

Steady-State Thermodynamics and Thermal Dissipation

Prologue

“With thermodynamics, one can calculate almost everything crudely; with kinetic theory, one can calculate fewer things, but more accurately; and with statistical mechanics, one can calculate almost nothing exactly.” — Eugene Paul Wigner

This essay began as an attempt to consolidate and expand upon, for personal reference, notions which have attracted my attention in recent years.¹ Explicit interest is in steady-state energy fluxes arising from thermal gradients in systems far from equilibrium. At the most fundamental level, we must assume such systems exhibit reproducible properties independent of the path by which their steady state is achieved. Mathematically, the path integral for some function must be independent of paths taken from A to B. This state function, should it exist, is called entropy and its conjugate integrating function is temperature. Qualitatively, the thermodynamic state has lost information of its past history.

This description has served well to understand one special steady state, equilibrium, a state of maximum entropy and uniform temperature. The factor kT is ubiquitous in the literature for analysis of equilibrium systems and first-order perturbations thereof, for such perturbations involve the populations of unperturbed equilibrium states. That assumption of the existence of a non-equilibrium steady state implies an inhomogeneous scalar temperature potential seems plausible if yet to be proved.

As a cardinal formulation of thermodynamics we adopt the Onsager expression^{2,3}

$$\nabla \cdot \vec{J}_s(r) = \vec{J}_U(r) \cdot \nabla \left(\frac{1}{T(r)} \right) = \nabla \cdot \left(\frac{\vec{J}_U(r)}{T(r)} \right) - \frac{1}{T(r)} \nabla \cdot \vec{J}_U(r) \quad (1)$$

which describes the divergence of an entropy flux density in terms of a scalar temperature potential and an energy flux density. Partial integration resolves entropy creation into a surface term describing a flux between isotherms and a bulk term describing local absorption. $\vec{J}_U(r)$ should include all fluxes that may alter a system's internal energy, including radiation. Traditionally, thermodynamics is presented in terms of densities of extensive parameters such as energy and mass. While this works well for static systems, e.g. equilibrium, dynamic descriptions are better expressed in terms of fluxes of extensive parameters and their conjugate intensive potentials.

A maxim of thermodynamics is that non-equilibrium states strive to relax towards equilibrium. To maintain a steady state requires the continuous expenditure of energy by external sources. This work, dissipation, is both elegantly and simply expressed by the Carnot Equation as a decrease in a flux of free energy on flowing through a system from T_0 to T_1 .

¹ <http://quondam.000webhostapp.com/Notebook.html>

² Lars Onsager, *Equation 5.9*, (Phys. Rev. 37, 405, 1931)

³ A more complete formulation would include mass and coulomb fluxes and their associated potentials.

$$\Delta J_F = -\frac{J_{F0}}{T_0}(T_0 - T_1) \quad (2)$$

This equation follows rigorously from *Eq. 1* when free energy flux is defined by $\vec{J}_U = \vec{J}_F + T\vec{J}_S$ and the condition $\nabla \cdot \vec{J}_U(r) = 0$ defines the steady state.

In the following section we discuss several one-dimensional models intended to illustrate and clarify perhaps less than obvious aspects of thermal dissipation. We first look at how the distinction between fluxes of free and internal energy is manifest in systems far from equilibrium. We then consider several examples involving radiative dissipation *in vacua*. Photon fluxes are intrinsically bi-directional in contrast to those of molecular origin.⁴ We conclude this section with a rather lengthy mathematical description of the gray gas. This is a theoretical concept in which all radiation is characterized by a single absorption coefficient. It then becomes possible to analyze a system with coupled radiative and conductive/convective transport processes, the latter being approximated by mechanisms proportional to local temperature gradients. Our algorithm considers the temperature profile as a variational parameter and seeks that solution for which a combined energy flux density is uniform throughout a one-dimensional cell.

In summary, we contrast this methodology with the traditional initial value approach based on iterative radiation calculations of local heating and cooling rates to adjust thermal profiles until temporal convergence is achieved. These alternatives represent parametrically distinct physical representations for the steady state. On one hand it is described by the decay of linked thermal and radiation transients, heat capacity, *etc.* On the other, it is described by a non-divergence constraint for a flux composed of two divergent energy streams jointly characterizing a bi-directional and a uni-directional process.

4 Photons are bosons, molecules *aka* electrons are fermions.

One-Dimensional Cells

In this section we explore the consequences of several one-dimensional models for energy transport in thermal gradients using idealized cells bounded by thermal reservoirs. We axiomatically define such reservoirs with these properties:

Axiom: All energy exiting a thermal reservoir is considered to be thermodynamic free energy.

Axiom: All energy, free or otherwise, impinging upon a thermal reservoir is absorbed without reflection.

Consider a basic one-dimensional cell bounded by thermal reservoirs at $10K$ and $100K$ (Fig. 1).

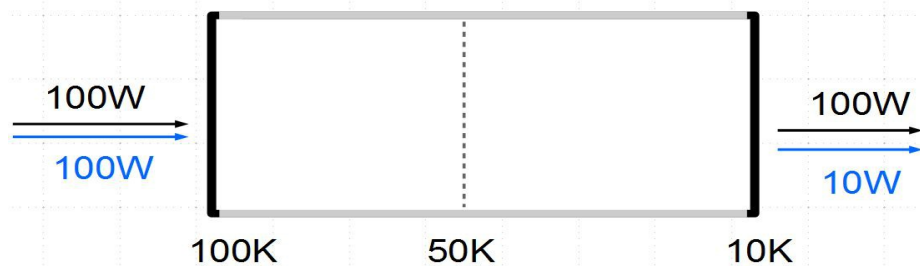


Figure 1: Two-terminal thermal cell. Net energy fluxes in black, free energy fluxes in blue, $90W$ dissipation.

A steady state is observed with a $100W$ energy flux. What is the rate of dissipation? By definition, all energy furnished by the input reservoir is free energy. From the Carnot equation (Eq. 2), we calculate a dissipation of $90W$. As all energy entering the system must exit through the $10K$ interface, $90W$ of this flux must be counted as dissipated energy while $10W$ remains free. This does not imply two distinct microscopic flavors for energy 'fluxons' but a non-Boltzmann redistribution of populations of less than maximum entropy. A $90W$ dissipation stream represents a $10K$ entropy flux.

Let us now suppose a scalar temperature potential exists within this cell. We ask, "What is the rate of dissipation between the $100K$ boundary and the intermediate $50K$ isotherm? Equation 2 says $50W$, with $50W$ of free energy remaining. Should we assume $100W$ flux remains available for dissipation between this isotherm and the $10K$ boundary, we should get an additional $80W$, a total dissipation of $130W$, exceeding the rate at which energy is entering the cell! Should we assume, however, that only the remaining $50W$ free energy is available for dissipation, we obtain a dissipation of $40W$, and total dissipation then equals the sum of its parts!

Theorem: Energy once dissipated within a system can not be re-dissipated without external intervention.

Imagine next that we insert a metal plate which intercepts flux at a position where it happens to reach a steady-state temperature of $50K$ (Fig. 2). If necessary, we can make dimensional adjustments to retain a $100W$ energy flux so that total dissipation remains $90W$.

