<u>Today</u>

- I. Last Time
- II. Historical Interlude
- III. Constant Temperature Reservoirs and Equilibrium at Constant Temperature
- IV. Setting Up the Computation of the Black Body Spectrum
 - I. We studied gas of photons, reviewed spherical coordinates, and were able compute

$$P = \frac{1}{3}\frac{U}{V} = \frac{1}{3}u.$$

We also found a relationship between energy density and temperature:

$$u = AT^4$$
.

II. At the dawn of the 20th century researchers were deeply intrigued by this "black body" radiation:

$$u(T) = \int u(T,\lambda)d\lambda = AT^4 \quad \text{``Stefan-Boltzmann Law''} (1879, 1889)$$

This "spectral energy density" depends on wavelength and temperature in a very particular way, that is, through the product λT , at least after you factor out a term:

 $u(T, \lambda) = \frac{1}{\lambda^5} \phi(\lambda T)$. (Note: I goofed the factor in class. Sorry!) They had a nice concrete way of thinking about this: how does the maximum of the spectral energy density vary with temperature? The max wavelength moves linearly with temperature, "Wien displacement law". At the turn of 1900 no one knew the functional form of $u(T, \lambda)$ or equivalently of $\phi(\lambda T)$. Lots of people had thought about it and good suggestions for ... II. Lots of people had thought about it and good suggestions for the long wavelength limit had been made (Rayleigh-Jeans). In 1900 Planck guesses the right functional form:

$$u(T,\lambda) = \frac{1}{\lambda^5} \frac{A}{e^{\frac{b}{\lambda T}} - 1}$$



Planck writes a remarkable paper that introduces a new constant with units of position times momentum, h, and this eventually leads to the introduction of quantum mechanics. This paper derives the functional form for the black body "energy spectral density" above.

II. A more careful plot of the black body spectrum and its dependence on Temperature.



III. Equilibrium at a constant temperature. You can think thermodynamics as a bridge from the microscopic to the macroscopic. In particular

U can be seen as the total energy of the micro constituents
T average kinetic energy of micro constituents
P average momentum transfer from the micro constituents
S a count of all microstates consistent with the macroscopic configuration (up to this point usually characterized by U).

We say that our system is in contact with a "Temperature reservoir" when it exchange energy with a big "reservoir system that is at a fixed temperature *T*. Our idealization is that the reservoir is so big that it doesn't change temperature when it exchanges energy.

III. Equilibrium is characterized by the maximum entropy of the reservoir plus box system.

According to Boltzmann: $S = k \ln \Omega$, turning this around we can solve for the multiplicity $\Omega = e^{S/k}$.

Boltzmann's insight was that every state that is allowed is equally probable. This means that we can study

$$\frac{P(E_1)}{P(E_2)} = \frac{\Omega(E_1)}{\Omega(E_2)} = \frac{e^{S_1/k}}{e^{S_2/k}} = e^{(S_1 - S_2)/k} = e^{\frac{\Delta S}{k}}.$$

Recall our relationship for thermodynamics

$$dS = \frac{1}{T}dU + \frac{P}{T}dV,$$

For small changes in volume dV = 0



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Recall our relationship for thermodynamics

$$dS = \frac{1}{T}dU + \frac{P}{T}dV,$$

For small changes in volume dV = 0, and we have

$$\Delta S_R = \frac{\Delta U_R}{T} = \frac{U_{R1} - U_{R2}}{T}$$

We also have conservation of energy, $U_{R1} + E_1 = U_{R2} + E_2$, so $U_{R1} - U_{R2} = -(E_1 - E_2)$



III. Plugging in our result from conservation of energy we have:

$$\frac{P(E_1)}{P(E_2)} = \frac{\Omega(E_1)}{\Omega(E_2)} = \frac{e^{S_1/k}}{e^{S_2/k}} = e^{(S_1 - S_2)/k} = e^{\frac{\Delta S}{k}} = e^{-\frac{(E_1 - E_2)}{kT}} = \frac{e^{-\frac{E_1}{kT}}}{e^{-\frac{E_2}{kT}}}.$$

We can interpret this result as saying that the relative probability of states at different energies is exponentially related to their energy. Specifically,

$$P(E_1) = \frac{e^{-\frac{E_1}{kT}}}{Z},$$

Where *Z* is unknown constant that normalizes the probability.