12.815 Atmospheric Radiation
Fall 2008

Thermodynamic concepts of radiation

(a) Black-body radiation – classical theory predicted (wrongly) increasing emission with increasing frequency (v) from an amorphous black surface. Quantum theory introduced by Planck agreed with observations. The blackbody radiation is defined by the Planck function.

$$B_v(T) = \frac{2hv^3}{c^2} \frac{1}{e^{hv/KT} - 1} \left(\frac{\left(\frac{Joule}{erg} \right)}{\left(\frac{cm^2}{m^2} \right) sec.\, freq.\, ster.} \right)$$

$$B_\lambda(T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda KT} - 1} = \left(\frac{v^2}{c} \text{ or } \frac{v}{\lambda} \right) B_v$$
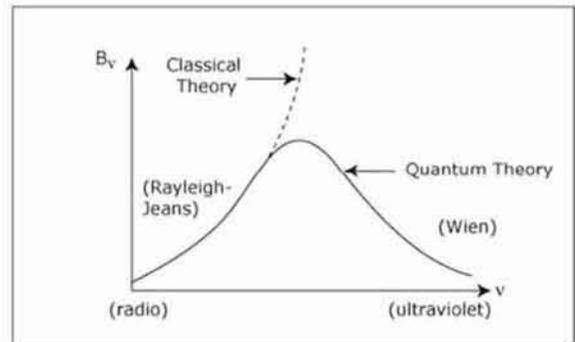
which agrees with observation and provided the first evidence for the quantum theory (h = Planck constant; K = Boltzmann constant).

Asymptotes: $\lambda \to 0$, $B_\lambda \to \frac{2hc^2}{\lambda^5} e^{-hc/\lambda KT}$; Wien wing (UV)

$\lambda \to \infty$, $B_\lambda \to \frac{2KTc}{\lambda^4}$; Rayleigh-Jeans wing (radio)

Stefan's Law:
  Kondratyev:

$$\int_0^\infty B_\lambda \, d\lambda = \frac{2K^4 T^4}{c^2 h^3} \overbrace{\int_0^\infty \frac{x^3 \, dx}{e^x - 1}}^{\pi^4/15} \qquad \left(x = \frac{hc}{\lambda KT} \right)$$

$$= \underbrace{\left[\frac{2\pi^5 K^4}{15 c^2 h^3} \right]}_{\text{Stefan's constant } (\sigma)} \frac{T^4}{\pi} \qquad \left(\frac{erg}{cm^2 . sec . steradian} \right)$$

$$= \frac{\sigma T^4}{\pi}$$

<u>Wien law:</u>

(defines the maximum in B)

$$\underbrace{\frac{dB_\nu(T)}{d\nu} = 0,}$$

$$\frac{cT}{\nu} = 0.51 \ (cm.\ °K)$$

(peak in flux per unit frequency)

$$\underbrace{\frac{dB_\lambda(T)}{d\lambda} = 0}$$

$$\lambda T = 0.29 \ (cm.\ °K)$$

(peak in flux per unit wavelength)

(b) <u>ideal black body</u>: one which is in equilibrium with the Planck distribution. It absorbs <u>all</u> the radiation incident upon it and emits the Planck distribution for its temperature.

<u>Practical Examples</u>:

(i) <u>a hole in a blackened sphere</u> (radiation entering the hole is totally absorbed and the hole radiates the Planck distribution).

(ii) <u>an infinite crystal</u> (oscillator energies are very closely spaced and possess a Boltzmann distribution of energy levels – solid and liquid particles, where dimensions >> wavelength of radiation of interest are <u>good black bodies</u> in regions covered by their oscillator energies – that is, in regions where they <u>absorb very strongly</u>).

(iii) <u>a multiple scattering cloud</u> (see later)

(c) <u>application to real gases</u> – providing the discrete energy levels in the molecule are populated according to Boltzmann's distribution, we can show these levels will be in = m with black body radiation. Consider an <u>enclosed</u> gas at <u>constant</u> temperature (i.e. in <u>local thermodynamic equilibrium</u> (LTE)) – consider 2 energy levels
i (excited) ↔ 0 (ground state)