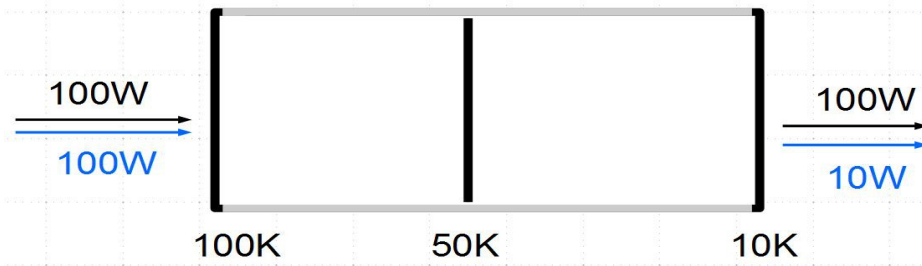


Figure 2: Two-terminal cell with an internal floating shield at 50K, 90W dissipation.

Externally, boundary conditions remain unchanged and thus also dissipation. But, let us now connect this 50K plate to an external 50K thermal reservoir. No net energy will flow through this isothermal connection, yet we expect dissipation to increase to 130W for we have created two thermally decoupled cells. We are forced to conclude that, while there is no net energy flux through this new connection, the plate is nevertheless exchanging 50W of dissipated energy for 50W of free energy from the reservoir.

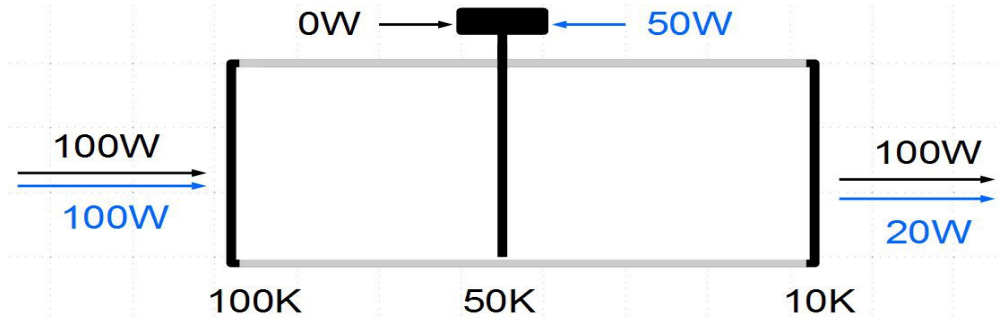


Figure 3: Connecting the shield in Fig. 2 to an external 50K reservoir, 130W dissipation.

LEMMA: Dissipated energy may be restored as free energy by intervention of an external reservoir.

It is perhaps worth noting that the rate of entropy creation is independent of this intervention, for

$$\frac{\Delta S}{\Delta t} = J_U \left[\left(\frac{1}{T_3} - \frac{1}{T_2} \right) + \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] = J_U \left[\left(\frac{1}{T_3} - \frac{1}{T_1} \right) \right] \quad (3)$$

where J_U is the internal energy flux, not J_F . This result is independent of T_2 .

LEMMA: Entropy creation and dissipation are not equivalent in non-isothermal systems.

Results for the cells just discussed are independent of cell contents, be they fluid or solid, gas or metal for steady-state dissipation rigorously reduces to a boundary-value problem. But what about a vacuum? In a true vacuum with boundaries of different temperature, it is not possible to define a temperature at any point within the cell. Should one look in one direction, one would sense black-body radiation of that boundary's temperature. From the same position, looking in the opposite direction one would sense a quite different temperature. Nevertheless, we shall suppose that a vacuum cell also obeys the Carnot equation.⁵ But, how may a vacuum dissipate energy? Clearly it can't, but the emissions occur from and to black-body surfaces with skin depths corresponding to radiation absorption coefficients and it is within these regions that dissipation takes place. Energy radiated from the warmer interface must cool it, and energy absorbed at the cooler interface will warm it, effecting a net transfer of heat between boundaries.

In a two-terminal thermal cell each boundary radiates energy absorbed by the other. Consider such a cell between $200K$ and $300K$ thermal reservoirs (Fig. 4). Given a cell with $1m^2$ area, the corresponding Stefan-Boltzmann fluxes are $459W$ and $91W$.

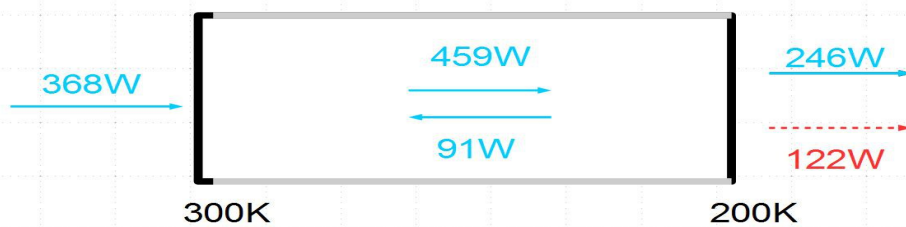


Figure 4: Two-terminal vacuum cell with thermostatted 'black-body' boundaries. Free energy fluxes in blue, dissipated energy fluxes in red.

Steady-state energy conservation requires a net flux of $368W$ throughout and the Carnot equation states that $1/3$ is dissipated. Note that this implies that dissipation depends not on the sum of fluxes absorbed at each interface, but on the net flux between interfaces.

In this cell, let us now insert a floating or unthermostatted black-body surface intercepting all flux flowing between boundaries.

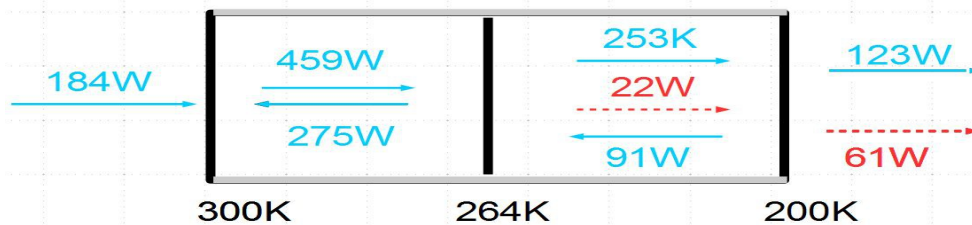


Figure 5: The vacuum cell of Fig. 4 with a 'black-body' baffle inserted at an arbitrary position.

This baffle will have assume a temperature of $264K$ no matter its position between cell boundaries.⁶ The Stefan-Boltzmann flux for this temperature is $275W$. The $275W$ radiated towards the cooler

⁵ Should this not be true, one may suspect the possibility of creating a perpetual motion device from a concatenation of material and vacuum cells – but this remains just a suspicion.

⁶ The general solution for the temperatures of a set of n such baffles requires that T^4 differences between baffles be equal and independent of their physical separations. Thus the central element, with n odd will always be $264K$

boundary includes $22W$ dissipated. For the more general case with n such baffles inserted, the net flux transiting the cell decreases as $(1+n)^{-1}$.

