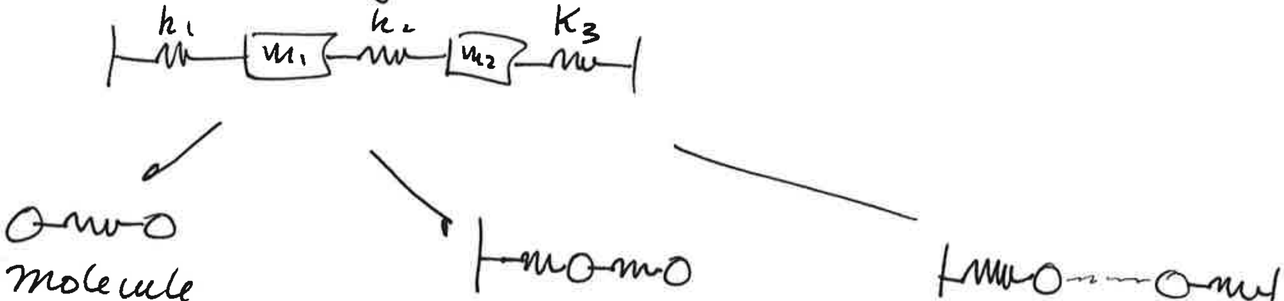
General problem again



molecule | absorbed molecule | weakly coupled osc

$$m_1\ddot{x}_1 = -k_1x_1 + k_2(x_2-x_1) = -(k_1+k_2)x_1 + k_2x_2$$
$$m_2\ddot{x}_2 = -k_3x_2 + k_2(x_1-x_2) = -(k_2+k_3)x_2 + k_2x_1$$

- even in general case, we'll presume there are steady-state sinusoidal solns, and we expect 2 of them $(\rightarrow\ \rightarrow)$, $(\rightarrow\ \leftarrow)$ symmetric and antisymmetric as normal modes
- try $x_1 = A_1e^{i\omega t}$ $x_2 = A_2e^{i\omega t}$, plug in above

$$m\ddot{x}_1 = -m_1\omega^2 A_1 e^{i\omega t} = -k_1A_1e^{i\omega t} + k_2(A_2-A_1)e^{i\omega t}$$
$$m_2\ddot{x}_2 = -m_2\omega^2 A_2e^{i\omega t} = -k_3A_2e^{i\omega t} + k_2(A_1-A_2)e^{i\omega t}$$

cancel $e^{i\omega t}$

$$-m_1\omega^2A_1 = -k_1A_1 + k_2(A_2-A_1)$$
$$-m_2\omega^2A_2 = -k_3A_2 + k_2(A_1-A_2)$$

rearrange...

$$(m_1\omega^2 - k_1 - k_2)A_1 + k_2A_2 = 0$$
$$k_2A_1 + (m_2\omega^2 - k_3 - k_2)A_2 = 0$$

now eqns for amplitudes can write as matrix again

$$\begin{bmatrix} m_1\omega^2-k_1-k_2 & k_2 \\ k_2 & m_2\omega^2-k_3-k_2 \end{bmatrix}\begin{bmatrix} A_1 \\ A_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$(\underline{\underline{K}} - \omega^2\underline{\underline{M}})\vec{A} = 0$ as before, k_2 = off diagonal = coupling

• nontrivial solutions if determinant of coeff matrix vanishes

$$\det(\underline{\underline{K}} - \omega^2 M) = (m_1\omega^2 - k_1 - k_2)(m_2\omega^2 - k_3 - k_2) - k_2^2 = 0$$

... tedium ensues ...

$$m_1 m_2 \omega^4 - \left[(k_2+k_3)m_1 + (k_1+k_2)m_2\right]\omega^2 + (k_1+k_2)(k_2+k_3) - k_2^2 = 0$$

quadratic in ω^2 ... more tedium

$$\omega^2 = \frac{(k_2+k_3)m_1 + (k_1+k_2)m_2 \pm \sqrt{\left[(k_2+k_3)m_1 - (k_1+k_2)m_2\right]^2 + 4m_1m_2k_2^2}}{2m_1m_2}$$

Case $k_1 = k_3$? (only coupling spring different)

$$\omega^2 = \frac{(k_1+k_2)(m_1+m_2) \pm \sqrt{(k_1+k_2)^2(m_1-m_2)^2 + 4m_1m_2k_2^2}}{2m_1m_2}$$

with $m_1 = m_2$? $\quad \omega^2 = \frac{k_1+k_2 \pm k_2}{m} = \frac{k_1}{m}, \frac{k_1+2k_2}{m}$ (as before w/ $k_1 = k_2$)

look above: if $m_1 \neq m_2$, correction to 2^{nd} mode is larger!

