COMPUTATIONAL PHYSICS : MOLECULAR DYNAMICS SIMULATION

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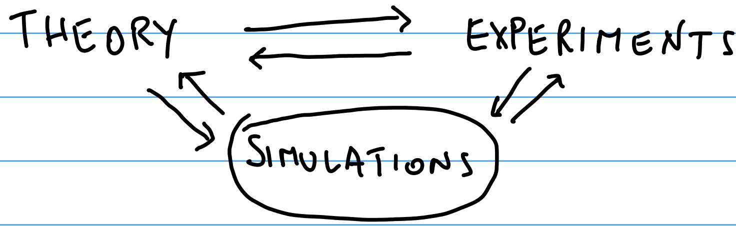
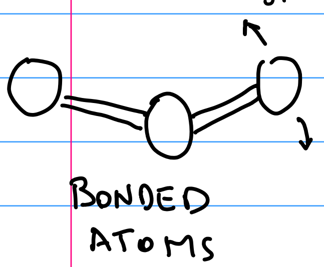


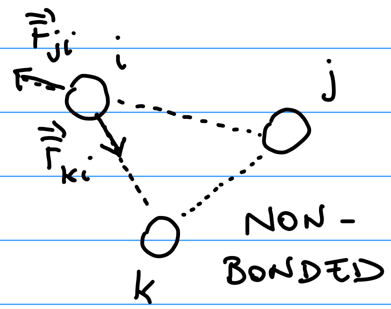
MONTE CARLO : STOCHASTIC METHOD

MOLECULAR DYNAMICS : DETERMINISTIC METHOD TO SOLVE CLASSICAL EQUATIONS OF MOTION

$$m_i \vec{a}_i = \vec{F}_i \qquad i = 1, 2, 3, \ldots, N$$

$$\vec{F}_i = \sum_{j \neq i} \vec{F}_{ji}$$





POTENT. ENERGY

$$V(\vec{r}_1, \ldots, \vec{r}_N) = \sum_{i \neq j} \varphi(|\vec{r}_i - \vec{r}_j|)$$

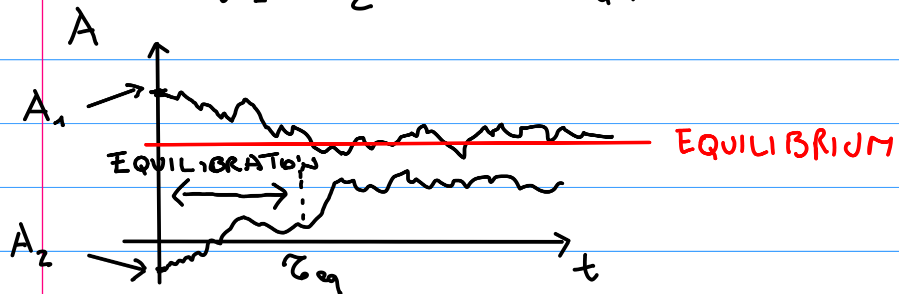
$$\boxed{m_i \ddot{\vec{r}}_i(t) = \vec{F}_i(\vec{r}_1, \ldots, \vec{r}_N)}$$

DISCRETE TIME STEP Δt

$$\begin{matrix} \vec{r}_i(t) \\ \vec{v}_i(t) \end{matrix} \xrightarrow{MD} \begin{matrix} \vec{r}_i(t+\Delta t) \\ \vec{v}_i(t+\Delta t) \end{matrix}$$

OBSERVABLES $\quad A(\vec{r}_1, \ldots \vec{r}_N, \vec{v}_1, \ldots \vec{v}_N)$

$K = \sum_{i=1}^{N} \frac{m_i \vec{v}_i^{\,2}}{2}$ KINETIC ENERGY $\qquad V(\vec{r}_1, \ldots, \vec{r}_N)$ POTENTIAL ENERGY



$$\langle A \rangle_{eq} = \frac{1}{M} \sum_{m=1}^{M} A(t_0 + m\Delta t)$$

2

VERLET ALGORITHM

$$\vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)\Delta t^2 + \frac{1}{6}\vec{g}_i(t)\Delta t^3 + O(\Delta t^4)$$

$$\vec{r}_i(t-\Delta t) = \vec{r}_i(t) - \vec{v}_i(t)\Delta t + \frac{1}{2}\vec{a}_i(t)\Delta t^2 - \frac{1}{6}\vec{g}_i(t)\Delta t^3 + O(\Delta t^4)$$