Suppose we now fill this vacuum cell with a thermally conducting fluid (Fig.6). We assume this fluid to be infrared inactive and transparent to radiation but to support an energy flux proportional to the local

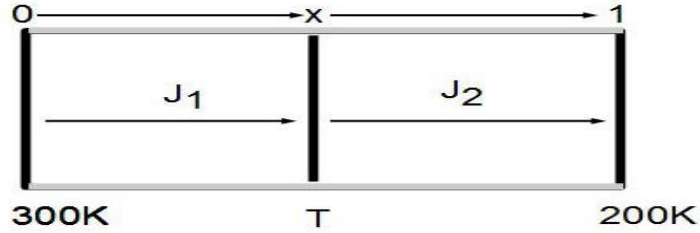


Figure 6: The cell of Fig. 5 now filled with a conducting fluid to establish an internal temperature gradient.

thermal gradient. The non-divergent net energy flux within each section is the sum of a Stefan-Boltzmann term and a gradient term, *i.e.*

$$J_1 = \sigma * (T_0^4 - T^4) + \kappa * \frac{T_0 - T}{x} \tag{4}$$

$$J_2 = \sigma * (T^4 - T_1^4) + \kappa * \frac{T - T_1}{1-x}$$

In a steady state, energy conservation at the internal boundary requires these be equal and, with given boundary temperatures, provides us a relationship between the baffle temperature and x . Setting $J_1=J_2$ gives an equation quadratic in x , permitting an analytic solution for x given T . The actual plot is nearly linear and best shown by its ratio to a linear variation (Fig. 7). It intersects the linear solution at 263.8976K, the temperature the baffle would have in vacuum Fig. 4).

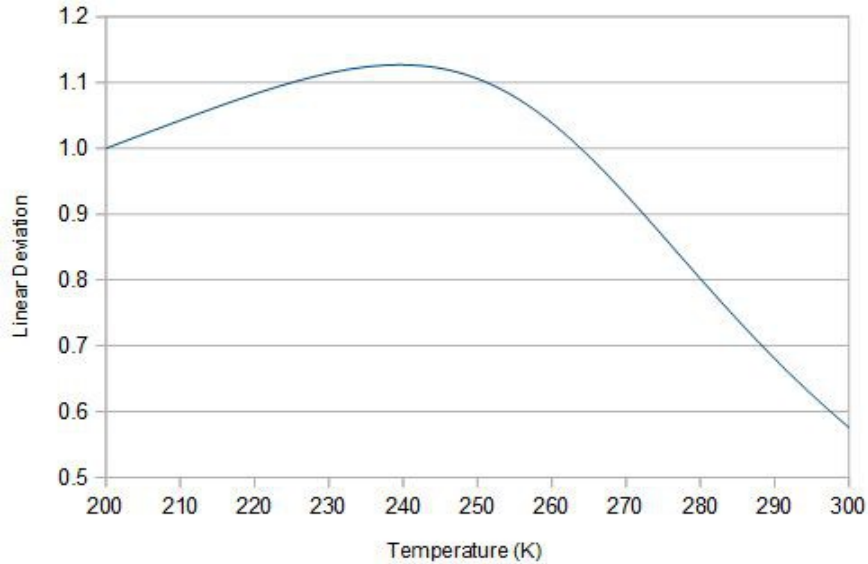


Figure 7: Solutions to Eqs. 4 for $\kappa=5$. Plotted is the ratio of the position of the baffle with a given temperature to the position for that temperature in a linear approximation.

As all energy input is considered to be free energy, dissipation is readily calculated as a function of x_0 and T from the Carnot equation (Eq. 2). Results plotted in Fig. 8 shown a minimum dissipation of $227.16W$ at $x=0.429459$ or $259.00K$.

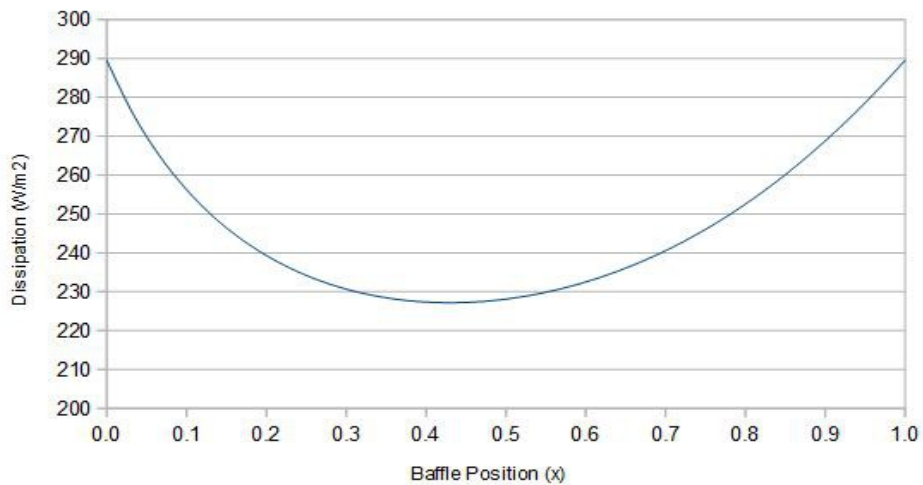


Figure 8: Variation of dissipation with position of baffle ($\kappa=5$).

Heuristically, the baffle's position may be viewed as an internal parameter which, if unconstrained, would drift towards this variational minimum. The identical boundary maxima of $289.53W$ correspond to Fig. 4, with a radiative dissipation contribution of $122.86W$. The conductive contribution is $\kappa (T_1 - T_2)^2 / T_1 = 166.67W$, and addition reproduces the plotted limits. At any intermediate baffle position, radiation contributes $61.43W$ (Fig. 4). Adding this value to the conductive contribution gives $228.10W$, $0.94W$ greater than the minimum possible.

This minimum can be qualitatively understood by a dissipation calculation for a very small conductivity (Fig. 9). Were the baffle at either extremity, one would have a system similar to Fig. 4, with $122W$ dissipation.. At any intermediate position, however (Fig. 5), the dissipation is reduced to $61W$, leading to a very broad minimum. For high conductivity, dissipation is dominated by conduction, with only a minor dependence on radiation and the baffle position.

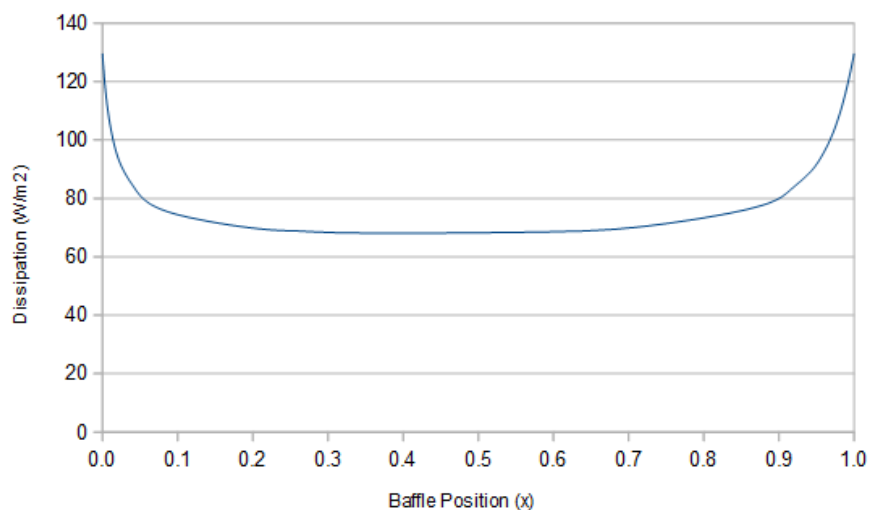


Figure 9: Variation of dissipation with baffle position ($\kappa=0.2$).

