Now, all these allow us to talk about energy density spectrum.

$$W \sim \int_{-\infty}^{+\infty} E^2(t)\,dt = \int_{-\infty}^{+\infty} E(t)\left[\frac{1}{2\pi}\int_{-\infty}^{+\infty} E(\omega)\, e^{i\omega t}\,d\omega\right]dt =$$

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} E(\omega)\left[\int_{-\infty}^{+\infty} E(t)\, e^{i\omega t}\,dt\right]d\omega =$$

we exchanged integration

$$= \frac{1}{2\pi}\int_{-\infty}^{+\infty} E(\omega)\,E(-\omega)\,d\omega = \frac{1}{2\pi}\int_{0}^{\infty} 2|E(\omega)|^2\,d\omega$$

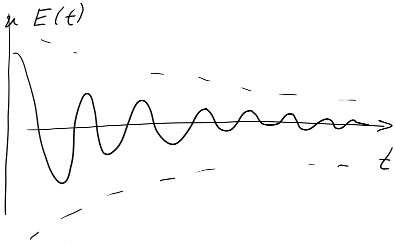
What does it mean?

Total energy of non-monochromatic wave is the integral of energy density on all the frequencies.

It would be important to look into the model of decaying oscillator. In order to understand its spectrum we need to know its time evolution:

$$E(t) \to E(\omega) \to S(\omega)$$

$$E(t) = \begin{cases} E_0\, e^{-\beta t}\cos\omega_0 t & t \geq 0 \\ 0 & t < 0 \end{cases}$$



$$E(\omega) = \int_0^{+\infty} E_0 e^{-\beta t} \cos\omega_0 t \, e^{-i\omega t} \, dt =$$

$$= E_0 \int_0^{+\infty} e^{-\beta t} \, \frac{e^{i\omega_0 t} + e^{-i\omega_0 t}}{2} \, e^{-i\omega t} \, dt =$$

$$= \frac{E_0}{2} \int_0^{+\infty} e^{[-\beta - i(\omega-\omega_0)]t} \, dt + \frac{E_0}{2} \int_0^{+\infty} e^{[-\beta - i(\omega+\omega_0)]t} \, dt =$$

$$= \frac{E_0}{2} \, \frac{e^{-\beta t} e^{-i(\omega-\omega_0)t}}{-\beta - i(\omega-\omega_0)} \Bigg|_0^{\infty} + \frac{E_0}{2} \, \frac{e^{-\beta t} e^{-i(\omega+\omega_0)t}}{-\beta - i(\omega+\omega_0)} \Bigg|_0^{\infty} =$$

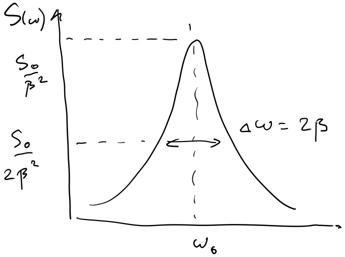
$$= 0 + \frac{E_0}{2} \cdot \underbrace{\frac{1}{\beta + i(\omega-\omega_0)}}_{\sim 10^{-8}} + 0 + \frac{E_0}{2} \cdot \underbrace{\frac{1}{\beta + i(\omega+\omega_0)}}_{\sim 10^{-15}}$$

$$E(\omega) = \frac{E_0}{2} \, \frac{1}{\beta + i(\omega-\omega_0)}$$

Thus,

$$S(\omega) = E(\omega) \cdot E^*(\omega) = \frac{E_0^2}{4} \, \frac{1}{\beta^2 + (\omega-\omega_0)^2}$$

$$\boxed{S(\omega) = \frac{S_0}{\beta^2 + (\omega-\omega_0)^2}}$$



$$\frac{S_0}{2\beta^2} = \frac{S_0}{\beta^2+(\omega-\omega_0)^2}$$

$$\beta^2+(\omega-\omega_0)^2 = 2\beta^2$$

$$\omega-\omega_0 = \beta$$

Natural broadening is the width of the spectrum if we excite the atom and let it decay.

$$\Delta\omega = \omega_1 - \omega_2$$

$$\omega = \frac{2\pi c}{\lambda} \Rightarrow |\Delta\omega| = \left|\frac{2\pi c}{\lambda^2}\cdot\Delta\lambda\right|$$

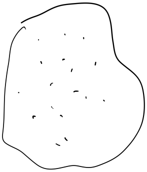
$$\Delta\lambda = \frac{\lambda^2\cdot\Delta\omega}{2\pi c} = \frac{\lambda^2}{\cancel{2}\pi c}\cdot\frac{\cancel{2}}{\tau} \approx \frac{500\cdot 500\cdot 10^{-18}}{\pi\cdot 3\cdot \cancel{10^8}\cdot\cancel{10^{-8}}} \approx$$

$$\approx 10^{-5}\ \text{nm}$$

From quantum point of view the broadening of spectral line is explained the energy width of the states itself. Excited state has the finite width. This width is inverse proportional to lifetime at this state.