SUM UP:

VERLET ALGORITHM

$$\boxed{\vec{r}_i(t+\Delta t) = 2\vec{r}_i(t) - \vec{r}_i(t-\Delta t) + \vec{a}_i(t)\Delta t^2 + O(\Delta t^4)}$$

$$\vec{a}_i(t) = \frac{1}{m_i}\vec{F}_i(\vec{r}_1(t), \vec{r}_2(t), \dots \vec{r}_N(t))$$

$$\begin{matrix}\vec{r}_i(t) \\ \vec{r}_i(t-\Delta t)\end{matrix} \longrightarrow \vec{r}_i(t+\Delta t)$$

NO VELOCITIES !

$$\vec{v}_i(t) = \frac{\vec{r}_i(t) - \vec{r}_i(t-\Delta t)}{\Delta t}$$

THE VELOCITY VERLET ALGORITHM

VELOCITY VERLET ALGORITHM

$$\boxed{\begin{cases} \vec{r}_i(t+\Delta t) = \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{\vec{a}_i(t)}{2}\Delta t^2 & (1) \\ \vec{v}_i(t+\Delta t) = \vec{v}_i(t) + \frac{\vec{a}_i(t) + \vec{a}_i(t+\Delta t)}{2}\Delta t & (2) \end{cases}}$$

THIS REPRODUCES EXACTLY VERLET (SEE LECTURE NOTES)

a) IMPLEMENT (1) $\vec{r}_i(t) \longrightarrow \vec{r}_i(t+\Delta t)$

b) $\vec{v}_i\left(t+\frac{\Delta t}{2}\right) = \vec{v}_i(t) + \frac{\vec{a}_i(t)}{2}\Delta t$

c) CALCULATE $\vec{a}_i(t+\Delta t)$ FROM $\vec{r}_i(t+\Delta t)$

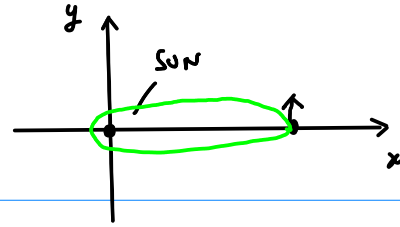
d) FINAL UPDATE $\vec{v}_i(t+\Delta t) = \vec{v}_i\left(t+\frac{\Delta t}{2}\right) + \frac{\vec{a}_i(t+\Delta t)}{2}\Delta t$

$\Longrightarrow$ APPROXIMATING EQ. (2) WITH $\vec{v}_i(t+\Delta t) \approx \vec{v}_i(t) + \vec{a}_i(t)\Delta t$ IS A VERY BAD IDEA

CHECK CONSERVATION OF TOTAL ENERGY $E = K + V$ MUST BE (ALMOST) CONSTANT IN TIME

VELOCITY VERLET IS A SYMPLECTIC ALGORITHM

TIPS ABOUT MD



Problem 13.1 - Halley's comet

① RESCALE UNITS

$$\cancel{m}\frac{d^2\vec{r}}{dt^2} = -\frac{GM\cancel{m}}{r^3}\vec{r}$$

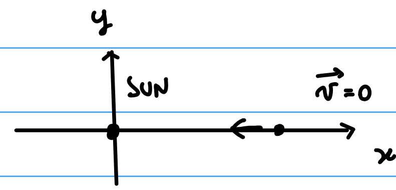
1 YEAR $\quad T = 3.156 \cdot 10^7\,s$

AU. $\quad L = 1.50 \cdot 10^{11}\,m$

$$\frac{1}{T^2}\frac{d^2\vec{R}}{d\tau^2} = -\frac{GM}{L^3R^3}\vec{R}$$

$$\frac{d^2\vec{R}}{d\tau^2} = -\Gamma\frac{\vec{R}}{R^3} \qquad \Gamma \simeq 39$$

