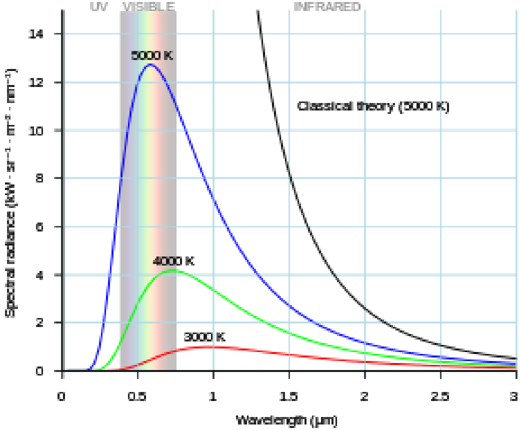
PREVIOUSLY ON *...Thermodynamics*

- Paramagnetic Cooling
- Entropy and degrees of freedom
- Many types of entropy

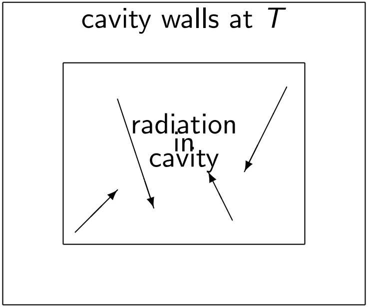


Ultraviolet Catastrophe

Allowing equipartition of energy in all wavelentghs requires infinite energy.

Thermal radiation as a thermodynamic system

System: radiation inside a cavity,
Surroundings :
Cavity walls = heat bath temperature T.

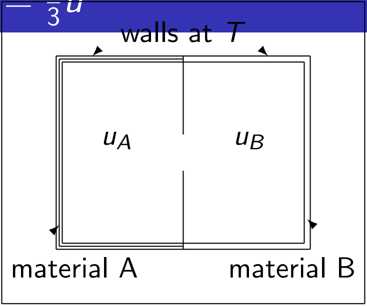


State Variables for radiation
Fixed T, $V \rightarrow U(T, V)$

Equation of state
(handwavingly treat photons using kinetic theory,
or in relativity, momentum in 3 dimensions
or properly in Electromagnetism):

$$\boxed{P = \frac{1}{3}u}$$

Thermodynamic Equilibrium with $P = \frac{1}{3}u$



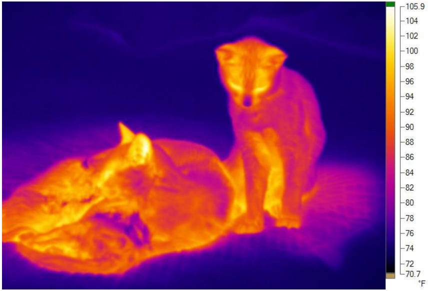
- Regions A and B, same T.
- Equilibrium: $P_A = P_B \implies u_A = u_B$
- Heat flows A to B. if $u_A > u_B$:
- Clausius violation unless $u(T, v) = u(T)$

Now consider a different system for *each* wavelength.

- Same argument: Heat flows between different λ systems until... ...at equilibrium, all T_λ are the same.
- $u_\lambda = u_\lambda(\lambda, T)$. (n.b. λ not a state variable)

$u_\lambda(T)$ is a thermodynamic function of T only, form valid for all λ

Peak moves to shorter wavelength with temperature



Cats at room temperature (IR).

"Red hot" iron (visible)

What is the total energy of blackbody radiation?

Consider all wavelengths separately

$$u = \int_0^\infty u_\lambda(\lambda, T) d\lambda$$

("area under the curve") is observed to be very strongly **temperature**-dependent, but cannot blow up for high or low λ

From the central equation of thermodynamics, + a Maxwell relation.

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

Stefan's Law is Thermodynamics

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

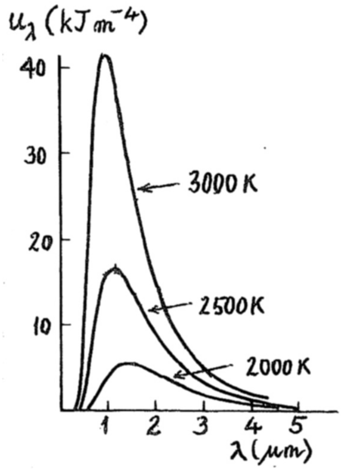
$P = \frac{1}{3}u$, $U = uV$ and $u = u(T)$

$$u = \frac{1}{3}T\frac{du}{dT} - \frac{1}{3}u \implies 4\frac{dT}{T} = \frac{du}{u}$$

Integrate and take logs

$$u(T) = \left(\frac{4\sigma}{c}\right)T^4$$

Flux $= u.(c/4) = \sigma T^4$
Introducing Stefan's constant σ .



