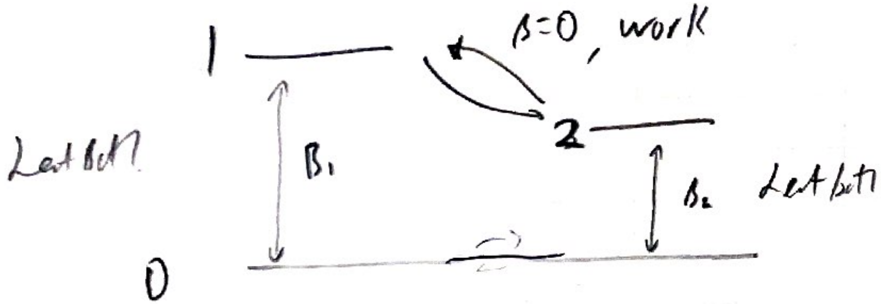
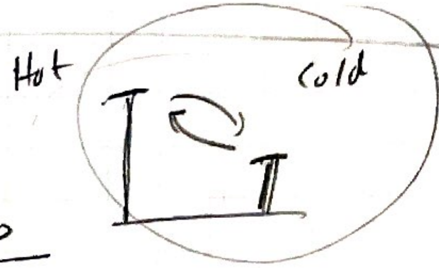
#12

12.0

$$\frac{\lambda_{01}^{\leftarrow}}{\lambda_{10}^{\rightarrow}} = e^{+\beta_1 \Delta E} \qquad T_1 = 2T_2 \qquad \beta_1 = \tfrac{1}{2}\beta_2$$



Heat engine



Heat Pump

Useless machine

$$Q = \begin{array}{c|ccc} & 0 & 1 & 2 \\ \hline 0 & \cdot & \lambda_{01} & \lambda_{02} \\ 1 & \lambda_{10} & \cdot & 1 \\ 2 & \lambda_{20} & 1 & \cdot \end{array}$$

$$\frac{P[X \mid x_0]}{P[\tilde{X} \mid \tilde{x}_t]} = e^{\Sigma^{env}} = e^{-\beta Q} \quad \text{(one bath)}$$

$$= e^{-\beta_1 Q_1 - \beta_2 Q_2}$$

$p^{ss} \neq$ canonical

$$S = -\sum p \ln p \quad \leftarrow \text{ensemble average}$$

$$s(x) = -\ln p \qquad S = \langle s \rangle$$

$$\frac{P[X]}{P[\tilde{X}]} = e^{-\beta_1 Q_1 - \beta_2 Q_2 + \Delta s}$$

$$\Delta s^{sys} = \left(-\ln p(x;t)\right) - \left(-\ln p(x;0)\right)$$

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1'

Classical Mechanics

momenta positions

Hamiltonian $H(p, q, t)$ general coordinates

[more than just cartesian ...]

Hamilton's equations $\frac{\partial p}{\partial t} = -\frac{\partial H}{\partial q}$ $\frac{\partial q}{\partial t} = \frac{\partial H}{\partial p}$

Cartesian coordinates $H = K + U$

$H(v, r)$ $= \frac{1}{2}mv^2$

$p = mv$

$\frac{\partial v}{\partial t} = -\frac{1}{m}\frac{\partial U}{\partial r}$ $\frac{\partial r}{\partial t} = v$