Rate of <u>induced</u> emission = $N_i \ b_{i0} \ I_{\nu_{i0}}$

Rate of <u>induced</u> absorption = $N_0 \ b_{i0} \ I_{\nu_{i0}}$

where b_{i0} = <u>Einstein "b" coefficient</u> (see later)

and $\dfrac{N_i}{N_0} = g_i \ e^{-h\nu_{i0}/KT}$ (g_i = 1 for vibrations

= 2J+1 for rotations)
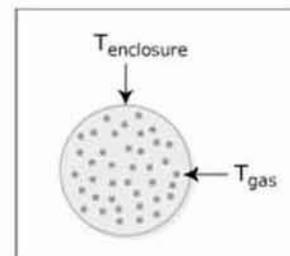
For vibrations $N_i \ll N_0$ (room temp.) so induced absorption far exceeds induced emission. Einstein argued (from the fact that molecules do not fall apart at low pressures) that the statistical Boltzmann distribution for energy should be maintained even at very low pressures where collisions do not occur. He therefore proposed the existence of <u>spontaneous emission</u> with a rate = a_{i0} (sec^{-1} ster^{-1}). Equivalently define the <u>radiative relaxation time</u> $\tau_{i0} = 1/ \ 4\pi a_{i0}$.

Therefore in LTE (in absence of collisions):

$$\overset{\underset{\text{Dominant}}{\downarrow}}{4\pi N_i \left(b_{i0} I_{v_{i0}} + a_{i0} h v_{i0}\right)} = 4\pi N_0 \left(b_{i0} I_{v_{i0}}\right)$$
$$\text{(total rate of emission)} \qquad \text{(total rate of absorption)}$$

i. e.
$$\frac{N_i}{N_0} = \frac{b_{i0} I_{v_{i0}}}{b_{i0} I_{v_{i0}} + a_{i0} h v_{i0}} = e^{-h v_{i0}/KT}$$

i. e.
$$I_{v_{i0}} = \frac{a_{i0}}{b_{i0}} \frac{h v_{i0}}{\left(e^{h v_{i0}/KT} - 1\right)} \qquad \left(\equiv B_{v_{i0}}\right)$$

From time-dependent quantum theory $a_{i0} = \dfrac{2 v_{i0}^2}{c^2} b_{i0}$ so that $I_{v_{i0}} = B_{v_{i0}}$. Hence **total rate of emission** given by

$$4\pi N_0 b_{i0} B_{v_{i0}} \quad \underline{\text{(Kirchoff's Law)}}$$

$$= 4\pi \beta_{i0} B_{v_{i0}} \quad (\beta_{i0} = N_0 b_{i0} = \underline{\text{integrated absorption coefficient}})$$

in LTE (as well as non-LTE). Also due to "broadening" of absorption and emission lines (discussed later) we allow for absorption or emission over a range of frequencies by generalizing v_{i0} to v.

$$4\pi N_0 \int_0^{\Delta v} k_v \, B_v \, dv \qquad (k_v = \underline{\text{absorption cross-section}})$$
$$\qquad\qquad\qquad\qquad (m^2)$$

$$= 4\pi \int_0^{\Delta v} \beta_v \, B_v \, dv \qquad (\beta_v = \underline{\text{absorption coefficient}})$$
$$\qquad\qquad\qquad\qquad (m^{-1})$$

(d) <u>Application to the real atmosphere</u> – the atmosphere is a <u>non-enclosed</u> space and generally has <u>external</u> radiation (e.g. solar; thermal from ground or distant atmosphere). Clearly, $I_v \neq B_v$ (as defined by T_{local}).

If $\quad 4\pi \int_0^\infty \beta_v \, I_v \, dv > 4\pi \int_0^\infty \beta_v \, B_v \, dv \qquad$ get <u>radiative heating</u>
$\qquad$ (absorption) $\qquad$ (emission)

$4\pi \int_0^\infty \beta_v \, I_v \, dv < 4\pi \int_0^\infty \beta_v \, B_v \, dv \qquad$ get <u>radiative cooling</u>
$\quad$ (absorption) $\quad$ (emission)

(a) <u>Rotational Energies</u> (quantum no. J=0, 1, 2, ...)