Let's go back to classic theory. Why in experiment we observe much broader lines?

Let's see, if this is because in real life the emission comes from ensemble of atoms.



Each atom emits its wave train (photon in quantum theory).

$$E(t-t_k)$$

where t_k is spontaneous time of k atom emission.

The total field is

$$E=\sum_{k=1}^{N}E(t-t_k)$$

Thus the spectrum

$$E(\omega)=\int_{-\infty}^{+\infty}E(t)e^{-i\omega t}dt=\int_{-\infty}^{+\infty}\sum_{k=1}^{N}E(t-t_k)e^{-i\omega t}dt=$$

$$=\sum_{k=1}^{N}\underbrace{\int_{-\infty}^{+\infty}E(t-t_k)e^{-i\omega(t-t_k)}dt}_{E(\omega)}\,e^{-i\omega t_k}=$$

$$=E(\omega)\sum_{k=1}^{N}e^{-i\omega t_k}$$

Since $S(\omega)=|E(\omega)|^2$

$$S(\omega)=|E(\omega)|^2\left|\sum_{k=1}^{N}e^{-i\omega t_k}\right|^2=$$

$$=|E(\omega)|^2\left|\sum\cos\omega t_k-i\sum\sin\omega t_k\right|^2=$$

$$=|E(\omega)|^2\left[\left(\sum_{k=1}^{N}\cos\omega t_k\right)^2+\left(\sum_{k=1}^{N}\sin\omega t_k\right)^2\right]=$$

$= |E(\omega)|^2 N$

1) The terms $\cos^2 \omega t_k$ and $\sin^2 \omega t_k$ will give 1.

2) The terms $\cos \omega t_i \cos \omega t_j$ and similar in $\Sigma = 0$, as t_i and t_j are spontaneous numbers.

Thus

$$S_E(\omega) = N S(\omega)$$

It seems it is just increase of overall intensity, without changing the spectral width.

What are potential mechanisms of spectral broadening then.

① Collision broadening

Let's see what spectral line shape collision broadening may result.

$$E(t) = \begin{cases} E_0 \cos \omega_0 t & -\frac{\delta}{2} < t < \frac{\delta}{2} \\ 0 & t > \frac{\delta}{2} \end{cases}$$

δ – the length of the wave train in time

For single emitter:

$$E(\omega) = \int_{-\infty}^{+\infty} E(t) e^{-i\omega t} dt = E_0 \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} \cos \omega_0 t \, e^{-i\omega t} dt =$$

$$= \frac{E_0}{2} \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} e^{i(\omega - \omega_0)t} dt + \int_{-\frac{\delta}{2}}^{\frac{\delta}{2}} e^{-i(\omega - \omega_0)t} dt =$$

$$= \frac{F_0}{2}\,\frac{e^{i(\omega-\omega_0)t}}{i(\omega-\omega_0)}\Bigg|_{-\frac{\gamma}{2}}^{\frac{\gamma}{2}} + \frac{E_0}{2}\,\frac{e^{-i(\omega+\omega_0)t}}{-i(\omega+\omega_0)}\Bigg|_{-\frac{\gamma}{2}}^{\frac{\gamma}{2}} =$$

$$= E_0\,\frac{\sin\left[(\omega-\omega_0)\frac{\gamma}{2}\right]}{\omega-\omega_0} + E_0\,\cancel{\frac{\sin\left[(\omega_0+\omega)\frac{\gamma}{2}\right]}{\omega+\omega_0}}$$

$\swarrow$

0 as $(\omega_0+\omega) \gg (\omega_0-\omega)$

$$S(\omega) = 2\left|E(\omega)\right|^2 = 2E_0^2\,\frac{\sin^2\left[(\omega-\omega_0)\frac{\gamma}{2}\right]}{(\omega-\omega_0)^2}$$

Since we have ensemble of emitting oscillators, the probability that wave train will be between γ and $\gamma+d\gamma$ is

P_γ - probability to collide for γ length photons

$$P_\gamma = \frac{1}{\tau}e^{-\frac{\gamma}{\tau}}$$

$$P_{\gamma,\gamma+d\gamma} = P_\gamma\,d\gamma = \frac{1}{\tau}e^{-\frac{\gamma}{\tau}}\,d\gamma$$