② CHECK SIMPLER INITIAL CONDITION



CHECK ENERGY CONSERVATION

③ MINIMIZE THE NUMBER OF CALCULATIONS

SYMPLECTIC ALGORITHMS

HAMILTONIAN MECHANICS

$$\boxed{m\ddot{\vec{r}}_i = \vec{F}_i} \implies \text{HAMILTON}$$

$H = T + V$

$H(\vec{p}_i, \vec{q}_i) \qquad \vec{p} = m\vec{v}$

1D PARTICLE $\quad p, q \quad H(q,p)$

$$\boxed{\dot{q} = \frac{\partial H}{\partial p} \qquad \dot{p} = -\frac{\partial H}{\partial q}}$$

HAMILTONIAN

$$H = \frac{p^2}{2m} + V(q)$$

KINETIC ENERGY $\qquad$ POTENTIAL ENERGY

$$\dot{q} = \frac{p}{m} \qquad \dot{p} = -\frac{\partial V}{\partial q} = F$$

$\Downarrow$

$$\dot{p} = m\ddot{q} \qquad m\ddot{q} = F$$

NEWTON'S EQ.

$f(q,p) \quad g(q,p)$

POISSON BRACKET

$$\{f,g\} \stackrel{\text{def}}{=} \frac{\partial f}{\partial q}\frac{\partial g}{\partial p} - \frac{\partial f}{\partial p}\frac{\partial g}{\partial q}$$

$$\dot{q} = \{q,H\} \qquad \dot{p} = \{p,H\} \qquad z = (q,p) \qquad \dot{z} = \{z,H\} = D_H z$$

LINEAR

FORMAL $\quad z(t) = e^{tD_H}\,z(0)$

APPLY TO A SHIFT Δt

$$z(t+\Delta t) = e^{\Delta t D_H} z(t) \qquad H = T + V$$

$$D_H z = \{z, H\} = \{z, T+V\} = \{z,T\} + \{z,V\} = D_T z + D_V z$$

$$e^{\Delta t D_H} = e^{\Delta t (D_T + D_V)}$$

FOR COMPLEX NUMBERS
(FOR COMMUTING VARIABLES)

$$e^{x+y} = e^x e^y = e^y e^x$$

$$e^{\varepsilon(A+B)} = \sum_{m=0}^{+\infty} \frac{\varepsilon^m (A+B)^m}{m!}$$

$\varepsilon = \Delta t$ (SMALL QUANTITY)

EXACT EVOLUTION

$$e^{\varepsilon(A+B)} = 1 + \varepsilon(A+B) + \frac{\varepsilon^2}{2}(A+B)^2 + \mathcal{O}(\varepsilon^3)$$

$$(A+B)^2 = (A+B)(A+B) = A^2 + AB + BA + B^2$$

$$= 1 + \varepsilon(A+B) + \frac{\varepsilon^2}{2}(A^2 + \underline{AB + BA} + B^2) + \mathcal{O}(\varepsilon^3)$$

APPROX. 1

$$e^{\varepsilon A} e^{\varepsilon B} = \left(1 + \varepsilon A + \frac{\varepsilon^2}{2} A^2\right)\left(1 + \varepsilon B + \frac{\varepsilon^2}{2} B^2\right) + \mathcal{O}(\varepsilon^3)$$

$$= 1 + \varepsilon(A+B) + \frac{\varepsilon^2}{2}(A^2 + B^2 + \underline{2AB}) + \mathcal{O}(\varepsilon^3)$$

APPROX. 2

$$e^{\frac{\varepsilon}{2}A} e^{\varepsilon B} e^{\frac{\varepsilon}{2}A} = \dots = 1 + \varepsilon(A+B) + \frac{\varepsilon^2}{2}(A^2 + \underline{AB + BA} + B^2) + \mathcal{O}(\varepsilon^3)$$

$$e^{\varepsilon(A+B)} = e^{\varepsilon A} e^{\varepsilon B} + \mathcal{O}(\varepsilon^2) = e^{\varepsilon B} e^{\varepsilon A} + \mathcal{O}(\varepsilon^2)$$

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

....

