PHYS 5210
Graduate Classical Mechanics
Fall 2024

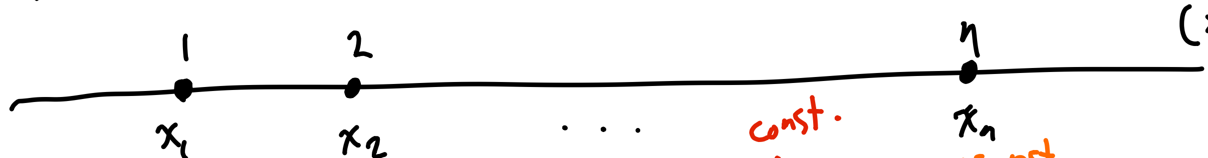
Lecture 5
Diatomic molecule

September 6

Recall: single particle w/ Galilean invariance:

$$L = \frac{1}{2}m\dot{x}^2 + \cancel{f(\dot{x}, \dots)}$$

What if n interacting particles?



config space $(x_1, \dots, x_n) \in \mathbb{R}^n$.

Galilean boost/ x,t -trans:

$$x_i \to x_i + \underset{\text{const.}}{v}t + \underset{\text{const.}}{b}$$

$$t \to t + t_0 \leftarrow \text{const.}$$

Most general Lagrangian?

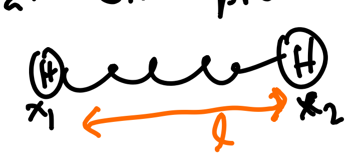
$(x_i + b) - (x_j + b) = x_i - x_j$

$$L = \sum_{i=1}^{n} \frac{1}{2} m_i \dot{x}_i^2 + F(x_i - x_j, \dot{x}_i - \dot{x}_j \dots)$$

Assume time-reversal symmetry $(t \to -t)$: $\dot{x}_i \to -\dot{x}_i$

↳ L must depend on even powers of velocity.

Minimal example: $(n=2)$ [diatomic molecule H_2]



From above: if H atoms are "same" $(x_1 \leftrightarrow x_2$ discrete sym)

$$L = \frac{1}{2} m(\dot{x}_1^2 + m\dot{x}_2^2) + F(x_1 - x_2, \dot{x}_1 - \dot{x}_2)$$

$$(x_1 - x_2)^2$$

Effective theory? Already exhausted symmetries...

State? "bound state" of x_1, x_2

$|x_2 - x_1| \approx \ell$ (bond length)

Regime of validity: $\big||x_2 - x_1| - \ell\big| \ll \ell$

To Taylor series in regime of validity:

$x_1 \approx z_1$ ← "small"?

$x_2 \approx z_2 + \ell$ ← "small"?

$\frac{|z_2 - z_1|}{\ell} \ll 1$

$$L = \frac{1}{2} m(\dot{z}_1^2 + \dot{z}_2^2) + \left[F_0 + \cancel{F_1 \boxed{\frac{z_2 - z_1}{\ell}}} + F_2 \frac{(z_2 - z_1)^2}{2\ell^2} + \dots \cancel{F_1' \left(\frac{\dot{z}_2 - \dot{z}_1}{\ell}\right)}\right]$$

small dimensionless

Euler-Lagrange equations:

$$\frac{\delta S}{\delta z_1} = 0 = \frac{\partial L}{\partial z_1} - \frac{d}{dt}\frac{\partial L}{\partial \dot{z}_1}$$

$$m\ddot{z}_1 = \cancel{\boxed{-\frac{F_1}{\ell}}} + \frac{F_2}{\ell^2}(z_1 - z_2) + \dots$$

Similar: $$m\ddot{z}_2 = \cancel{\boxed{\frac{F_1}{\ell}}} + \frac{F_2}{\ell^2}(z_2 - z_1) + \dots$$

ℓ = equilibrium bond length.

if $F_1 \neq 0$ $z_1 - z_2 = 0$ is not steady-state. !!

So take $F_1 = 0$ (correctly define equilibrium)

Our Lagrangian (simplified):

$$L \approx \frac{1}{2} m(\dot{z}_1^2 + \dot{z}_2^2) + \frac{F_2}{2\ell^2}(z_1 - z_2)^2$$

This problem is exactly solvable: (coupled) harmonic oscillator:

general solution:

$$L = \frac{1}{2} M_{ij} \dot{z}_i \dot{z}_j - \frac{1}{2} K_{ij} z_i z_j = \frac{1}{2} \dot{z}^T M \dot{z} - \frac{1}{2} z^T K z$$

① choose $q_i = (\sqrt{M})_{ij} z_j$:

$$L = \frac{1}{2} \dot{q}_i \dot{q}_i - \frac{1}{2} W_{ij} q_i q_j \quad \text{where} \quad W = M^{-1/2} K M^{-1/2}$$

(Lec 9)

(W, K, M symmetric)

② Find orthogonal R such that $q'_\alpha = R_{\alpha i} q_i$

and $RWR^T =$ diagonal [eigenvalues of W on diag].