τ - time between the collisions

In this case for ensemble of oscillators spectral density of radiation:

$$F(\omega) = \int^{\infty} P(\gamma)\,S(\omega,\gamma)\,d\gamma =$$

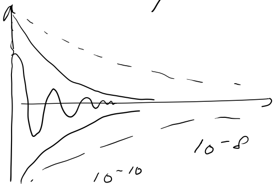
$$= \underbrace{\frac{1}{\tau} 2E_0^2 \frac{1}{(\omega-\omega_0)^2}}_{c} \int_0^\infty e^{-\frac{\gamma}{\tau}} \sin^2\left[(\omega-\omega_0)\frac{\gamma}{2}\right] d\gamma =$$

$$= \frac{c}{2} \int_0^\infty e^{-\frac{\gamma}{\tau}} \left[1-\cos\left[(\omega-\omega_0)\gamma\right]\right] d\gamma =$$

$$= \frac{c\tau}{2} - \frac{c}{2} \left. \frac{e^{-\frac{\gamma}{\tau}}\left[(\omega-\omega_0)\sin(\omega-\omega_0)\gamma - \frac{1}{\tau}\cos(\omega-\omega_0)\gamma\right]}{\frac{1}{\tau^2}+(\omega-\omega_0)^2} \right|_0^\infty =$$

$$= \frac{E_0^2}{\cancel{(\omega-\omega_0)^2}} \cdot \frac{\cancel{\frac{1}{\tau^2}} + \cancel{(\omega-\omega_0)^2} - \cancel{\frac{1}{\tau^2}}}{\frac{1}{\tau^2}+(\omega-\omega_0)^2} = \frac{E_0^2}{\left(\frac{1}{\tau}\right)^2+(\omega-\omega_0)^2}$$

In this case atom collide 10^{10} times per second.



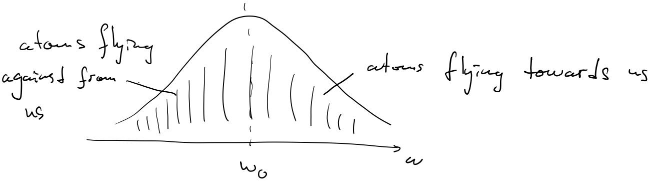
$$S(\omega) = \frac{S_0}{\left(\frac{1}{\tau_c}\right)^2 + (\omega-\omega_0)^2}$$

However, if we use low pressure gas, the spectral width should come back to 10^{-5} nm. In experiments it is not the case.

② Doppler broadening.

Frequency is dependent on speed and

speed vector.



For atoms, the speed is temperature dependent, hence kinetic energy.

The probability that the speed will be dV_x

$$dP_{v_x,\, v_x+dv_x} = A e^{-\frac{mV_x^2}{2kT}} dV_x$$

Maxwell - Boltzmann distribution

$$w = w_0 \left(1 + \frac{V_x}{c}\right)$$

We exchange arguments:

$$\begin{cases} V_x = (w - w_0)\frac{c}{w_0} \\ dV_x = \frac{c}{w_0} dw \end{cases}$$

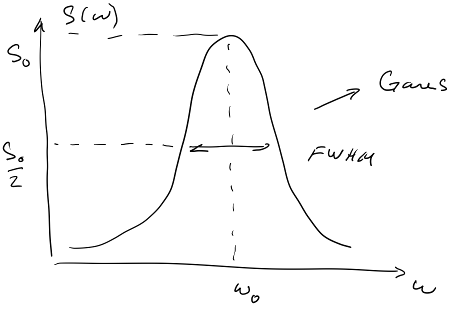
What would be the probability to determine that frequency is dw:

$$dP_{w,\, w+dw} = A \frac{c}{w_0} e^{-\frac{mc^2(w-w_0)^2}{2kTw_0^2}} dw$$

Energy of light wave confined between ω and $\omega + d\omega$

$$dW_{\omega,\omega+d\omega} \sim dP_{\omega,\omega+d\omega} = S(\omega)\,d\omega$$

$$\boxed{S(\omega) = S_0\, e^{-\frac{mc^2}{2kT}\left(\frac{\omega-\omega_0}{\omega_0}\right)^2}}$$



Let's now check how broad the spectral line is due to the Doppler effect.

$$\frac{S_0}{2} = S_0\, e^{-\frac{mc^2}{2kT}\left(\frac{\omega_{1,2}-\omega_0}{\omega_0}\right)^2}$$

$$\ln 2 = \frac{mc^2}{2kT}\left(\frac{\omega_{1,2}-\omega_0}{\omega_0}\right)^2$$

$$\omega_{1,2} = \omega_0 \pm \sqrt{\frac{\ln 2 \cdot 2kT}{mc^2}\omega_0^2}$$

$$\Delta\omega = 2\,\frac{\omega_0}{c}\sqrt{\frac{2\ln 2\, kT}{m}}$$

Since $\omega = \frac{2\pi c}{\lambda}$

$$\left|\frac{\Delta\omega}{\omega_0}\right| = \left|\frac{\Delta\lambda}{\lambda}\right| \Rightarrow \Delta\lambda = 2\,\frac{\lambda_0}{c}\cdot\sqrt{\frac{2\ln 2\, RT}{M}} \sim$$

$\sim 10^{-3}$ nm

How we can check Doppler broadening?

We can vary temperature.