APPROX. 1

$$z(t+\Delta t) = e^{\Delta t (D_V + D_T)} z(t) \approx e^{\Delta t D_V} e^{\Delta t D_T} z(t)$$

$z \equiv (q, p)$

$$e^{\Delta t D_T} q(t) = \left(1 + \Delta t D_T + \overline{\frac{\Delta t^2}{2} D_T^2 + \dots}\right) q(t) \overset{\text{EXACT}}{=} \left(1 + \Delta t D_T\right) q(t)$$

$$D_T q = \{q, T\} = \left\{q, \frac{p^2}{2m}\right\} = \frac{\partial q}{\partial q} \frac{\partial}{\partial p} \frac{p^2}{2m} = \frac{p}{m}$$

$$D_T^2 q = D_T(D_T q) = D_T \frac{p}{m} = \left\{\frac{p}{m}, T\right\} = \left\{\frac{p}{m}, \frac{p^2}{2m}\right\} = 0 \qquad \underset{n \geq 2}{D_T^n q = 0}$$

$$e^{\Delta t D_T} q(t) = \left(1 + \Delta t D_T\right) q(t) = q(t) + \Delta t \frac{p(t)}{m}$$

$$q(t+\Delta t) = e^{\Delta t D_V}\left(e^{\Delta t D_T} q(t)\right) = e^{\Delta t D_V}\left(q(t) + \Delta t \frac{p(t)}{m}\right) =$$

$$= \left(1 + \Delta t D_V\right)\left(q(t) + \Delta t \frac{p(t)}{m}\right) = q(t) + \Delta t \frac{p(t)}{m} + \cancel{\Delta t D_V q(t)} + \frac{\Delta t^2}{m} D_V p(t)$$

$$D_V p(t) = \{p, V\} = \cancel{\frac{\partial p}{\partial q} \frac{\partial V}{\partial p}} - \frac{\partial p}{\partial p} \frac{\partial V}{\partial q} = -\frac{\partial V}{\partial q} = F(q)$$

$$(1) \quad q(t+\Delta t) = q(t) + \Delta t \frac{p(t)}{m} + \Delta t^2 \frac{F(q(t))}{m}$$

$$(2) \quad p(t+\Delta t) = e^{\Delta t D_V} e^{\Delta t D_T} p(t) = e^{\Delta t D_V} p(t) = \left(1 + \Delta t D_V\right) p(t)$$

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

$$v \equiv \frac{p}{m}$$

REWRITE (1) & (2) AS FUNCTIONS OF q AND v

$$(1) \quad q(t+\Delta t) = q(t) + \Delta t\, v(t) + \Delta t^2 a(q(t)) \overset{\text{Eq.(2)}}{=} q(t) + \cancel{\Delta t\, v(t)} + \Delta t\left(v(t+\Delta t) - \cancel{v(t)}\right)$$

$$(2) \quad v(t+\Delta t) = v(t) + \Delta t\, a(q(t))$$

$$= q(t) + \Delta t\, v(t+\Delta t)$$

FIRST ORDER SYMPLECTIC INTEGRATOR

$$\begin{cases} q(t+\Delta t) = q(t) + \Delta t\, v(t+\Delta t) \\ v(t+\Delta t) = v(t) + \Delta t\, a(q(t)) \end{cases}$$