The Gray Gas Model

Aequationes loqui plus valet quam verba — Quondamus

The basic gray-gas equations describing radiative energy transfer through a medium absorbing and emitting thermal radiation are:⁷

$$\begin{aligned}\lambda(x) \frac{dJ_r^+}{dx} &= -J_r^+ + \sigma T(x)^4 \\ \lambda(x) \frac{dJ_r^-}{dx} &= J_r^- - \sigma T(x)^4\end{aligned}\tag{14}$$

where $\lambda(x)$ is a distance characterizing an absorption coefficient for all radiative energy. When $\lambda(x)$ is much longer than the physical size of a system, gradients are small and the bidirectional fluxes equal boundary-value emissions (*Fig. 4*). When much shorter, they equal the Stefan-Boltzmann terms. For real gases, absorption is frequency-dependent and the spectrum must be partitioned into individual regions of unique absorption. The gray-gas approximation is frequently employed as a generic device to explore a common behavior.

Assuming monotonic variations in a one-dimensional cell, we may scale the physical coordinate x to a dimensionless parameter $d\zeta = dx/\lambda(x)$ ranging from 0 to l which is related to the physical cell length, L , by

$$l = \int_0^l d\zeta = \int_0^L \frac{dx}{\lambda(x)}\tag{15}$$

With the substitutions

$$\begin{aligned}J_r^+(x) &\rightarrow J_r^+(\zeta) \\ J_r^-(x) &\rightarrow J_r^-(\zeta) \\ \sigma T(x)^4 &\rightarrow \varphi(\zeta)\end{aligned}\tag{16}$$

and introduction of the differential operator, $D = d/d\zeta$, *Eqs. 14* may be written as

$$\begin{aligned}[D + 1]J_r^+(\zeta) &= \varphi(\zeta) \\ [D - 1]J_r^-(\zeta) &= -\varphi(\zeta)\end{aligned}\tag{17}$$

The net radiative energy flux is $J_r(\zeta) = J_r^+(\zeta) - J_r^-(\zeta)$ and it then follows that

$$(D^2 - 1)J_r(\zeta) = 2\varphi'(\zeta)\tag{18}$$

We seek steady-state solutions for which $D J_r(\zeta) = 0$, in which case $J_r(\zeta) = -2\varphi'(\zeta)$, with $\varphi'(\zeta)$ a constant independent of ζ . Thus the function T^4 will vary linearly with ζ , and

$$T^4(\zeta) = T^4(0) + [T^4(l) - T^4(0)](\zeta/l)\tag{19}$$

A plot of T vs. ζ is non-linear, with a slope decreasing as the cooler boundary is approached (*Fig. 10, top curve*). It should be emphasized that ζ coordinates do not scale linearly with laboratory coordinates unless $\lambda(x)$ is independent of x . *Figure 10* also plots cases where $\lambda(x)$ increases exponentially with x as might be expected should density and absorption decrease with temperature.

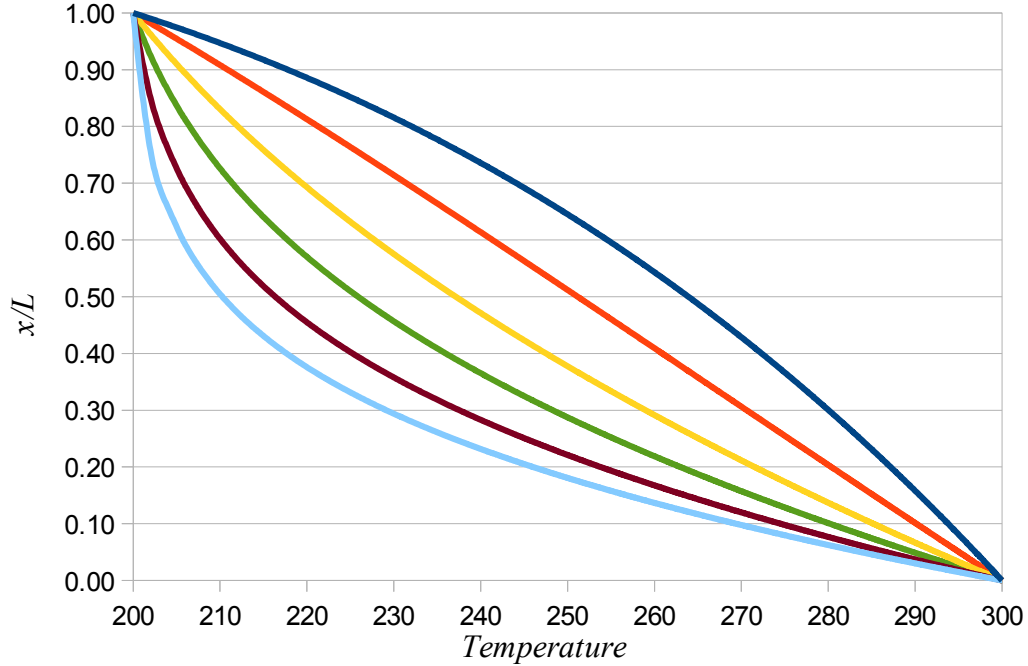


Fig 10: Plots of temperature vs. laboratory coordinates for $\lambda(x)$ increasing exponentially with x by factors of 1, 3, 10, 20, 100 and 300, top to bottom.

The steady-state flux, $-2\varphi'(\zeta)$, becomes

$$J_r(\zeta) = (2/l) \sigma [T^4(0) - T^4(l)] \quad (20)$$

with steady-state dissipation following from the Carnot Equation

$$W = J_r(0) \left[1 - \frac{T(l)}{T(0)} \right] \quad (21)$$

Note the correspondence of this solution with that for the vacuum cell depicted in *Fig. 5* containing n floating black-body baffles, $l/2 \Leftrightarrow n+1$.

Suppose, now, another energy flux process co-exists with this radiative flux which is determined by the gradient of another local function, *i.e.* $J_c(\zeta) = -\psi'(\zeta)$.⁸ Were this the only flux, a steady state would require that $\psi'(\zeta)$ be constant. But, it is now the total flux that defines the steady state,

$$D[J_r(\zeta) + J_c(\zeta)] = D J_{tot} = 0 \quad (22)$$

⁸ For descriptive convenience, we shall refer to processes contributing to J_c as convective and J_r as radiative, bearing in mind that true convection is a highly nonlinear function restricted to gradients exceeding the adiabatic threshold.

By inversion of Eq. 18, $J_r(\zeta) = -2[1-D^2]^{-1} \varphi'(\zeta)$ and the steady-state constraint may be written as

$$J_{tot} = -2[1-D^2]^{-1} \varphi'(\zeta) - \psi'(\zeta) = constant \quad (23)$$

Upon reversion,

$$[1-D^2]J_{tot} = -2\varphi'(\zeta) - \psi'(\zeta) + \psi'''(\zeta) \quad (24)$$

Operating now on each side with $[1+D^2]$ we find an expression for J_{tot} with a residual of order $D^4 J_{tot}$ for this presumably constant function.

$$J_{tot} = [1+D^2][-2\varphi'(\zeta) - \psi'(\zeta) + \psi'''(\zeta)] + \epsilon(D^4 J_{tot}) \quad (25)$$

Equation 25 is useful for analyzing flux profiles when a temperature profile is sought to fit parameters assigned $\varphi(\zeta)$ and $\psi(\zeta)$.⁹

Integration of Eq. 25, again assuming J_{tot} constant (and dropping $\psi''''(\zeta)$), provides an alternative method for evaluation,

$$\begin{aligned} J_{tot} &= -\frac{1}{l} \int_0^l d\zeta [2\varphi'(\zeta) + \psi'(\zeta) + 2\varphi'''(\zeta)] \\ &= -\frac{1}{l} [2\varphi(\zeta) + \psi(\zeta) + 2\varphi''(\zeta)]_0^l \end{aligned} \quad (26)$$

and J_{tot} reduces to a boundary value evaluation. In the absence of convection, the first term describes radiative flux, for $\varphi'''(\zeta)$ is then zero. In the absence of radiation, the second term describes convective flux. It is the last term which introduces a synergy of fluxes.