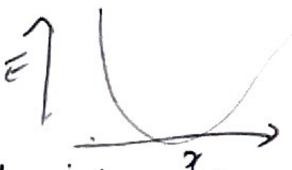
Newton

$F = ma$ $= \frac{1}{m}F$

$F = m\frac{dv}{dt}$

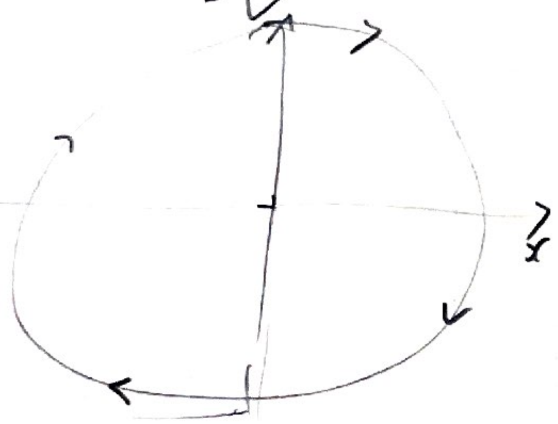
Integrable System

(1) Harmonic Oscillator



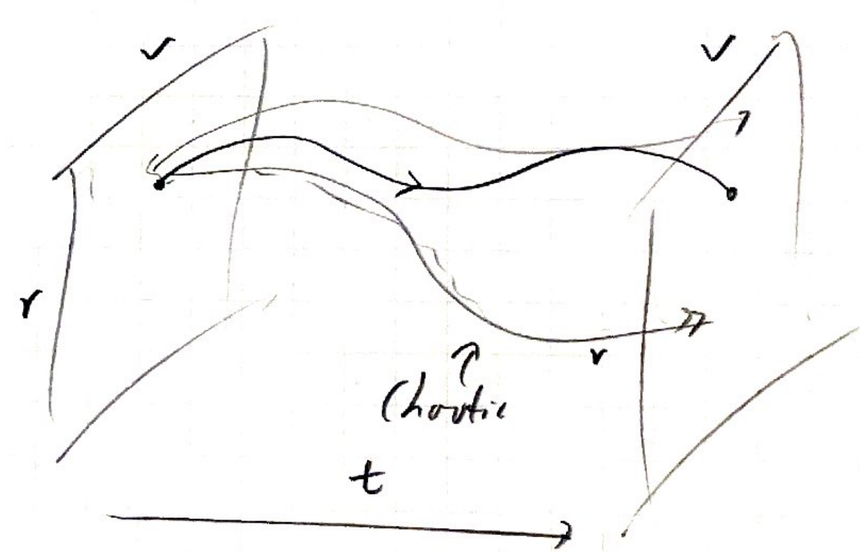
$F = -Kx \quad U = \frac{1}{2} K x^2$

phase space



$\omega = \sqrt{\frac{K}{m}} \quad x(t) = A \cos(\omega t + c)$

Chaotic ~~System~~



deterministic & invertable

Chaotic

Liouville's eq

Liouvillian

$$\frac{\partial}{\partial t}\rho(p;q;t) = -\mathcal{L}\rho \qquad \rho(p;q;t+\Delta t) = e^{-\Delta t\mathcal{L}}\rho(p,q;t+\Delta t)$$

$$\mathcal{L}\,\square = \frac{\partial H}{\partial p}\frac{\partial}{\partial q}\square - \frac{\partial H}{\partial q}\frac{\partial}{\partial p}\square$$

[this is why $e^{+tQ}p$ convention]

cartesian

$$\mathcal{L}(v,r) = \underbrace{\mathcal{L}_r}_{v\frac{\partial}{\partial r}} + \underbrace{\mathcal{L}_v}_{\frac{F}{m}\frac{\partial}{\partial v}}$$

Discussion: Jarzynski Eq for Deterministic eq.

2nd Law Problem of, Each 3 meanings (Wolfram)

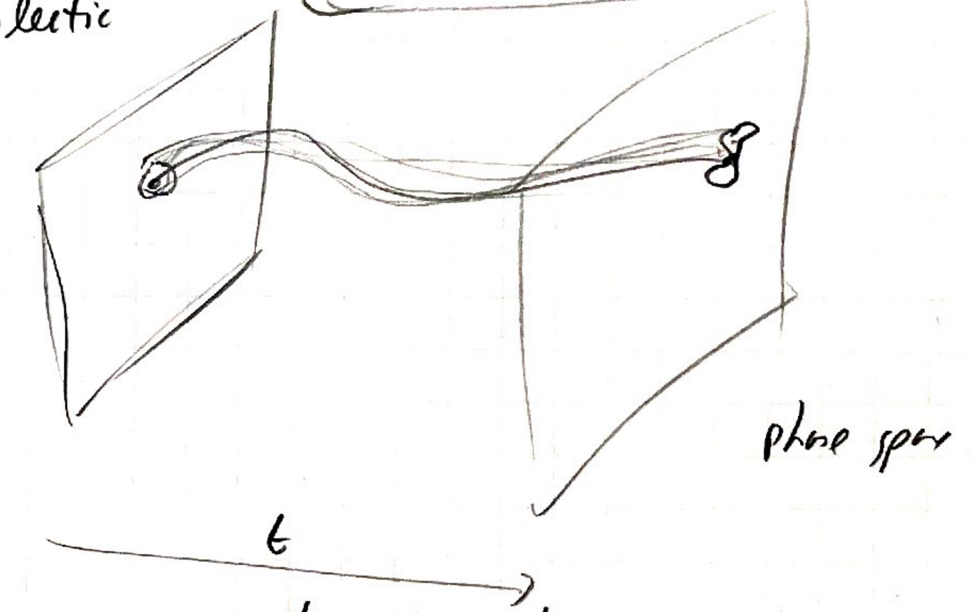
($\ddot{p}$, $\ddot{q}$) vector field

Divergence free

[Incompressible flow e.g. water]