PROBLEM 2 USES THIS FOR HARMONIC OSCILLATOR

$k = m = 1 \qquad F = -kq$

$$a = \frac{F}{m} = -\frac{k}{m} q$$

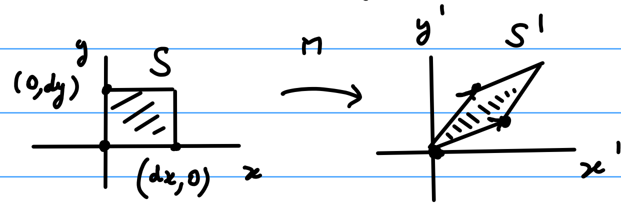
FOR HARMONIC OSCILLATOR THIS BECOMES A LINEAR SYSTEM

$$\begin{pmatrix} q(t+\Delta t) \\ v(t+\Delta t) \end{pmatrix} = M \begin{pmatrix} q(t) \\ v(t) \end{pmatrix}$$

PROPERTY OF SYMPLECTIC ALGORITHM: VOLUME IN PHASE SPACE IS CONSERVED

FIRST SIMPLE EXAMPLE ON LINEAR MAP (2D)

$$M = \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}$$



$$\begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}\begin{pmatrix} dx \\ 0 \end{pmatrix} = \begin{pmatrix} \alpha\, dx \\ \gamma\, dx \end{pmatrix} \qquad \begin{pmatrix} \alpha & \beta \\ \gamma & \delta \end{pmatrix}\begin{pmatrix} 0 \\ dy \end{pmatrix} = \begin{pmatrix} \beta\, dy \\ \delta\, dy \end{pmatrix}$$

$S: \ dx dy$

$$\hat{x} \times \hat{y} = \hat{z} \qquad \hat{x}\times\hat{x} = \hat{y}\times\hat{y} = 0$$
$$\hat{y} \times \hat{x} = -\hat{z}$$

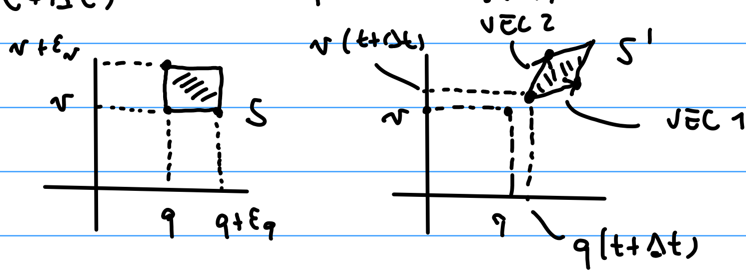
$$(\alpha dx, \gamma dx) \times (\beta dy, \delta dy) = \alpha\delta\, dxdy\, \hat{z} - \gamma\beta\, dxdy\, \hat{z}$$

$$S': \ \left| \alpha\delta\, dxdy - \gamma\beta\, dxdy \right| = \underbrace{|\alpha\delta - \gamma\beta|}_{\det M} dx\, dy$$

$$\det M = \underbrace{\lambda_1 \lambda_2}_{\text{eigenvalues}} = \pm 1$$

THIS IS ALSO VOLUME PRESERVING

$$q(t+\Delta t) = q(t) + \Delta t\, v(t) + \Delta t^2 a(q(t))$$
$$v(t+\Delta t) = v(t) + \Delta t\, a(q(t))$$



$$(q, v) \longrightarrow (q + \Delta t\, v + \Delta t^2 a(q),\ v + \Delta t\, a(q))$$
$$(q+\varepsilon_q, v) \longrightarrow (q + \varepsilon_q + \Delta t\, v + \Delta t^2 a(q+\varepsilon_q),\ v + \Delta t\, a(q+\varepsilon_q))$$
$$(q, v+\varepsilon_v) \longrightarrow (q + \Delta t\,(v+\varepsilon_v) + \Delta t^2 a(q),\ v + \varepsilon_v + \Delta t\, a(q))$$

$$\left| \left(\varepsilon_q + \Delta t^2 \left[a(q+\varepsilon_q) - a(q)\right],\ \Delta t\left[a(q+\varepsilon_q) - a(q)\right]\right) \times \left(\Delta t\, \varepsilon_v, \varepsilon_v\right) \right| =$$