For purposes of discussion, let us assume an explicit function for J_c ,

$$J_c(x) = -\kappa(x) \frac{dT(x)}{dx} = -\frac{\kappa(\zeta)}{\lambda(\zeta)} \frac{dT(\zeta)}{d\zeta} = -\gamma(\zeta) \frac{dT(\zeta)}{d\zeta} = -\frac{d\psi(\zeta)}{d\zeta} \quad (27)$$

The local function, $\gamma(\zeta)$, is a positive ratio reflecting the relative strengths of convection and radiation. Should we assume $\gamma(\zeta)$ to be a known function, we can calculate fluxes for hypothetical thermal profiles and seek that profile best matching the condition that J_{tot} be constant. The function

$$T^n(\zeta) = T^n(0) + [T^n(l) - T^n(0)] (\zeta/l) \quad (28)$$

seems a natural choice as it is exact in the limits of pure convection ($n=1$) and radiation ($n=4$). Table 1 lists results for a constant $\gamma=7$, a value for which both fluxes are about equal. Perhaps surprisingly, results are essentially independent of the thermal profile.

⁹ If a function $F(i)$ has been tabulated at a sequence of equally spaced differential intervals, the function $[1+D^2]F(i)$ is obtained replacing $F(i)$ by $F(i-1)-F(i)+F(i+1)$. In practice, this embellishment becomes unimportant as one converges towards a steady-state solution for $DF \rightarrow 0$.

n	J_c	J_r	J_{rc}	J_{tot}
4.0	7.0000	7.3710	0.0000	14.3710
3.9	7.0000	7.3710	0.0000	14.3710
3.8	7.0000	7.3710	0.0000	14.3710
3.7	7.0000	7.3710	0.0000	14.3710
3.6	7.0000	7.3710	0.0000	14.3710
3.5	7.0000	7.3710	0.0000	14.3710
3.4	7.0000	7.3710	-0.0001	14.3709
3.3	7.0000	7.3710	-0.0001	14.3709
3.2	7.0000	7.3710	-0.0001	14.3709
3.1	7.0000	7.3710	-0.0001	14.3709
3.0	7.0000	7.3710	-0.0001	14.3709
2.9	7.0000	7.3710	-0.0001	14.3709
2.8	7.0000	7.3710	-0.0001	14.3709
2.7	7.0000	7.3710	-0.0002	14.3708
2.6	7.0000	7.3710	-0.0002	14.3708
2.5	7.0000	7.3710	-0.0002	14.3708
2.4	7.0000	7.3710	-0.0002	14.3708
2.3	7.0000	7.3710	-0.0002	14.3708
2.2	7.0000	7.3710	-0.0003	14.3707
2.1	7.0000	7.3710	-0.0003	14.3707
2.0	7.0000	7.3710	-0.0003	14.3707
1.9	7.0000	7.3710	-0.0003	14.3707
1.8	7.0000	7.3710	-0.0004	14.3706
1.7	7.0000	7.3710	-0.0004	14.3706
1.6	7.0000	7.3710	-0.0004	14.3706
1.5	7.0000	7.3710	-0.0005	14.3705
1.4	7.0000	7.3710	-0.0005	14.3705
1.3	7.0000	7.3710	-0.0005	14.3705
1.2	7.0000	7.3710	-0.0006	14.3704
1.1	7.0000	7.3710	-0.0006	14.3704
1.001	7.0000	7.3710	-0.0007	14.3703

Table 1: Gray-gas fluxes from Eq.26 and parameters $T(0)=300K$, $T(l)=200K$, $\gamma=7$, $l=100$ and $T^n(\zeta)=T^n(0)+[T^n(l)-T^n(0)](\zeta/l)$.

To find the profiles for J_r , J_c and J_{tot} , we have used Eq. 25 for point-by-point calculations with temperature profiles described by Eq. 28. Values for n were chosen to minimize *rms* deviations of J_{tot} using trapezoidal integration.¹⁰ Results are plotted in Fig. 11 and their associated parameters are listed in Table 2.

γ	n	$J_{tot}(rms)$	RMS Deviation	Eq. 26
0.7	3.723	8.0709	0.016%	8.0710
7.0	2.494	14.3709	0.257%	14.3708
70.0	1.273	77.3715	0.156%	77.3705

Table 2: Parameters for Fig. 11 plots.

¹⁰ This procedure assigns only half the weights to the two endpoints as does a summation average and differences are not trivial when only 100 points are used and endpoints lie farthest from mean values.