"normal modes"

$$L = \sum_\alpha \left[\frac{1}{2} (\dot{q}'_\alpha)^2 - \frac{1}{2} \underbrace{W_\alpha}_{\text{e-val}} q_\alpha^2 \right]$$

③ Euler-Lag: $\ddot{q}'_\alpha = -W_\alpha q_\alpha$

if $W_\alpha > 0$: $q'_\alpha(t) = A \cos(\sqrt{W_\alpha} t) + B \sin(\sqrt{W_\alpha} t)$

~~$W_\alpha < 0$: $e^{\sqrt{-W_\alpha} t}$ $e^{-\sqrt{-W_\alpha} t}$~~

unstable problem

$W_\alpha = 0$: interesting, later...

Back to diatomic molecule:

$$M = \begin{pmatrix} m & 0 \\ 0 & m \end{pmatrix} \qquad K = -\frac{F_2}{\ell^2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}$$

since $L = \frac{m}{2}(\dot{z}_1^2 + \dot{z}_2^2) + \frac{F_2}{2\ell^2}(z_1 - z_2)^2$

① $q_i = \sqrt{m}\, z_i \rightsquigarrow L = \frac{1}{2}(\dot{q}_1^2 + \dot{q}_2^2) - \underbrace{\left(-\frac{F_2}{2m\ell^2} \right)}_{\text{call this } \frac{1}{4}\omega_0^2} (q_1 - q_2)^2$

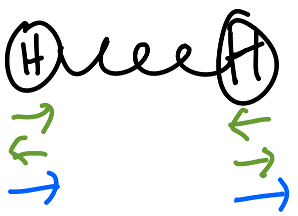
② Eigenvector/val of $\frac{K}{m} = W$: $\frac{1}{2}\omega_0^2 \underbrace{\begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}}_{\mathbb{1} - \sigma^x}$

since eigenvectors of σ^x: $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ 1 \end{pmatrix}$, $\frac{1}{\sqrt{2}}\begin{pmatrix} 1 \\ -1 \end{pmatrix}$

W's eigenval: 0 , ω_0^2

Rewrite $q'_\pm = \frac{1}{\sqrt{2}}(q_1 \pm q_2)$:

$$L = \frac{1}{2}\left(\dot{q}'^2_+ + \dot{q}'^2_-\right) - \frac{1}{2}\omega_0^2 q'^2_-$$

③ 

vibrational mode at freq. ω_0:

$$q'_-(t) = A\cos(\omega_0 t) + B\sin(\omega_0 t)$$

translational mode has frequency 0:

$$q'_+(t) = a + bt$$

Effective theory remarks:

① On long time scales... $\Delta t \gg 1/\omega_0$, $L_{eff} = \frac{1}{2}\dot{q}'^2_+$

$$x_1(t) \approx \frac{1}{\sqrt{2}}(a + bt) + \text{oscillations}$$

↑ $\Delta t \gg 1/\omega_0$

② Slow DoF (translation) predictable by symmetry:

$$\begin{pmatrix} z_1 \\ z_2 \end{pmatrix} \to \begin{pmatrix} z_1 + a \\ z_2 + a \end{pmatrix} \rightsquigarrow \begin{pmatrix} z_1 & z_2 \end{pmatrix} K \begin{pmatrix} z_1 \\ z_2 \end{pmatrix}$$

$$= \begin{pmatrix} z_1 + a & z_2 + a \end{pmatrix} K \begin{pmatrix} z_1 + a \\ z_2 + a \end{pmatrix}$$

implies $\begin{pmatrix} a & a \end{pmatrix} K \begin{pmatrix} a \\ a \end{pmatrix} = 0$,

or K has null vector → 0 eigenval.

Most effective theory: slow DoF are consequences of symmetry

③ Do we stay in regime of validity?

translation only ✓

include vibration?

$$L = \frac{1}{2}m\left(\dot{z}_1^2 + \dot{z}_2^2 - \frac{1}{2}\omega_0^2(z_1 - z_2)^2 + a\,\omega_0^2 \frac{(z_1 - z_2)^3}{\ell} + \cdots + b\frac{1}{\omega_0 \ell}(\dot{z}_1 - \dot{z}_2)^3 + \cdots\right)$$

To stay in our regime of validity, Taylor series converge?

Parameters a & b $\lesssim 1$