systems for which only energy fluxes are allowed to cross system boundaries and therefore only contribute to steady-state dissipation. Internal material fluxes remain important for determining the rate at which transitions between steady states occur.

⁸ We later relax this local constraint to an integral constraint in discussion of internal fluctuations and steady-state stability.

The rate at which the integrated entropy of the system changes reduces to a surface integral of flux and temperature. It does not depend on knowledge of explicit internal functions for fluxes and gradients or their functional relationship. It is a state function, dependent only on surface values of flux and temperature. (The relationship between these parameters does depend on system internals.) In the case of transport through two interfacial regions, each of constant temperature,

$$\dot{S} = (J_{UI}/T_1 + J_{U2}/T_2) = J_{U2}(1/T_2 - 1/T_1)$$

By convention, outward fluxes are taken as positive and entropy is increasing when $T_1 > T_2$. The Clausius definition for entropy changes follows from Onsager's expression and the assumption of local energy conservation.

In similar fashion, we may derive an equation for the dissipation of the Helmholtz free energy flux, J_F ,

$$\overrightarrow{J}_{U}(r) = \overrightarrow{J}_{F}(r) + T(r)\overrightarrow{J}_{S}(r)$$

and dissipation then equals the negative of the normal surface integral of $J_F(r)$.

In the steady state, the flux functional $J_F(r)/T(r)$ is non-divergent by virtue of the Onsager expression,

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

It is this relation which is key to our analysis of nonlinear steady-state phenomena. For a surface with two active regions,

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

This simple expression for thermal dissipation is no more than a restatement of Carnot's equation for the work performed by a thermal engine operating reversibly. Dissipation is a state function dependent only on boundary parameters. Partition into 'useful' work and 'waste' energy is by human artifice.

An important corollary is that energy can only be dissipated once within a system. Consider two Carnot cells connected in series with interfacial temperatures $T_1 > T_2 > T_3$. The first interface is connected to a thermal reservoir and, for the energy flux transfered across this interface, $J_F = J_U$. In a steady state, energy conservation requires that J_U be the same for all interfaces. Not so for J_F which dissipates as flux flows towards the cooler interface. If dissipation is to be additive, only free energy flux crossing the T_2 isotherm can be dissipated in the second cell, for only then will the combined dissipations of the two cells equal that of a single cell operating between T_1 and T_3 .

As a hypothetical case, consider a thermal cell bounded by two thermal reservoirs at 280K and 210K dissipating energy at a steady 240W rate. The internal energy flux must then be 960W no matter the cell's shape or content, be it solid, liquid or gas. While 960W of energy, J_U , transits the cell, at the cooler interface only 720W free energy, J_{F2} , remains. Imagine now that only dissipated energy can escape the system at the cooler boundary. Energy undissipated will accumulate and be recycled until building up to a steady state for which dissipated energy escapes at the same rate as free energy enters. The Carnot expression still holds provided J_{F1} includes both recycled and incoming free energy.

These numbers have clearly been chosen to mimic the troposphere, but are the derived flux values consistent with known values? For the thermodynamic dissipative model, the down-to-up flux ratio at the surface is T_2/T_1 . MODTRAN calculations for the US Std Atmosphere give surface radiation fluxes of 259W/m² down and 360W/m² up, close to the ratio assumed above.⁹ MODTRAN spectra show no window suggesting photons emitted from the surface might avoid being absorbed and their energy dissipated among various modes of internal energy. However, the thermodynamic expressions apply to the total energy flux which must also include convective transport, dominant near the surface (960-360W/m²), and agreement is contingent upon a similar ratio existing for convection.

A function of particular interest is the variation of dissipation with surface temperature. Differentiation of the above equation leads directly to:

$$\frac{\delta W}{\delta T_{I}} = \frac{W}{\Delta T} \left[\frac{d \ln (J_{I})}{d \ln (\Delta T)} + \frac{T_{2}}{T_{I}} \right]$$

where W is the rate of dissipation, $J_I = |J_{FI}|$ and $\Delta T = T_I - T_2$. For CO₂ doubling, δW is generally accepted to be 3.7W/m² and the major question is what δT_I shall be. As estimates of W, T_I and T_2 , we'll take 240W/m², 280K and 210K. J_I may depend explicitly on parameters other than temperature which are themselves temperature dependent. If the derivative is partial, *i.e.* these parameters are held constant, one has 'transient' sensitivity, if total, 'equilibrium' sensitivity (which has nothing to do with equilibrium in the thermodynamic sense.) Our default assumption is unit slope for a log-log plot. Larger slopes lead to lesser temperature changes (negative feedback in the climatologist's jargon), lesser slopes to greater changes (positive feedback). These are, however capped by the T_2/T_1 term. Only when the derivative changes sign, a hypothetical negative resistance regime, is it theoretically possible for positive feedbacks to have catastrophic consequences and the very stability of a steady state and the meaning of temperature become questionable. For slopes 1 to 0, δT ranges 0.62K to 1.44K. For slopes less than unity, surface temperature increases will be less than 0.62K.¹⁰