$u(T) = \left(\frac{4\sigma}{c}\right) T^4 \implies$ Other thermodynamic quantities

Heat capacity.

$$C_v = \left(\frac{\partial uV}{\partial T}\right)_V = 4\sigma_o VT^3$$

with $\sigma_o = 4\sigma/c$,
Entropy

$$S = \int \frac{C_v dT}{T} = \frac{4}{3}\sigma_o VT^3$$

Enthalpy

$$H = U + PV = \frac{4}{3}\sigma_o VT^4 = TS$$

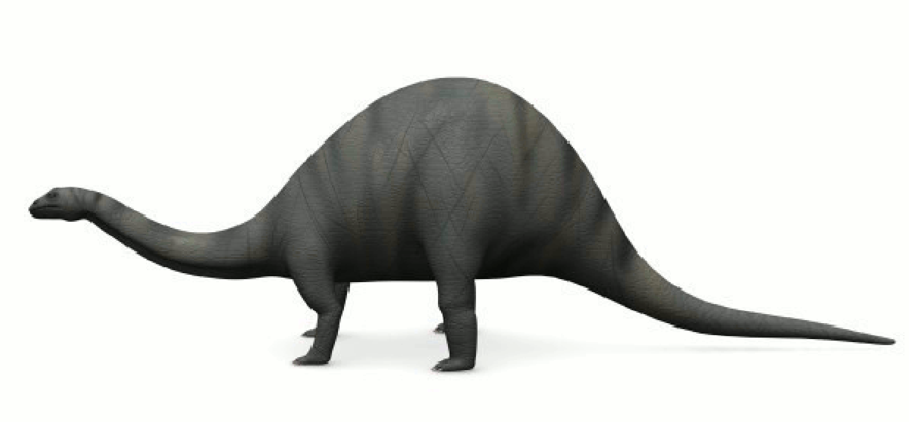
And finally

Gibbs Free Energy,

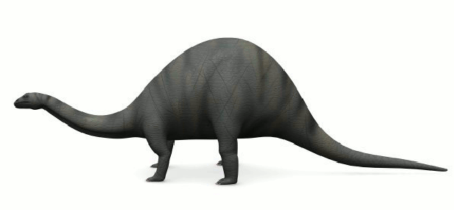
$$G = uV - TS + PV = \sigma_o VT^4 - \frac{4}{3}\sigma_o VT^4 + \frac{1}{3}\sigma_o VT^4 = 0$$

Photons have zero Gibbs Free energy.

What is the function?



Brontosaurus



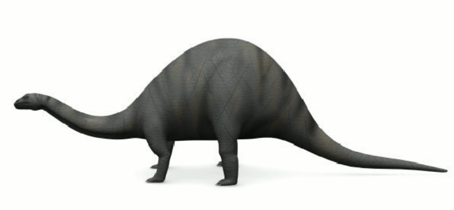
157-145,000,000 B.P.
1879-1903
2015-

Anne Elk's Theory on Brontosauruses

All brontosauruses are thin at one end; much, much thicker in the middle and then thin again at the far end.

Easily measured bits of brontosaurus:

Peak, total energy, and fit the head and tail using power laws.