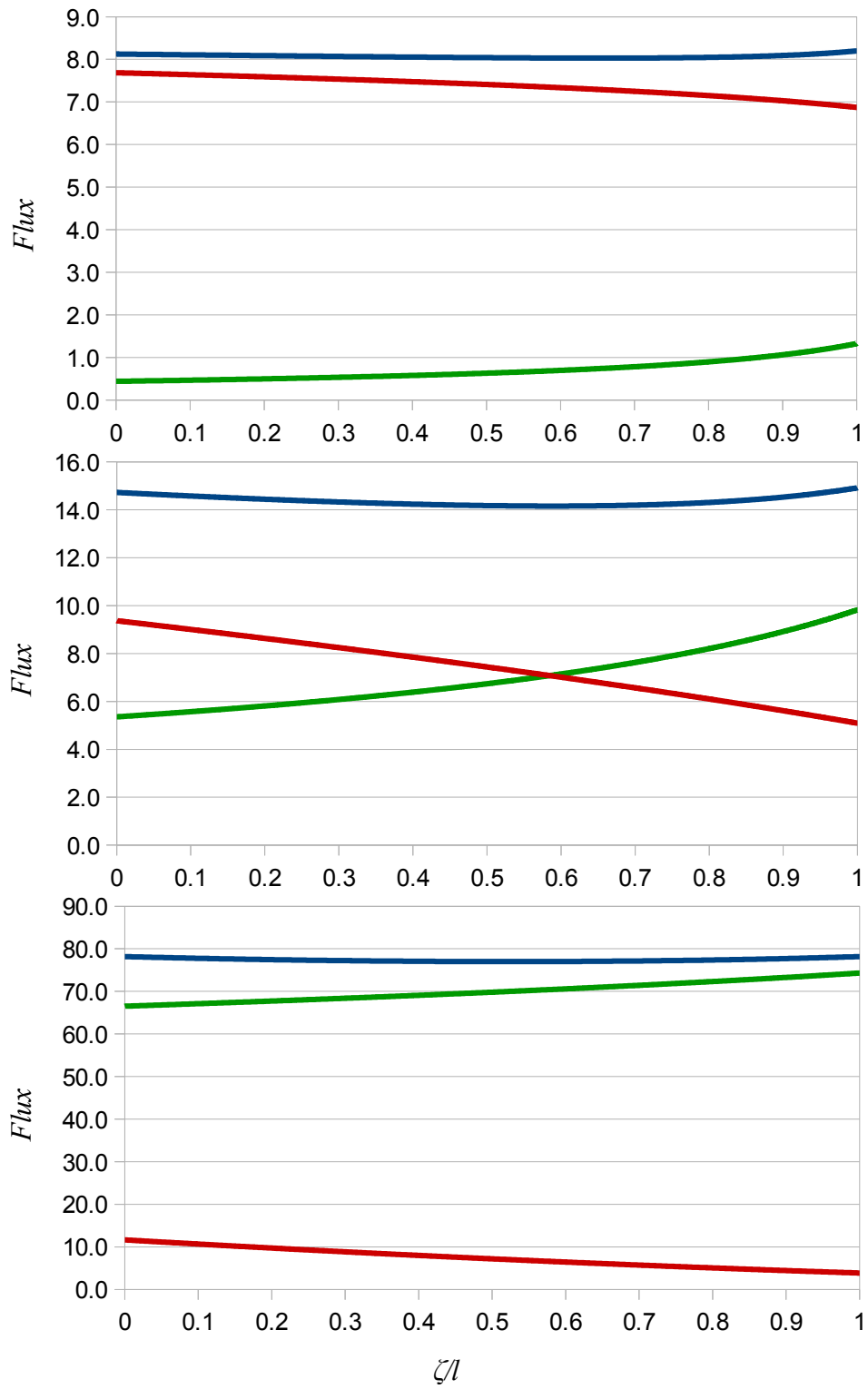


Fig 11a-c: From top to bottom, $\gamma = 0.7, 7.0$ and 70.0 . Red= J_{rad} , Green = J_c , Blue = J_{tot}

In all plots, as flux flows towards the cooler interface, a decreasing radiative flux is balanced by increasing convection. For $\gamma=0.7$, radiation dominates transport and n is close to 4. For $\gamma=70$, convection is the more important process and n is close to 1. Total flux values are virtually identical with those found using only boundary parameters (Eq.27). $D^4 J_{tot}$ values were of order 10^{-7} , supporting their omission in Eq. 25.¹¹

The simplicity of the profiles in Fig. 11, which are based on a single fitting parameter, n , suggests that a basic power series with multiple adjustable coefficients might provide more accurate results. The function ($\xi=\zeta/l$),

$$T(\xi) = T(0) + [T(l)-T(0)] \cdot [\xi + \xi(1-\xi)(a+b\xi+c\xi^2+d\xi^4)] \quad (29)$$

has four adjustable parameters and matches fixed boundary temperatures. Results fitting these coefficients to the case, $\gamma=7$ are listed in Table 3. The plots in Fig. 12 and 13 show, in comparison with Fig. 11b, more constant J_{tot} values expected for the steady-state solution.

J_{tot}	RMS%	a	b	c	d
14.37173	0.690%	-0.28600			
14.37065	0.005%	-0.24970	-0.09680		
14.37060	0.000%	-0.25350	-0.07460	-0.02476	
14.37059	0.000%	-0.25357	-0.07471	-0.02472	0.00031

Table 3: Polynomial coefficients minimizing rms variations of J_{tot} for $\gamma=7$.

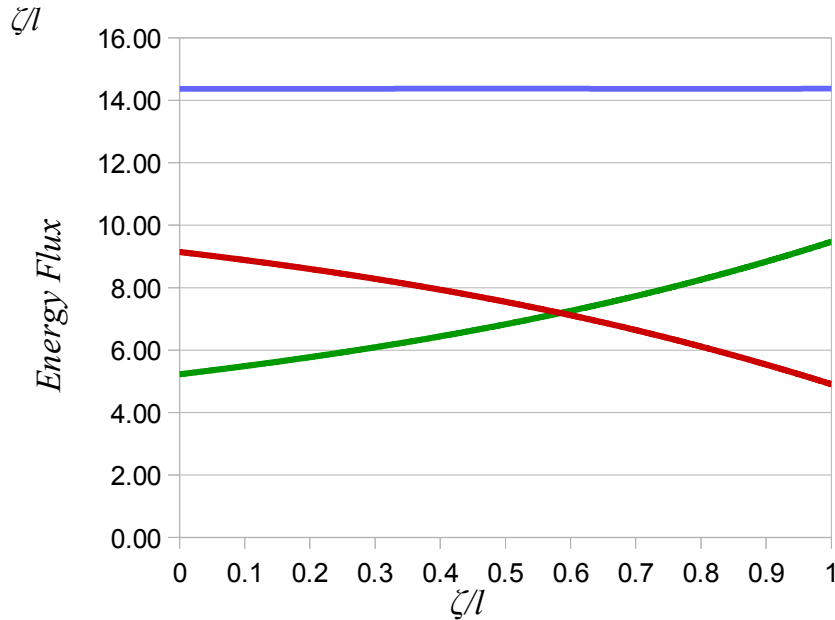


Fig 12: Flux components calculated using a polynomial thermal profile with $\gamma = 7.0$. Red= J_{rad} , Green = J_c , Blue = J_{tot}

11 The differential operator for D^4 is $6f(x) - 4[f(x+\Delta)+f(x-\Delta)] + [f(x+2\Delta)+f(x-2\Delta)]$

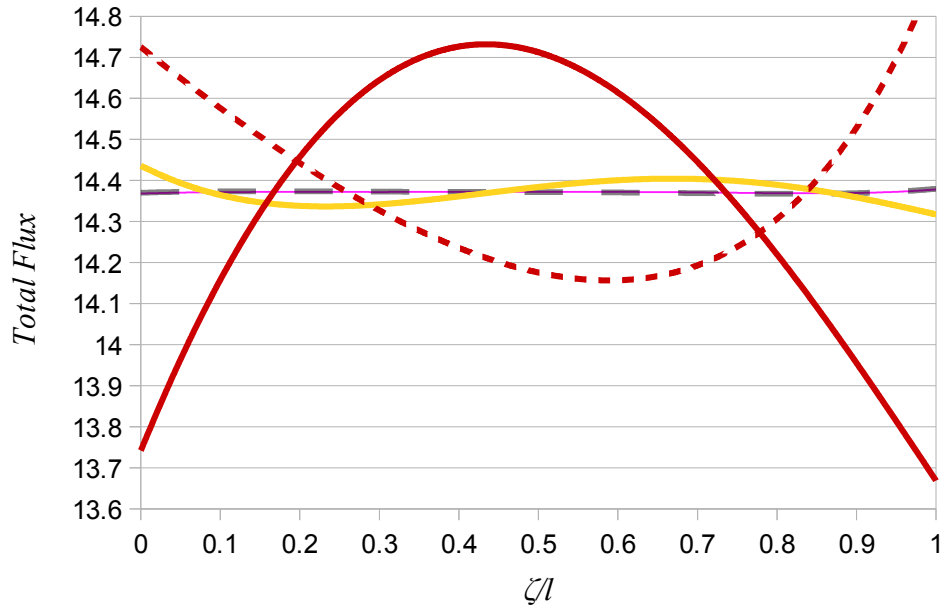


Fig 13: Variation of J_{tot} for various approximations, $\gamma = 7.0$: Power (n) – red dash; Polynomial parameters (1) red, (2) yellow, (3) gray dash, (4) fine magenta.

Perhaps the most striking aspect of these various solutions is their agreement to six significant figures, no matter the functional approximations made. In part this may be because the solutions must lie somewhere between extremes in Fig. 11 which themselves are rather featureless functions.