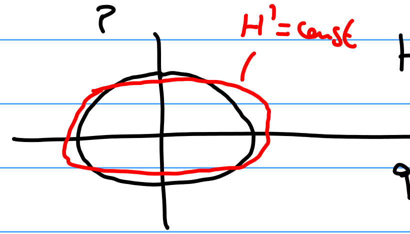
$$= \left| \varepsilon_q \varepsilon_v + \cancel{\varepsilon_v \Delta t^2 [\ldots]} - \cancel{\Delta t^2 \varepsilon_v [\ldots]} \right| = \varepsilon_q \varepsilon_v$$

RELATED TO THIS THERE IS A CONSERVED QUANTITY

IN HAMILTONIAN DYNAMICS $H = T + V$

IN SYMPLECTIC ALGORITHMS H' (PSEUDO-HAMILTONIAN)

$$H' = H + O(\Delta t^m)$$

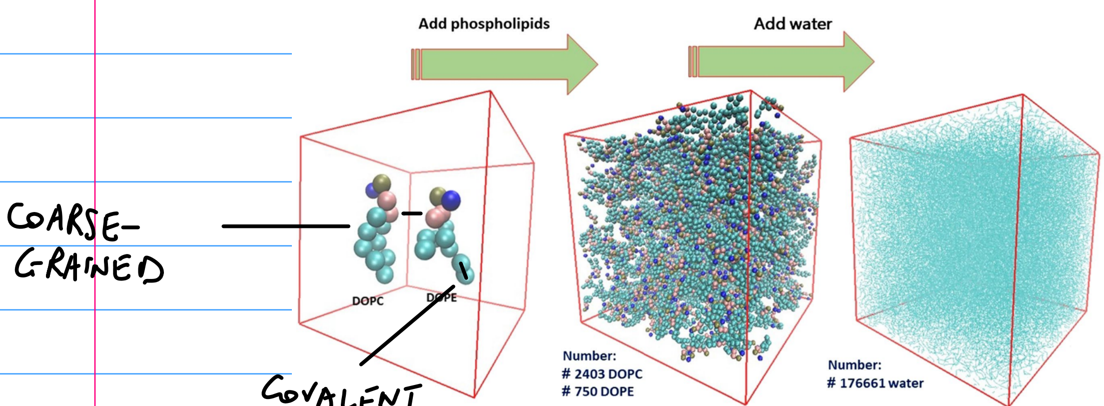


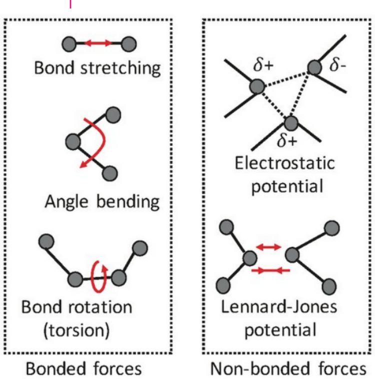
$$H = \frac{p^2}{2m} + \frac{m\omega^2}{2} q^2$$

1 October 2025

FORCE FIELDS

$$m_i \vec{a}_i = \vec{F}_i = \sum_{j \neq i} \vec{F}_{ji} = -\vec{\nabla}_i V(\vec{r}_1, \dots, \vec{r}_N)$$

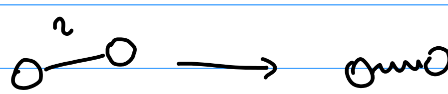




$$V(\vec{r}_1, \dots, \vec{r}_N) = V_{bonded}(\vec{r}_1, \dots, \vec{r}_N) + V_{non-bonded}(\vec{r}_1, \dots, \vec{r}_N)$$