antisymm → − mode cares if $m_1 \neq m_2$,

symmetric → + mode does not so much

with $k_1 = k_2$, $\omega^2 = \left\{\frac{k}{m}, \frac{3k}{m}\right\}$ as before

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Diatomic molecule : $k_1 = k_3 = 0$, $k_2 \equiv k$, $m_1 \neq m_2$ — no coupling

$$\omega^2 = \frac{k(m_1+m_2) \pm \sqrt{k^2(m_1-m_2)^2 + 4m_1m_2k^2}}{2m_1m_2} = \frac{k(m_1+m_2) \pm k(m_1+m_2)}{2m_1m_2}$$

$$\omega^2 = \left\{0, \frac{k(m_1+m_2)}{m_1m_2}\right\} = \left\{0, \frac{k}{\mu}\right\} \qquad \mu = \frac{m_1m_2}{m_1+m_2}$$

! diatomic molecule has only antisymmetric mode, because symmetric mode is just a translation, & is transl invariant

- behaves as a single particle of mass μ connected to k
- if $m_1 = m_2$ (e.g. H_2), $\omega^2 = \frac{2k}{m}$ – has to be $2k$ because $\rightarrow \leftarrow$ motion, both masses act in the same way
- diatomic molecule on a surface? $k_3 = 0$, $m_1 = m_2 = m$ for simplicity
  now k_1 = coupling!

$$\omega^2 = \frac{(k_1+2k_2)m \pm \sqrt{m^2(k_2-k_1-k_2)^2 + 4m^2k_2^2}}{2m^2} =$$

$$\omega^2 = \frac{(k_1+2k_2)m \pm \sqrt{m^2(4k_2^2+k_1^2)}}{2m^2} = \frac{k_1+2k_2 \pm \sqrt{4k_2^2+k_1^2}}{2m}$$

- if $k_1 = k_2$, $\omega^2 = \left(\frac{3\pm\sqrt{5}}{2}\right)\frac{k}{m}$ – but coupling to surface (e.g. van der Waals) is far weaker than bond – $k_1 \ll k_2$
- with $(1+x)^n \simeq 1+nx$ for $x \ll 1$,

$$\sqrt{4k_2^2+k_1^2} = 2k_2\sqrt{1+\frac{k_1^2}{4k_2^2}} \simeq 2k_2\left(1+\frac{1}{2}\cdot\frac{k_1^2}{4k_2^2}\right)$$

$$\Rightarrow \omega^2 \simeq \frac{k_1+2k_2 \pm 2k_2\left(1+\frac{k_1^2}{8k_2^2}\right)}{2m} = \left\{\frac{k_1-\frac{k_1^2}{4k_2}}{2m},\ \frac{k_1+4k_2+\frac{k_1^2}{4k_2}}{2m}\right]$$

presuming $k_1 \gg k_1\left(\frac{k_1}{4k_2}\right)$, neglect $\frac{k_1^2}{4k^2}$

$$\Rightarrow \omega^2 \approx \left\{\frac{k_1}{2m},\ \frac{k_1}{2m} + \underset{\text{original freq}}{\frac{2k}{m}}\right\} = \{\delta\omega,\ \omega_0+\delta\omega\}$$

spectroscopic shift due to absorption

Weak coupling $k_1 = k_3 \gg k_2$ back to 2 masses, 3 springs

$$\omega^2 = \frac{(k_1+k_2)(m_1+m_2) \pm \sqrt{(k_1+k_2)^2(m_1-m_2)^2+4m_1m_2k_2^2}}{2m_1m_2}$$

with $m_1 = m_2$, $\omega^2 = \left\{\frac{k_1}{m}, \frac{k_1+2k_2}{m}\right\} = \{\omega_1, \omega_2\}$

- if $k_2 \ll k_1$, then these 2 frequencies are very close together.

$$\omega_2 = \sqrt{\frac{k_1+2k_2}{m}} = \sqrt{\frac{k_1}{m}}\sqrt{1+\frac{2k_2}{k_1}} \simeq \sqrt{\frac{k_1}{m}}\left(1+\frac{k_2}{k_1}\right)$$

or $\omega_2 = \omega_1\left(1+\frac{k_2}{k_1}\right)$, but remembering $\frac{k_2}{k_1} \ll 1$