A formal solution to Eq. 18 could be expressed in terms of a characteristic solution embodying two constants of integration and a particular solution, *i.e.*

$$F(\zeta) = Ae^{-\zeta} + Be^{-(l-\zeta)} + \Phi(\zeta) \quad (30)$$

In our analysis these constants are implicit in the constraint that J_r is constant and the parameter, l (Eq. 15), which maps ζ to laboratory coordinates. In examples discussed we have chosen $l=100$, which sets the magnitude of radiation fluxes to order 10 W/m^2 . Should we choose $l=5$, the plots in Fig. 14 follow (*cf.* Fig 11). That these flux levels emulate tropospheric values suggests an 0.7% (*i.e.* $\exp(-5)$) probability of surface radiation escaping absorption and dissipation within the troposphere.

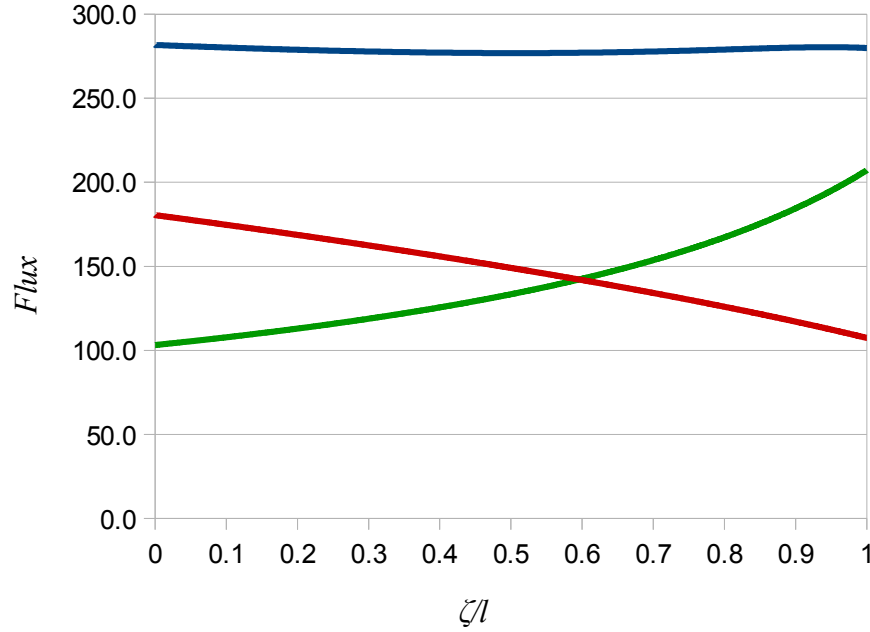


Fig 14; Parameters: $l=5$, $\gamma=7$, $n=2.72$. Red= J_{rad} , Green = J_c , Blue = J_{tot}

The intent of this rather extended discussion of the gray-gas equations was not to establish accurate solutions to hypothetical models but to explore the properties of these solutions when parallel transport processes coexist. Specifically, our interest has been in solutions to the two equations

$$(D^2 - 1)J_r(\zeta) = 2\varphi'(T(\zeta)) \quad (31)$$

$$J_c(\zeta) = -\psi'(T(\zeta))$$

when coupled by the constraint

$$D[J_r(\zeta) + J_c(\zeta)] = 0 \quad (32)$$

The equation for $J_r(\zeta)$ describes a flux which is the superposition of two fluxes traveling in opposing directions, *e.g.* radiation. That for $J_c(\zeta)$ describes a flux wholly defined by a local gradient, *e.g.* conduction or convection. It is this distinction that makes our problem nontrivial. The two *rhs* functions of temperature incorporate the physics specific to each flux.

Our solutions are for a one-dimensional cell of fixed length and given boundary temperatures. Any position within this cell can be identified by either its temperature, its laboratory coordinate, x , or its radiation coordinate, ζ . The units of the latter correspond to absorption coefficients. We have assumed these, $\lambda(\zeta)$, to be temperature independent. Thus, our results all show a steady decrease in radiative flux, compensated by increasing convection as energy flows towards the cooler interface. This is wholly a consequence of the T^4 dependence of Stefan-Boltzmann radiation and in direct contrast to behavior within the troposphere. There, the pressure decreases by an order of magnitude and the corresponding absorption distance might be expected to increase proportionately.

Epilogue

The purpose of computation is insight, not numbers – R. Hamming

In this note, we have attempted to examine the implications of several well-defined mathematical models to better understand the physics of energy transport in thermal fields. Among topics explored are distinctions between energy fluxes and free energy fluxes by both generic radiative and non-radiative mechanisms, the essential difference between these mechanisms being that radiative transport involves bi-directional fluxes whereas non-radiative fluxes are unidirectional. Attention has been restricted to one-dimensional models. A mechanism such as convection without net material transport, a purely rotational flux, is not easily described in one-dimension. At best, we can assume a model invoking a net convective flux, reserving for later discussion the reality that this flux is really the difference of two larger numbers. That this arcane matter strikes us as of uncommon interest is that it forms the core for understanding the influence of greenhouse gases on atmospheric temperatures. To place our analysis in perspective, we should briefly describe *Radiative-Convective Equilibrium* which lies at the heart of current climate science.

The juxtaposition of convection and equilibrium should properly provoke premonition of pending paradox. Anyone remotely familiar with thermodynamic fundamentals is aware that a thermal system in equilibrium is necessarily isothermal and lacking static fluxes. A non-isothermal system is ever endeavoring to relax towards isothermality and, to maintain a *steady state*, requires the constant expenditure of energy to counter relaxation. This work, dissipation in the thermodynamic lexicon, is the prime property of a steady state and is expressed by Carnot's equation. Unfortunately, the misuse of 'equilibrium' when 'steady state' is intended has led to perhaps unintended presumptions that other properties of equilibrium systems may be ascribed to the atmosphere.

Semantics aside, much of the early work attempting to describe temperatures and radiation within the troposphere traces back to Manabe and colleagues.^{12a-c} Their basic calculation was to take an isothermal profile as an initial value, calculate corresponding fluxes of radiant energy to determine local heating and cooling rates from flux divergences and then iteratively revise the profile until convergence was reached. Typically, up to 1000 iterations were involved.^{12b} This was identified as a state of *radiative equilibrium*. We presume this corresponds to finding that profile exhibiting a non-divergent radiation flux. Manabe and Strickler then extended this methodology to adjust for convection. As described in their own words,

“b. Thermal equilibrium with convective adjustment. The procedure of convective adjustment is to adjust the lapse rate to the critical lapse rate whenever the critical lapse rate is exceeded in the course of the numerical integration of the initial value problem. The observed tropospheric lapse rate of temperature is approximately 6.5 deg km⁻¹. The explanation for this fact is rather complicated. It is essentially the result of a balance

12 a) S. Manabe and F. Möller, Mon. Weather Rev. **89**, 503 (1961);
b) S. Manabe and R. F. Strickler, J. Atmos. Sci. **21**, 361 (1964);
c) S. Manabe and R.T. Wetherald, J. Atmos. Sci. **24**, 241 (1967).

between (a) the stabilizing effect of upward heat transport in moist and dry convection on both small and large scales and (b), the destabilizing effect of radiative transfer. Instead of exploring the problem in detail, we here accept this as an observed fact and regard it as a critical lapse rate for convection.”

