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Supplementary Information

TEACHING THERMODYNAMICS: THE CHALLENGE

Peter Atkins

THE THERMODYNAMICS OF THE ELECTROMAGNETIC FIELD

The Planck distribution is

$$\rho(\nu,T)=\frac{8\pi^5 h\nu^3}{c^3}\frac{1}{\mathrm{e}^{\frac{h\nu}{kT}}-1}$$

The energy density (the total energy of a region divided by the volume of the region) is therefore

$$\mathcal{E}(T)=\int_0^\infty \rho(\nu,T)\mathrm{d}\nu=aT^4 \quad \text{with } a=\frac{8\pi^5k^4}{15(hc)^3}$$

The constant a is related to the Stefan–Boltzmann constant σ by $a = 4\sigma = 7.573\times10^{-16}\ \mathrm{J\,K^{-4}\,m^{-3}}$.

The internal energy of a region of volume V is

$$U(T)=\mathcal{E}(T)V=aT^4V$$

It follows from $(\partial U/\partial S)_V = T$ that $\mathrm{d}S = \mathrm{d}U/T$, with $\mathrm{d}U = 4aT^3V$; therefore $\mathrm{d}S = 4aT^2V\mathrm{d}T$ and with $S(0) = 0$,

$$S(T)=S(0)+\int_0^T 4aT^2V\mathrm{d}T=\frac{4}{3}aT^3V$$

The Helmholtz energy of the region is therefore

$$A(T)=U(T)-TS(T)=-\frac{1}{3}aT^4V$$

and the radiation pressure is

$$p(T)=-\left(\frac{\partial A(T)}{\partial V}\right)_T=\frac{1}{3}aT^4$$

Note that the equation of state of the 'electromagnetic fluid' is p = const. × T^4, independent of V. It now follows that the enthalpy is

$$H(T)=U(T)+p(T)V=\frac{4}{3}aT^4V=4p(T)V$$

and the Gibbs energy is

$$G(T)=A(T)+p(T)V=0$$

We are now ready to calculate the solar constant, which is the energy flux at a distance equal to the orbital radius of the Earth from the Sun. Given that the energy density at the radius of the photosphere of the Sun is $\mathcal{E}(T)$, with T the temperature of the photosphere, the outward energy flux at the radius of the photosphere, R_{Sun}, is $(1/2)\mathcal{E}(T)\langle|v_\mathrm{r}|\rangle$, where v_r is the radial component of the velocity of light allowing for photons to move in all directions, not just on an outward radial trajectory. The factor of ½ is present because half the photons are travelling outwards and half are travelling inwards, and only the former contribute to the outward flux. The mean speed of photons (the components of the radiation) relative to the radial direction is

$$\langle|v_\mathrm{r}|\rangle = \int_0^\pi c\cos\theta\sin\theta\,\mathrm{d}\theta \Big/ \int_0^\pi \sin\theta\,\mathrm{d}\theta = \frac{1}{2}c$$

It follows that the outward energy flux at the radius of the photosphere is

$$J(T_\mathrm{Sun}, R_\mathrm{Sun}) = \frac{1}{4}\mathcal{E}(T_\mathrm{Sun})c$$

The energy flux is diminished in proportion to $1/R^2$, where R is the distance from the Sun, so at the mean orbit of the Earth

$$J(T_\mathrm{Sun}, R_\mathrm{orb}) = \frac{1}{4}\mathcal{E}(T_\mathrm{Sun})c\left(\frac{R_\mathrm{Sun}}{R_\mathrm{orb}}\right)^2$$

A similar calculation for the entropy flux at the distance of the Earth from the Sun gives

$$J'(T_\mathrm{Sun}, R_\mathrm{orb}) = \frac{4}{3}\frac{\mathcal{E}(T_\mathrm{Sun})}{T_\mathrm{Sun}}c\left(\frac{R_\mathrm{Sun}}{R_\mathrm{orb}}\right)^2$$

This inward entropy flux should be compared with the generation of entropy when the inward energy flux is dissipated at the mean temperature of the Earth:

$$\frac{\mathrm{d}S_\mathrm{diss}}{\mathrm{d}t} = \frac{J(T_\mathrm{Sun}, R_\mathrm{orb})}{T_\mathrm{Earth}}$$

With $R_\mathrm{Sun} = 6.955 \times 10^8$ m, $R_\mathrm{orb} = 1.5 \times 10^{11}$ m, $T_\mathrm{Sun} = 5800$ K, $T_\mathrm{Earth} = 288$ K:

Energy density at photosphere: $\mathcal{E}(5800\ \mathrm{K}) = 0.857$ J m^{-3}
Entropy density at photosphere: $S(5800\ \mathrm{K})/V = 1.97 \times 10^{-4}$ J K^{-1} m^{-3}
Radiation pressure at photosphere: $p(5800\ \mathrm{K}) = 0.286$ Pa
Energy flux on the Earth (solar constant): $J(5800\ \mathrm{K}, R_\mathrm{orb}) = 1.3$ kW m^{-2}
Entropy flux on the Earth: $J'(5800\ \mathrm{K}, R_\mathrm{orb}) = 0.30$ J K^{-1} m^{-2} s^{-1}