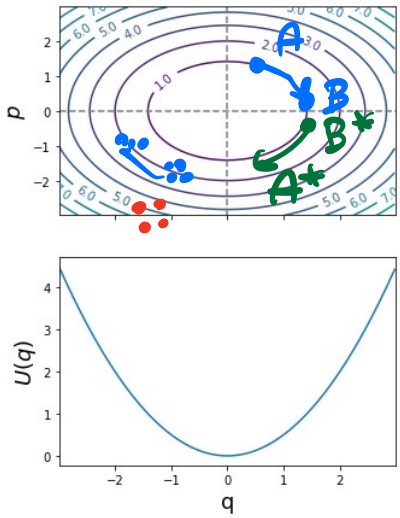
- MOLECULAR DYNAMICS
  - INTEGRATORS
  - THERMOSTATS
  - ENHANCED SAMPLING

q_i , p_i $\quad H(q,p)$

$$\rightarrow \begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} = \dfrac{\partial K}{\partial p_i} = \dfrac{p_i}{m_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} = -\dfrac{\partial U}{\partial q_i} \end{cases}$$

$$H = K(p) + U(q) = \sum_i \frac{p_i^2}{2m_i} + U(q)$$

1. TIME REVERSIBILITY
2. ENERGY CONSERVED
3. INCOMPRESSIBILITY



TROTTER SPLITTING

$$\begin{cases} \dot{q} = \frac{p}{m} \\ \dot{p} = f(q) \end{cases} = \begin{cases} \dot{q} = \frac{p}{m} \\ \dot{p} = 0 \end{cases} + \begin{cases} \dot{q} = 0 \\ \dot{p} = f(q) \end{cases}$$

$U = 0$ $\qquad$ $K = 0$

$$q(t+\Delta t) = q(t) + \frac{p}{m}\Delta t$$

$$p(t+\Delta t) = p(t) + f(q)\Delta t$$

	1.	2.	3.
$\frac{1}{2}$	✗	✗	✓
1	✓	✗	✗
$\frac{1}{2}$			

$\frac{1}{2}$ 1 $\frac{1}{2}$ V X V

VELOCITY VERLET

for i in range(nsteps):