The net result of this adjustment sets the thermal gradient within most of the troposphere to a prescribed value. What is most surprising, however, is that this adjustment remains today uncritically accepted as gospel. In 1978, a review on the subject refers to it as an empirical approach.¹³ As recently as 2015 one reads¹⁴

“Within the troposphere, the vertical mixing of sensible heat (where input of energy leads to an increase in temperature) and latent heat (where input of energy is used to induce a phase transition and thus there is no change in temperature) by large-scale motions and convection is quite rapid in comparison to the time scales associated with responses to radiative changes (e.g., see Ramanathan et al.). As a result dynamical processes largely govern the vertical distribution of the tropospheric temperature change, while the mass-weighted tropospheric temperature change is governed by the radiative forcing of the column”

which essentially asserts that convection (dynamics) determines gradients while radiation governs values. *Ergo*, gradients are set by convection, while radiation uniformly affects all temperatures within the troposphere.

The notion that constraint of a steady-state system may serve as a proxy for convection raises several interesting thermodynamic issues. Addition of a passive constraint, *i.e.* one that does not add or remove energy, can only reduce internal fluxes with given boundary parameters. Indeed, in their introduction, Manabe and Strickler assert “*It is expected that this process of convective adjustment will transfer heat energy from the earth's surface into the lower and upper troposphere and thereby permit more realistic temperatures to occur throughout the troposphere.*”^{12b} For calculations, they adopt the adiabatic lapse rate, g/C_B , as the critical thermal gradient. When radiative fluxes are recalculated with this *active* constraint, they no longer converge to a non-divergent stream, typically doubling in strength on transiting the troposphere (*MODTRAN* calculations). It is an *a priori* presumption that this divergence should define the convective flux. In principle, having specified the thermal profile, the function $\varphi(T(\zeta))$ is known and $J_r(\zeta)$ may be calculated (*Eqs. 31*). $J_c(\zeta)$ follows from *Eq. 32* and $\psi(T(\zeta))$ then deduced. To my knowledge this has yet to be done to find convective functions compatible with the assumed constraint.

But, more importantly, this critical thermal gradient has always been assumed to be invariant to greenhouse gas perturbation and thus not a variational parameter. No justification has been offered, except the tangential assertion of *convective equilibrium*. That a gradient may be calculated with equilibrium parameters is not proof this gradient characterizes an equilibrium system – a fundamental thermodynamic paradox. Should we dope a copper wire with a trace of antimony we expect an increased resistance due to reduced electron mean free paths and, under constant current conditions, an increase in internal potential gradients. By analogy, there should be a thermal gradient increase on tropospheric doping by trace amounts of greenhouse gases due to shortened photon mean free paths.

13 V. Ramanathan and J.A. Coakley Jr., *Rev. Geophys. And Space Phys.* **16**, 465 (1978).

14 “Physical Chemistry of Climate Metrics”, A.R. Ravishankara, Y. Rudich and D.J. Wuebbles, *Chem Rev.* **115**, 3682 (2015).

On a historic note, the term *convective equilibrium* can be traced back to Lord Kelvin (W. Thomson). In his classic treatise, J.C. Maxwell writes¹⁵

“This result is important in the theory of thermodynamics, for it proves that gravity has no influence in altering the conditions of thermal equilibrium in any substance, whether gaseous or not. For if two vertical columns of different substances stand on the same perfectly conducting horizontal plate, the temperature of the bottom of each column will be the same; and if each column is in thermal equilibrium of itself, the temperatures at all equal heights must be the same. In fact, if the temperatures of the tops of the two columns were different, we might drive an engine with this difference of temperature, and the refuse heat would pass down the colder column, through the conducting plate, and up the warmer column; and this would go on till all the heat was converted into work, contrary to the second law of thermodynamics.

“But we know that if one of the columns is gaseous, its temperature is uniform. Hence that of the other must be uniform, whatever its material.

“This result is by no means applicable to the case of our atmosphere. Setting aside the enormous direct effect of the sun's radiation in disturbing thermal equilibrium, the effect of winds in carrying large masses of air from one height to another tends to produce a distribution of temperature of a quite different kind, the temperature at any height being such that a mass of air, brought from one height to another without gaining or losing heat, would always find itself at the temperature of the surrounding air. In this condition of what Sir William Thomson has called Convective equilibrium of heat, it is not the temperature which is constant, but the quantity ϕ , which determines the adiabatic curves.”

Even in Maxwell's time, it is clear that, however one might wish to define convective equilibrium, it can not be the thermodynamic equilibrium of maximum entropy, but rather descriptive of a non-equilibrium or dissipative process. No present theory exists to predict the magnitude of convective flux at the critical lapse rate or its variation with lapse rate at this point.

The physical connection between convection and thermal gradients has been properly derived by Landau and Lifshitz.¹⁶

“§4. The condition that convection is absent

A fluid can be in mechanical equilibrium (i.e. exhibit no macroscopic motion) without being in thermal equilibrium. Equation (3.1), the condition for mechanical equilibrium, can be satisfied even if the temperature is not constant throughout the fluid. However, the question then arises of the stability of such an equilibrium. It is found that the equilibrium is stable only when a certain condition is fulfilled. Otherwise, the equilibrium is unstable, and this leads to the appearance in the fluid of currents which tend to mix the fluid in such a way as to equalise the temperature. This motion is called convection. Thus the condition for a mechanical equilibrium to be stable is the condition that convection is absent. It can be derived as follows.”

They go on to show that for a perfect gas this condition is $dT/dz > -g/c_p$, i.e. the lapse rate magnitude must be less than adiabatic to forestall convection. This gradient defines a condition for a convective breakdown of mechanical equilibrium. That atmospheric gradients fall near this limit, implies a flux of strong lapse-rate dependence with small gradient changes leading to large flux changes, buffering the gradient against large perturbation. The convective flux increase required to compensate for a radiative flux reduction by greenhouse gases could be accomplished with but a minor gradient tweak. In reality, both radiation and convection fluxes are of comparable magnitudes and are expected to jointly provide requisite compensation.

15 *Theory of Heat*, J. Clerk Maxwell, Longmans, Green and Co., 1872, p.330.

16 *Fluid Dynamics*, L.D. Landau and E.M. Lifshitz, Addison-Wesley (1959)

Increased absorption of radiation due to increasing concentrations of greenhouse gases will move the atmosphere yet further from isothermal thermodynamic equilibrium and entail increased rates for both free energy dissipation and entropy formation. Following Onsager (*Eq. 1*), the latter rate is

$$\frac{ds(r)}{dt} = \vec{J}_U(r) \cdot \nabla \left(\frac{1}{T(r)} \right) \quad (33)$$

With $J_U(r)$ fixed by solar energy influx, *thermal gradients must necessarily increase with greenhouse gas concentration.*

We should also note that the Stefan-Boltzmann constant contains an embedded kT factor to describe the populations of excited states undergoing spontaneous radiative decay. While one might argue a theory of local thermodynamic equilibrium as justification, the differences illustrated by *Figs. 2 and 3* belie this as a general concept. In principle, the relative populations of any two levels of known energy and degeneracy for a molecule can define a thermometer *via* this constant but it is only for an isothermal system that we may expect all such thermometers to agree.

Apart from the choice of a 200K to 300K temperature range, we have deliberately chosen not to attempt to emulate atmospheric behaviors by opening Pandora's box for adjustments. In the gray-gas case, we have γ , κ , λ and l at our disposal. *Fig. 6* tells us that l is useful for adjusting flux amplitudes. *Fig. 3* tells us that we can adjust the balance between convection and radiation with γ . Making γ position dependent would allow us to describe a system in which radiative fluxes increase at lower temperatures instead of decreasing as in those cases discussed herein.

With four parameters I can fit an elephant, and with five I can make him wiggle his trunk. – J. von Neumann (attr.)