- Total Energy/Power (Stefan)

$$u = \int_0^\infty u_\lambda(\lambda, T) d\lambda$$

- At long wavelength, (Rayleigh) $u_\lambda \propto \lambda^{-4} T$.
- At short wavelength (Wein)

$$u_\lambda(\lambda, T) \propto \lambda^{-5} e^{-const./\lambda T};$$

- The peak intensity $\lambda_{peak} = 2.898 \times 10^{-3}/T$ m

Closing in on the Planck distribution

Integrating the Black Body equation of state gives Stefan Law's

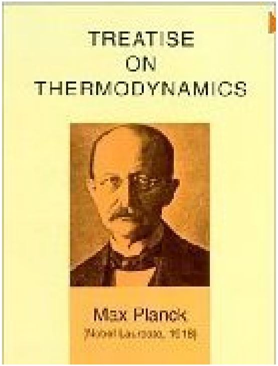
$$u(T) = \int_0^\infty u_\lambda(\lambda, T) d\lambda = \left(\frac{4\sigma}{c}\right) T^4$$

and requires for $u_\lambda(\lambda, T)$

- A 5^{th} power in λ for long wavelengths.
- A function which doesn't blow up at high ν (short wavelength)
- Gives the same $T = (\partial U_\lambda / \partial S_\lambda)_V$ for all λ.

... but what is the exact form of $u_\lambda(\lambda, T)$

How Planck discovered Quantum Theory



I had no alternative but to tackle the problem again ... from the side of thermodynamics. In fact, my previous studies of the Second Law of Thermodynamics came to stand me in good stead now, for at the very outset I hit upon the idea of correlating not the temperature of the oscillator but its entropy with the energy... While a host of outstanding physicists worked on the problem ... every one of them directed his efforts solely towards exhibiting the dependence of the intensity of radiation on the temperature. On the other hand, **I suspected that the fundamental connection lies in the dependence of entropy with the energy** *... Nobody paid any attention to the method which I adopted and I could work out by calculations completely at my leisure, with absolute thoroughness, without fear of interference or competition.*

Two leaps of intuition

Planck now considered how energy and entropy were related, $\left(\frac{\partial^2 s}{\partial u^2}\right)_V$ from the central equation ... $\left(\frac{\partial s}{\partial u}\right)_V = 1/T$.

$$\text{Rayleigh limit}: \left(\frac{\partial(1/T)}{\partial u}\right)_V \propto -1/u^2; \quad \text{Wein limit}: \left(\frac{\partial(1/T)}{\partial u}\right)_V \propto -1/u$$

The simplest way to bodge these together is

$$\left(\frac{\partial(1/T)}{\partial u}\right)_V = \left(\frac{\partial^2 s}{\partial u^2}\right)_V \propto \frac{c_1}{u(u+c_2)}$$

(n.b. all unknown constants are different) which after integrating wrt u

$$\frac{1}{T} = \int \frac{c_1}{u(u+c_2)} du = \frac{c_1}{c_2} \ln \frac{u}{u+c_2}$$

Rearranging, and reintroducing λs.

$$u_\lambda(\lambda, T) \propto \lambda^{-5} \left(\frac{1}{e^{const./\lambda T} - 1} \right)$$

Which fits the data perfectly - but what could it mean?

It looks like a geometric series and Ludwig

$$u_\lambda(\lambda, T) \propto \frac{1}{1 - e^{-const./\lambda T}}$$

Would look like

$$\sum_{n=0}^{\infty} r^n = \frac{1}{1-n}$$

If

$$u_\lambda(\lambda, T) \propto \sum_{n=0}^{\infty} e^{-nhc/\lambda k_B T}$$

Which is Boltzmann's distribution, if $E = nch/\lambda$

And gives for Stefan's Constant $\sigma = \frac{2\pi^5 k_B^4}{15h^3c^2}$

(we called the const. hc/k_B)

The reluctant Quantum Mechanic

I was desperate. I was compelled to consider statistical version of the second law $S = k.\log W$ that I rejected and hated the most...

"If E is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways."
i.e. Boltzmann's entropy would be infinite.
We consider, however - this is the most essential point of the whole calculation - E to be composed of a well-defined number of equal parts."
i.e. make energy countable, to make Boltzmann's entropy finite.

"Much though I hate thee, Let me count the ways."

Inventing Quantum Mechanics

To make this consistent with the Austro-Scottish statistical theory of entropy-as-counting, Planck had to assume that energy was quantised in lumps $nh\nu$ (or nhc/λ).

$$u_\lambda(\lambda, T) = \propto \lambda^{-5} \left(\frac{1}{e^{hc/\lambda k_B T} - 1} \right)$$

Planck later wrote in 1934: *My maxim is always this: consider every step carefully in advance, but then, if you believe you can take responsibility for it, let nothing stop you.*