$p+ = \frac{f}{2}\Delta t$

$q+ = \frac{p}{m}\Delta t$

$f = force(q)$

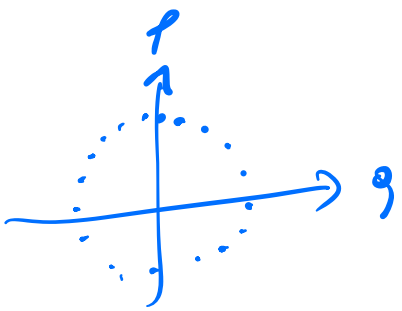
$p+ = \frac{f}{2}\Delta t$

ENSEMBLES

2. EN. CONSERVATION
+ 3. INCOMPRESSIBILITY

MICROCANONICAL

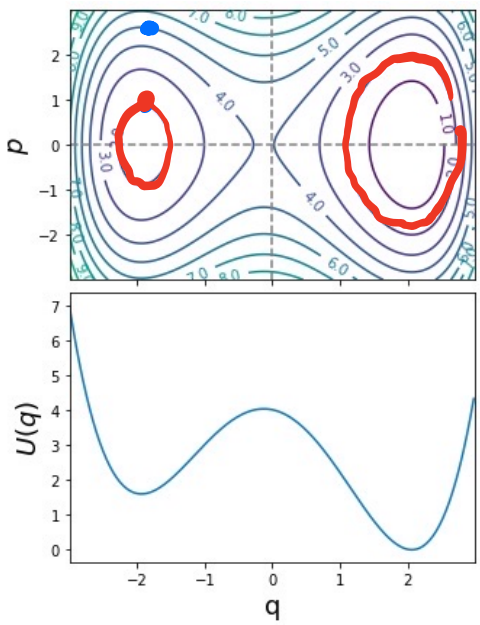
$P(p,q) \propto \delta(H(p,q) - E_0)$



1. STATIONARITY

2. + ERGODICITY

$$= \int dp\,dq\; P(p,q)\, O(q,p) = \frac{1}{\tau}\int_0^{\tau} dt\; O(t)$$

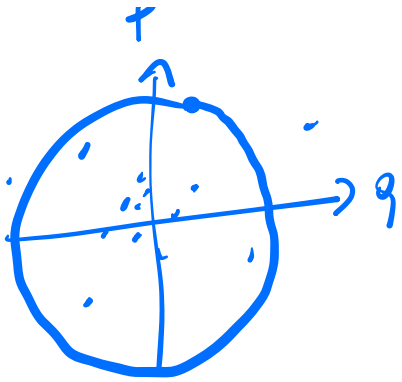


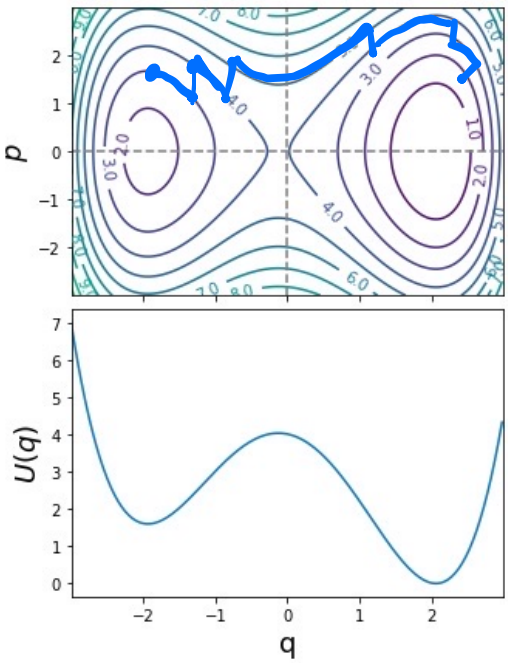
CANONICAL NVT

$$P(q,p) \propto e^{-\beta H(q,p)}$$

$$\beta = \frac{1}{k_B T}$$

$$P(q,p) \propto f(H(q,p))\; e^{-\beta H(q,p)}$$





- CONFIGURATIONAL
- KINETIC
  - LOCAL
  - GLOBAL

LANGEVIN

$$P(p,q) \propto e^{-\beta K} e^{-\beta U}$$

$$e^{-\sum_i \frac{p_i^2}{2m_i k_B T}}$$

$$p = c_1 p + c_2 \sqrt{m k_B T} * \text{normal}()$$

$$c_1^2 + c_2^2 = 1 \qquad c_1 = e^{-\gamma \Delta t}$$

$$c_1 \sim 1 - \gamma \Delta t$$

$$c_2 = \sqrt{1 - c_1^2} \sim \sqrt{2\gamma \Delta t}$$

$$\Delta p = -\gamma p \Delta t + \sqrt{2\gamma m k_B T}\, \sqrt{\Delta t} * \text{normal}()$$

$$dp = -\gamma p\, dt + \sqrt{2\gamma m k_B T}\, dW$$

ITO FORMALISM

for i in ... :

$p = c_1 p + c_2 \sqrt{\quad} * \text{normal}()$

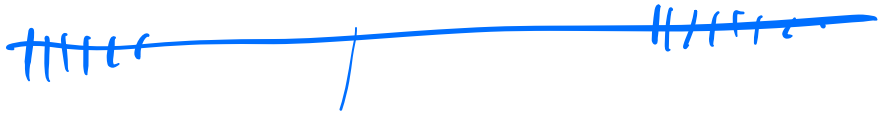
$p \mathrel{+}= \frac{f}{2} \Delta t$

$q \mathrel{+}= \frac{p}{m} \Delta t$

$p \mathrel{+}= \frac{f}{2} \Delta t$

$p = c_1 p + c_2 \sqrt{\quad} * \text{normal}()$

$c_1 = e^{-\gamma \frac{\Delta t}{2}}$



GLOBAL

$p \leftarrow \alpha p \qquad \alpha = \sqrt{\frac{K_{NEW}}{K_{CURRENT}}}$

$p_i' = c_1 p_i + c_2 \sqrt{m_i k_B T}\, R_i$

$\frac{p_i'^2}{2m_i} = \frac{c_1^2 p_i^2 + c_2^2 m k_B T R_i^2 + c_1 c_2 p_i \sqrt{m k_B T}\, R_i}{2m_i}$ ($R_i^2 \to 1$ ONLY FOR $\Delta t \to 0$)

$\sum_i \frac{p_i'^2}{2m_i} = \sum_i \frac{p_i^2}{2m_i}$

$K' = K$

$$K' = c_1^2 K + c_2^2 N_f \frac{k_B T}{2} + c_1 c_2 \sqrt{k_B T}\sqrt{2K}\,R$$

$c_1 \sim e^{-2\gamma \Delta t}$

$\bar{K} = \frac{N_f}{2} k_B T$

$$dK = -2\gamma(K - \bar{K})\,dt + \sqrt{\frac{8 K \bar{K} \gamma}{N_f}}\,dW$$

$\gamma = \frac{1}{2\tau}$

$$\boxed{dK = -\frac{K - \bar{K}}{\tau}\,dt + \sqrt{\frac{4K\bar{K}}{\tau N_f}}\,dW}$$

STOCHASTIC VELOCITY RESCALING

BERENDSEN

	L/G	S/D	OK
LANGEVIN	L	S	✓
SVR	G	S	✓
BERENDSEN	G	D	✗
ANDERSEN	L	S	✓
NOSE-HOOVER	G/L	D	✓*
" " CHAINS	G/L	D	✓

COLLECTIVE VARIABLES

plumed.org/masterclass