- mathematically nicer: let $\omega_0 = \frac{\omega_1+\omega_2}{2} \simeq \omega_1\left(1+\frac{k_2}{2k_1}\right)$
- then $\omega_{1,2} = \omega_0 \mp \epsilon$ w/ $\epsilon = \omega_0\left(\frac{k_2}{2k_1}\right)$ – half diff btw modes
- normal modes are then (complex form)

$$x(t) = C_1\begin{bmatrix}1\\1\end{bmatrix}e^{i(\omega_0-\epsilon)t}, \quad x(t) = C_2\begin{bmatrix}1\\-1\end{bmatrix}e^{i(\omega_0+\epsilon)t}$$

where $C_1, C_2 \in \mathbb{Z}$ are arbitrary complex numbers

- general soln is the sum of these 2 as before

$$x(t) = C_1\begin{bmatrix}1\\1\end{bmatrix}e^{i(\omega_0-\epsilon)t} + C_2\begin{bmatrix}1\\-1\end{bmatrix}e^{i(\omega_0+\epsilon)t}$$

get C_1, C_2 from $x(0)$ and $\dot{x}(0)$

but note $x(t) = \underbrace{\left\{ c_1 \begin{bmatrix} 1 \\ i \end{bmatrix} e^{-i\epsilon t} + c_2 \begin{bmatrix} 1 \\ -i \end{bmatrix} e^{i\epsilon t} \right\}}_{\epsilon \text{ small, so slowly varying}} e^{i\omega_0 t}$

$\Rightarrow$ for short time intervals, $x(t) \sim A e^{i\omega_0 t}$, carts oscillate with ω_0, but overall "constant" starts to vary slowly and the details change

- if C_1 or $C_2 = 0$, only one normal mode excited, easy case
- suppose $C_1 = C_2 = \frac{A}{2}$ - more interesting

$$x(t) = \frac{A}{2} \begin{bmatrix} e^{-i\epsilon t} + e^{i\epsilon t} \\ e^{-i\epsilon t} - e^{i\epsilon t} \end{bmatrix} e^{i\omega_0 t} = A \begin{bmatrix} \cos \epsilon t \\ -i \sin \epsilon t \end{bmatrix} e^{i\omega_0 t}$$

- actual motion is real part

$$Re(x_1(t)) = A \cos \epsilon t \cos \omega_0 t$$
$$Re(x_2(t)) = A \sin \epsilon t \sin \omega_0 t$$

- at $t=0$, $x_1 = A$ but $\dot{x}_1 = x_2 = \dot{x}_2 = 0$

$\Rightarrow$ Solution is 1 pulled to right a distance A and released @ $t=0$ w/ 2 stationary

because ϵ is small, for $0 \leq t \ll \frac{1}{\epsilon}$

$\cos \epsilon t \simeq 1$, $\sin \epsilon t \simeq 0$

$$\left. \begin{aligned} Re(x_1(t)) &\simeq A \cos \omega_0 t \\ Re(x_2(t)) &\simeq 0 \end{aligned} \right\} t \simeq 0$$

! initially cart 1 oscillates w/ ampl A and freq ω_0
while cart 2 is stationary

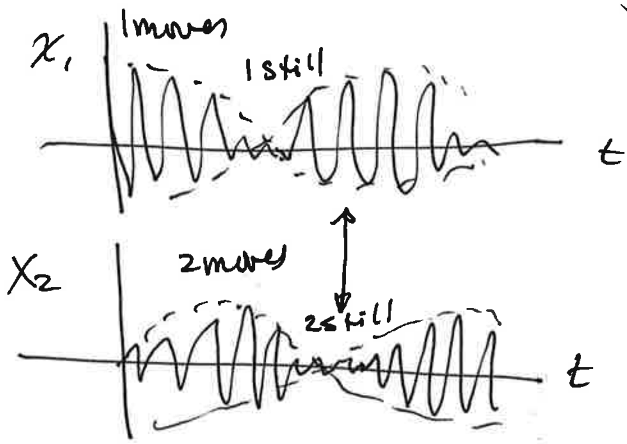
- after some time $\sim \frac{1}{\epsilon}$, coupling starts to wriggle cart 2
- when $t = \frac{\pi}{2\epsilon}$, $\sin \epsilon t = 1$ & $\cos \epsilon t = 0$ so

$$x_1(t) \simeq 0$$
$$Re(x_2(t)) \simeq A \sin \omega_0 t$$

! cart 2 osc @ max ampl and cart 1 sits still

continues indefinitely, 2 carts pass energy back & forth

another view: like beating in wave superposn



normal coord? each osc w/ normal freq

$$\xi_1(t) = \frac{1}{2} A \cos(\omega_1 t)$$
$$\xi_2(t) = \frac{1}{2} A \cos(\omega_2 t)$$

$$\left.\begin{aligned} X_1 &= \xi_1 + \xi_2 \\ X_2 &= \xi_1 - \xi_2 \end{aligned}\right\}$$ both are interference of $\omega_1 \simeq \omega_2$

but + vs − means phase opposite