For a <u>linear</u> molecule (e.g. CO_2, N_2O, O_2, CO, H_2, etc.)

$$E_{rot} = \left(\frac{h^2}{8\pi^2 I}\right) J(J+1)$$
$$= B\,J\,(J+1)$$

and $N_J/N_0 = \underbrace{(2J+1)}_{\text{degeneracy}} \exp(-BJ\,(J+1)/KT)$

where I = moment of inertia = $\sum_i m_i r_i^2$ and r_i is distance of atom i from center of mass:

center of mass
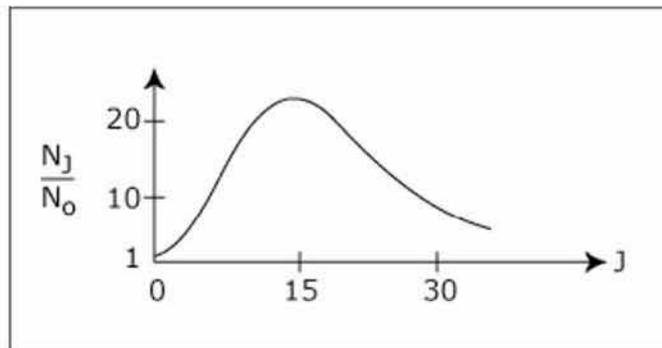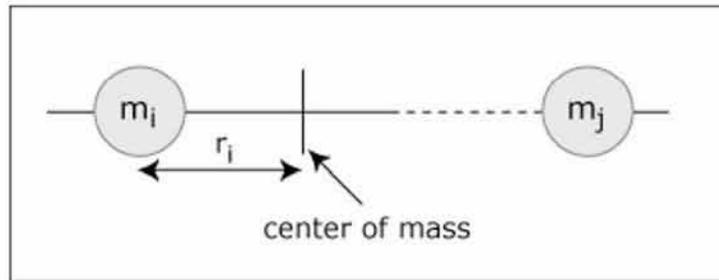
(b) <u>Vibrational Energies</u> (quantum no. v=0, 1, 2,.......)

For a <u>diatomic</u> molecule:

Fundamental Frequency

$$E_{vib} = \left(v+\frac{1}{2}\right) h \left[\frac{1}{2\pi}\sqrt{\frac{C}{\left(\frac{1}{m_1}+\frac{1}{m_2}\right)}}\right] = \left(v+\frac{1}{2}\right) h\nu_0$$

where potential energy $= \frac{1}{2}C(r-r_0)^2$ ("Hookes Law"), but note that a "spring" has a continuous set of energy states while a molecule does not. We can compare E_{vib} to the amplitude of the "spring" vibration.

Also $N_v/N_0 = \exp(-vhv_0/KT)$ (Boltzmann distribution). Note $N_1/N_0 \approx \exp(-5) \approx 0.01$ at room temperature so almost all molecules in ground state. For complex molecules:

Number of fundamental vibrations/frequencies

$$= 3N_{(atoms)} - 3_{(translation)} - \begin{bmatrix} 3 \ (\text{nonlinear}) \\ 2 \ (\text{linear}) \end{bmatrix} (\text{rotation})$$

Each fundamental vibration has a fundamental frequency v_i with its own set of quantum numbers (v_i = 0, 1, 2, etc.). Choose fundamentals using group theory or simple geometry so vector sets representing vibrations linearly independent :

Examples :

① **Water Vapor Molecule**

0.958 Å O
105°
H   H

(3N-6 = 3)

Vibratory States

Symmetric band stretching
$\nu_1 = 3657$ cm^{-1} = 2.73 μm

Bending
$\nu_2 = 1595$ cm^{-1} = 6.25 μm

Asymmetric band stretching
$\nu_3 = 3756$ cm^{-1} = 2.66 μm

② **Ozone Molecule**

1.26 Å O
117°
O   O

(3N-6 = 3)

Vibratory States

Symmetric band stretching
$\nu_1 = 1110$ cm^{-1} = 9.0 μm

Bending
$\nu_2 = 701$ cm^{-1} = 14.3 μm

Asymmetric band stretching
$\nu_3 = 1045$ cm^{-1} = 9.6 μm

③ **Carbon Dioxide Molecule**

O   C   O   (3N-5 = 4)

1.16 A

Vibratory States

Symmetric band stretching
No band

Bending
$\nu_2 = 667$ cm^{-1} = 15 μm

Asymmetric band stretching
$\nu_3 = 2349$ cm^{-1} = 4.3 μm

⊖   ⊕   ⊖

(c) Electronic Energies

These are also quantized but much more complex as we proceed from atoms, to diatomic molecules, to multiatomic molecules.

e.g. for linear molecules electronic states are conveniently designated by informative symbols: