Rewrite equation of motion:

for $F(t) = 0$

$Q(t) = e^{-\gamma t}\sin\Omega_{ot}$

$$\text{I} \qquad \frac{\partial^2 Q}{\partial t^2} + 2\gamma\frac{\partial Q}{\partial t} + \omega_0^2 Q = \frac{F_{ext}(t)}{m}$$

c) *Apply external driving force → interaction of molecule with EM field*

You know what to expect:

The effect depends on the frequency of the driving field . . . like pushing someone on a swing.

- The most efficient way to push someone higher is to push at a frequency corresponding to their swinging frequency
- This leads to a big displacement.
- If you push with arbitrary frequency, nothing will happen.

So you know that we should have a "resonance":

- When you drive the system with frequency $\omega \approx \omega_o$ there will be an efficient transfer of power and the displacement of the H.O. will increase

Indeed, that is what an absorption spectrum is! Measure the power absorbed by the system from the field.

Now let's solve the equation:

Set:

$$F_{ext}(t) = F_o \cos \omega t$$

$F_0 \propto E_0$

$Q = A_0 e^{i(\omega t - \varphi)} \rightarrow$ in (I) $\Rightarrow \times e^{i\varphi}$

$(\omega_0^2 + 2i\gamma\omega - \omega^2)A_0 = \frac{F}{m}e^{i\varphi} \rightarrow$

$$Q(t) = A\sin(\omega t + \beta) = \frac{F_o/m}{\left((\omega_o^2 - \omega^2)^2 + 4\gamma^2\omega^2\right)^{1/2}}\sin(\omega t + \beta)$$

$$\begin{cases} (\omega_0^2 - \omega^2)A_0 = \frac{F_0}{m}\cos\varphi \\ 2\gamma\omega A_0 = \frac{F_0}{m}\sin\varphi \end{cases}$$

$\Downarrow$

$$A_0 = \frac{F_0/m}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}}$$

$+ A e^{-\gamma t}\sin\Omega_0 t$, $\Omega_0 = \sqrt{\omega_0^2 - \gamma^2}$

$$\tan\beta = \frac{\omega_o^2 - \omega^2}{2\gamma\omega}$$

Notice that the coordinate oscillates at the driving frequency ω! $\beta = \frac{\pi}{2} - \varphi$

$$\tan\varphi = \frac{2\gamma\omega}{\omega_0^2 - \omega^2}$$

$$Q(t) = \frac{F_0/m}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}}\cos(\omega t - \varphi)$$

$$v = \frac{\partial q}{\partial t}$$

$$\langle P \rangle = \left\langle F(t) \frac{\partial q}{\partial t} \right\rangle_{avg} \Rightarrow P = F_0 \cos \omega t \times \frac{F_0/m}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}} (-\omega) \sin(\omega t - \varphi)$$

$$P = \frac{F_0^2}{m} \frac{\omega \cos \omega t}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}} \left[-\sin \omega t \cos \varphi + \sin \varphi \cos \omega t \right]$$

$$\langle \cos^2 \omega t \rangle = \frac{1}{2}$$

$$\langle \cos \omega t \sin \omega t \rangle = 0$$

$$\langle P \rangle = \frac{F_0^2}{m} \frac{\omega}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}} \frac{\sin \varphi}{2}$$

$$\tan \varphi = \frac{2\gamma\omega}{\omega_0^2 - \omega^2}$$

$$\sin \varphi = \frac{2\gamma\omega}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]^{1/2}}$$

$$\langle P \rangle = \frac{F_0^2}{m} \frac{\gamma\omega^2}{\left[(\omega_0^2-\omega^2)^2 + 4\gamma^2\omega^2\right]}$$

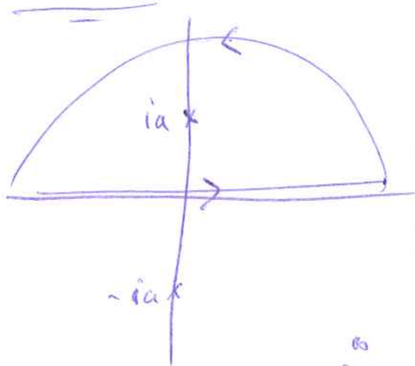
$\gamma \ll \omega_0$ &

$\omega \approx \omega_0$

$\left\{ (\omega_0^2 - \omega^2)^2 \simeq 4\omega_0^2(\omega_0 - \omega)^2 \right.$

If $\omega \approx \omega_0 \rightarrow$
$$\langle P \rangle \simeq \frac{F_0^2}{4m} \frac{\gamma}{(\omega-\omega_0)^2 + \gamma^2}$$

Remember:

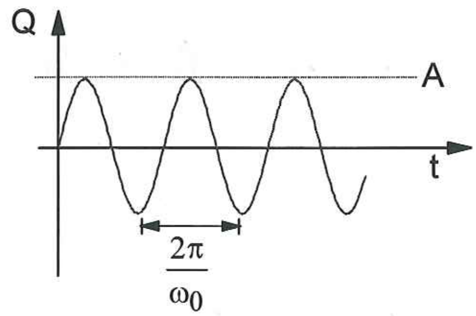


$$\int_{-\infty}^{\infty} \frac{a}{u^2+a^2} du = 2\pi i \sum \text{residues}$$

$$\int_{-\infty}^{\infty} \frac{a}{(u+ia)(u-ia)} du = 2\pi i \frac{a}{ia + ia} = \pi$$

$$\rightarrow \text{Area} = \int_{-\infty}^{\infty} \frac{F_0^2}{4m} \frac{\gamma}{(\omega-\omega_0)^2+\gamma^2} d\omega = \frac{\pi F_0^2}{4m}$$

Oscillations at ω_0 continue forever.



b) **<u>Now we add damping—H.O. may feel friction that reduces the amplitude of oscillation</u>**

$$m\frac{\partial^2 Q}{\partial t^2} = F_{res} + F_{damp} = -kQ - b\frac{\partial Q}{\partial t}$$

$$\frac{\partial^2 Q}{\partial t^2} + \frac{b}{m}\frac{\partial Q}{\partial t} + \frac{kQ}{m} = 0$$

Damping has two effects:

$$Q(t) = A\underbrace{e^{-\gamma t}}_{\text{damps}}\sin\underbrace{\Omega_o}_{\text{reduced freq.}} t$$

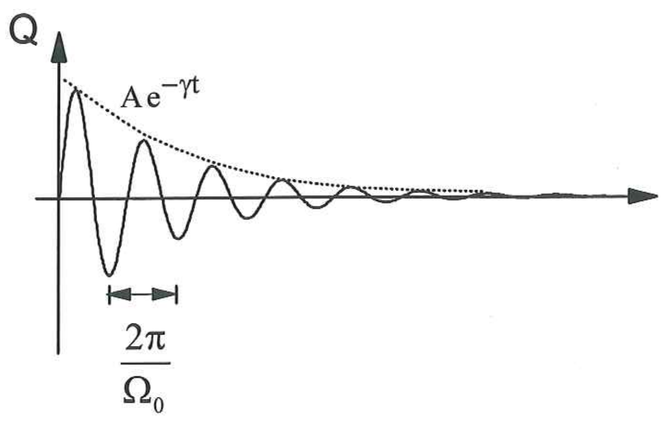
Now oscillation decays away exponentially

$\gamma = b/2m$

$\Omega_o = \sqrt{\omega_o^{\,2} - \gamma^2} \approx \omega_o$

reduced frequency

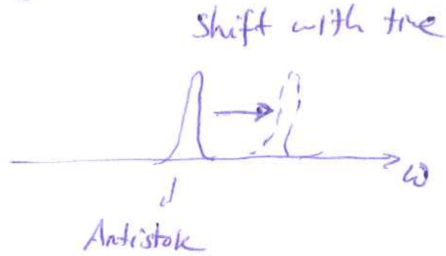
for weak damping



- Damping has two effects: educe amplitude & reduce frequency
- Damping can be due to heat dissipation.
- Can we use time resolved CARS to look at the shift in ω vs. time to extract the thermal diffusivity:

$$\omega = \sqrt{\omega_0^2 - \gamma(t)}$$

$\gamma(t) \propto$ thermal diffusivity



Notice that it oscillates 90° out of phase with field when driven on resonance. →
absorbing power from field.

If $\gamma << \omega_o$ and near resonance $\omega_o \approx \omega$

$$\left(\omega_o^2-\omega^2\right)^2=\left(\omega_o-\omega\right)^2\left(\omega_o+\omega\right)^2\approx 4\omega_o^2\left(\omega_o-\omega\right)^2$$

$$Q(t)=\frac{F_o}{2m\omega_o}\frac{1}{\left[\left(\omega_o-\omega\right)^2+\gamma^2\right]^{1/2}}\quad\sin\left(\omega t+\beta\right)+Ae^{-\gamma t}\sin\Omega_o t$$

$$\Omega_o \rightarrow \sqrt{\omega_o^2-\gamma^2}$$

Now we can calculate the absorption spectrum → power absorbed.

Power* = *force* x *velocity

$$P_{avg}=\left\langle F(t)\cdot\frac{\partial Q}{\partial t}\right\rangle_{avg}$$

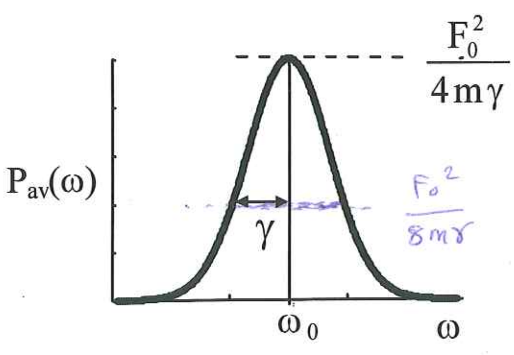
$$=\frac{\gamma F_0^2}{\cancel{2}4m}\frac{1}{\left(\omega-\omega_0\right)^2+\gamma^2}$$

Average over several cycles

(avera

Let's plot the power absorbed as a function of frequency:

LORENTZIAN LINESHAPE
peak is at $\omega=\omega_o$



At what frequency shift relative to maximum is the absorbed power reduced by ½?

$\omega-\omega_o=\pm\gamma$

The full-width at half-maximum intensity (FWHM) is 2γ .

peak → ω_o width → γ Area under lineshape → $\frac{\pi F_0^2}{4m}$