Hamiltonian flow "symplectic"

$$\boxed{P_\Omega[X] = P_{\tilde{\Omega}}[\tilde{X}] \quad H(t)}$$



Conservation of phase space!

Entropy does not change

THERMODYNAMICALLY REVERSIBLE!

Deterministic Thermostats

NOSÉ 1984 HOOVER 1985

"Nose - Hoover Thermostat"

$$m \frac{\partial v}{\partial t} = F - \lambda \frac{\partial g}{\partial v}$$

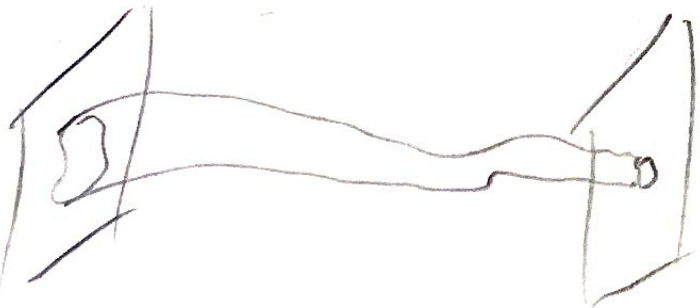
$$\frac{P_{\lambda}[x]}{\tilde{P}_{\tilde{\lambda}}[\tilde{x}]} = e^{+\Sigma}$$

constraint $g(\;, v, t) = 0$

constant kinetic energy

isokinetic $g = \left(\sum \frac{1}{2} m v^2 \right) - K = 0$

[λ is Lagrange multiplier to make constraint true]



phase space contraction →
Entropy production
[see early FTs]

12-6

6

Molecular Dynamics

Discrete time

$$\rho(r, v; t+\Delta t) = e^{-\Delta t \mathcal{L}} \rho(r, v; t)$$

$$\mathcal{L} = \mathcal{L}_V + \mathcal{L}_R$$

Strong (symmetric Trotter) operator splitting

$$e^{(A+B)\varepsilon} \approx e^{A\frac{\varepsilon}{2}} e^{B\varepsilon} e^{A\frac{\varepsilon}{2}} + O(\varepsilon^3)$$

(comes from taylor series expansion)

$AB \neq BA$

$$e^{-\Delta t \mathcal{L}} \approx \underbrace{e^{-\frac{\Delta t}{2}\mathcal{L}_V}}_{V} \underbrace{e^{-\frac{\Delta t}{2}\mathcal{L}_R}}_{R} e^{-\frac{\Delta t}{2}\mathcal{L}_R} e^{-\frac{\Delta t}{2}}$$

12.7

7

[BACK]4e

Velocity Verlet

"Leap frog"

V $\quad v(t+\frac{\Delta t}{2}) = v(t) + \frac{\Delta t}{2}\frac{f}{m}$

R $\quad r(t+\frac{\Delta t}{2}) = r(t) + \frac{\Delta t}{2} v(t+\frac{\Delta t}{2})$

R $\quad r(t+\Delta t) = r(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2} v(t+\frac{\Delta t}{2})$

← Evaluate Force!

V $\quad v(t+\Delta t) = v(t+\frac{\Delta t}{2}) + \frac{\Delta t}{2}\frac{f}{m}$

time ←

$$V \quad R \quad R \quad V \quad \underbrace{V \quad R \quad \overbrace{R \quad V}^{\text{position verlet}}}_{\text{velocity verlet}} \quad V \quad R \quad R$$

- Time Symmetric
- Symplectic (Conserves phase space!) Hamiltonian dynamics

[Discussion → Anomalies]

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Shadow Work

Shadow Hamiltonian $H^s \approx H^0 + O(\Delta t^3)$ (?)

MD

E_s shadow Energy conserved

Energy of system (with H^0) fluctuates

$$W_s^{shadow} = H[v(t), r(t)] - H[v(0), r(0)]$$

(David Sivak)

Metropolize