A) $\boxed{\text{BONDED INTERACTIONS}}$

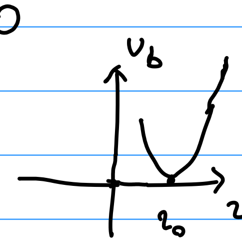
1 MOLECULAR BONDS



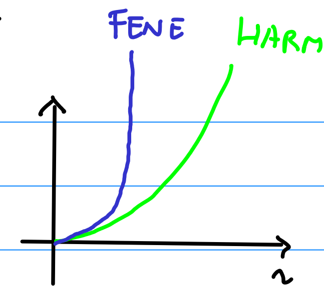
r_0 REST LENGTH

HARMONIC POTENTIAL $V_b = \frac{k_b}{2} (r - r_0)^2 + \dots$

POSSIBLY ANHARMONIC TERMS COULD BE ADDED



FENE: <u>F</u>INITE <u>E</u>XTENSIBLE <u>N</u>ON-LINEAR <u>E</u>LASTIC



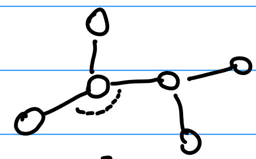
$$V_{FENE} = -\frac{k_F}{2} b^2 \log\left(1 - \frac{r^2}{b^2}\right)$$

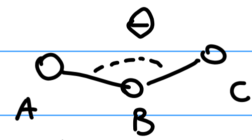
b IS A LENGTH $\quad r \ll b \quad V_{FENE} \approx \frac{k_F \cancel{b^2}}{2} \frac{r^2}{\cancel{b^2}}$

r CANNOT EXCEED b

C − C $\quad$ O − O $\quad$ .... $\quad$ A − B $\quad$ FOR EACH k_b, r_0

② ANGLES

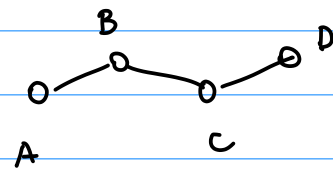




$$V_{angle} = \frac{K_a}{2}(\theta - \theta_0)^2$$

$$\cos\theta = \frac{\vec{AB} \cdot \vec{BC}}{|\vec{AB}|\,|\vec{BC}|}$$

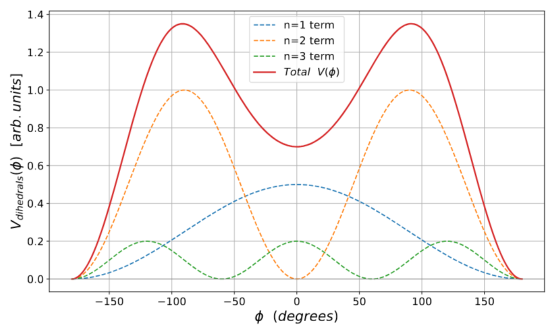
③ DIHEDRAL ANGLES

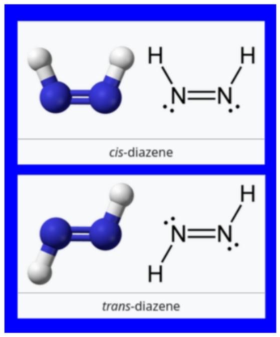


$$\left.\begin{array}{ll} ABC & \text{PLANE} \\ BCD & \text{PLANE} \end{array}\right\} \varphi \text{ ANGLE BETWEEN PLANES}$$

$$\cos\varphi = \frac{(\vec{AB} \times \vec{BC}) \cdot (\vec{BC} \times \vec{CD})}{|\vec{AB} \times \vec{BC}|\,|\vec{BC} \times \vec{CD}|}$$