This brings us to the question, "What determines the stability of a steady state?" So far, we have

⁹ D. Archer, <u>http://forecast.uchicago.edu/Projects/modtran_form.html</u>

¹⁰ That these changes are considerably below 'consensus' predictions is largely a consequence of constraints applied to the Carnot equation. We have assumed a constant T_2 implying the cooler interface represents a specific isotherm, not a physical surface. The 'consensus' constraint is that ΔT is invariant, the 'convective adjustment'. Literally, this leads to an unstable situation with surface cooling by added greenhouse gases. A constraint closer to 'consensus' models assumes a constant T_2/T_1 ratio. Then the second term disappears. The only argument of which I'm aware justifying the 'convective adjustment' harks back to the notion of 'convective equilibrium' once offered by Kelvin and shown by Maxwell to be inconsistent with a state of thermodynamic equilibrium. (*Theory of Heat*, p. 300, 1872 ed.) Should a non-equilibrium state exist with an invariant thermal gradient, we would have to assume that an infinitesimal gradient change results in an infinite flux change, overwhelming any possible greenhouse effect.

presumed a non-divergent flux of internal energy to define the steady-state. To explore fluctuations, we will require only that the total internal energy of the system be fixed, i.e. only that the surface integral of internal energy flux be zero. For convenience, we define a dissipation flux as

$$\vec{J}_{D}(r) \equiv \frac{\vec{J}_{F}(r)}{T(r)}$$

The volume integral for dissipation with variations for both $J_D(r)$ and T(r) included is

$$W = -\iiint d\tau \left(\left(\overrightarrow{J}_{D}(r) + \delta \overrightarrow{J}_{D}(r) \right) \cdot \overrightarrow{\nabla} \left(T(r) + \delta T(r) \right) \right)$$

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

and the second-order variation becomes

$$\langle \delta^2 W \rangle = - \iiint d\tau \left(\delta \overrightarrow{J}_D(r) \cdot \delta \overrightarrow{\nabla} T(r) \right)$$

while the first-order variation reduces to a surface integral, $\delta < W >$. Dissipation will be a minimum if, on average, a negative correlation exists.¹¹ Qualitatively, hot spots should then cool rather than grow. This need not be true everywhere as, for instance, condensation within a supersaturated vapor. The existence of a minimum implies that nature does its best to minimize thermal gradients and, therefore, surface temperatures.

One of the major challenges in discussing climate sensitivity is its presentation as a 'wicked' function of a litany of uncertainties. Our analysis reveals a simple surface function, with no explicit indication of such parameters. This solution is a first-order perturbation of an existent state, using observable properties of that state as input, thereby implicitly including all internal parameters in its basis. The reduction from a thermodynamic space expressed in statistical coordinates, *e.g.* isotherms, to corresponding physical coordinates lies beyond the limits of current analytic abilities. Similarly, does the resolution of energy fluxes into convective and radiative components. Reduction of nonlinear thermodynamic quantities to a molecular level remains one of the challenges facing 21st century thermodynamics.

Our thermal dissipation model for climate sensitivity is clearly bare-bones. Energy enters the troposphere from the surface and remains there, circulating about until dissipated, *i.e.* unable to do any further work within the troposphere. Only dissipated energy escapes. Eventually, with increasing temperatures, a steady-state is reached where dissipation matches energy influx. This suffices to provide a formal analytic expression for climate sensitivity and greenhouse effects without a more detailed resolution into the physical natures of energy fluxes, *etc*.

The assumption of a steady state is of theoretical concern. It is closely linked to the existence of a temperature function which renders path integrals for state functions path-independent. The steady-state properties of liquid water, both equilibrium and dissipative, are the same no matter whether once ice or steam. The dissipation of a 100W light bulb is independent of the path by which its operating potential is reached. But we recognize that other physical systems exhibit memory effects over anthropic temporal scales. Transitions between steady states are yet more hypothetical. Should they proceed slowly, one might suppose a path through a continuum of steady state configurations but, if

¹¹ Ilya Prigogine, TIME, STRUCTURE AND FLUCTUATIONS, Nobel Lecture, 8 December, 1977

otherwise, is the concept of a temperature still meaningful?

Perhaps our most important observations are that: (1) if the troposphere is a dissipative system, the consequences of positive feedback are severely restricted by lapse rate increases; (2) a variational theorem keeps surface temperatures to the minimum value consistent with constraints; (3) thermodynamics is the invisible 800lb gorilla in the climate science arena pending materialization.

P. D. Quondam 12/28/2014