$$V_{dih.} = \sum_m \frac{V_m}{2}\left[1 + \cos(m\varphi - \gamma_m)\right]$$





$m = 1, 2, 3$

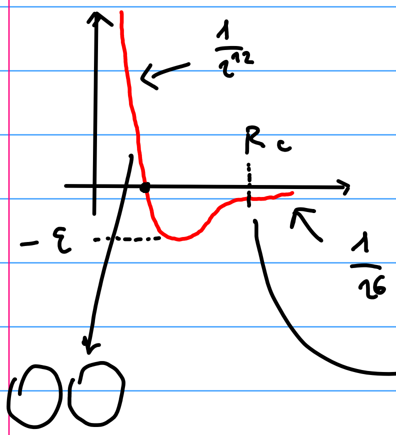
$V_1 = 0{,}5 \qquad \gamma_1 = 0$

$V_2 = 1 \qquad \gamma_2 = 180°$

$V_3 = 0{,}2 \qquad \gamma_3 = 0$

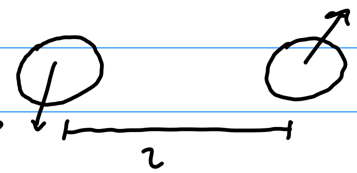
NON-BONDED INTERACTIONS

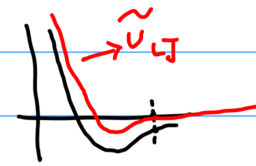
① LENNARD-JONES $\quad U_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$



AT LARGE DISTANCES $\sim \frac{1}{r^6}$ ATTRACTION

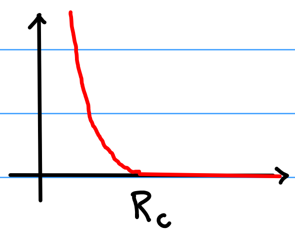
VAN DER WAALS INTERACTION



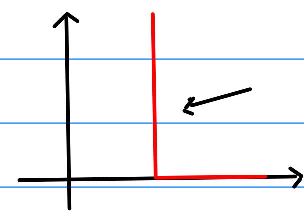


OFTEN TRUNCATED $\quad \tilde{V}_{LJ} = \begin{cases} V_{LJ}(r) - V_{LJ}(R_c) & r \leq R_c \\ 0 & r > R_c \end{cases}$

TRUNCATION AT MINIMUM (ALSO CALLED WCA)



SOFT REPULSIVE POTENTIAL



HARD SPHERES

② CHARGED SYSTEM $\quad i \underset{-}{O} \quad \underset{+}{O}\, j \quad U_{coul} = \frac{1}{4\pi\varepsilon}\frac{q_i q_j}{r_{ij}}$

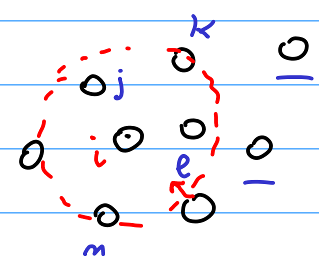
ADVANCED SCHEMES TO DEAL WITH $1/r$ INTERACTION

PARAMETRIZATION $\quad$ LJ ε, σ $\quad U_b \quad k_b, r_0$

SIMULATIONS ON A FEW WELL STUDIED EXPERIM SYSTEM FOR WHICH QM CALCULATIONS ARE AVAILABLE ARE USED TO FIX PARAMETERS

PERIODICALLY REVISED USING MORE EXPT. AND QUANTUM CHEMISTRY COMPUTATIONS

USE LISTS OF INTER. PARTICLES

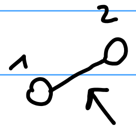


"MEASURING"

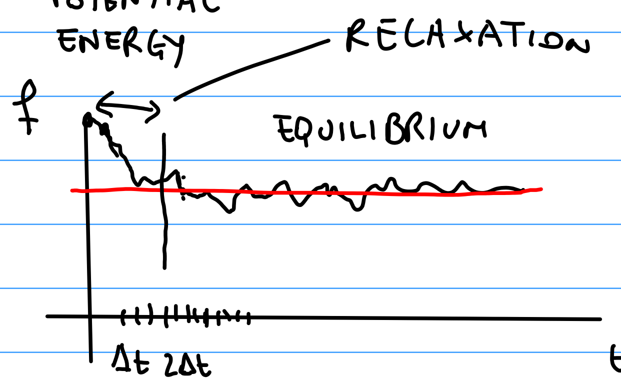
$f(\vec{r}_1, \dots, \vec{r}_N, \vec{v}_1, \dots, \vec{v}_N)$ OBSERVABLE

$$K_{TOT} = \sum_i \frac{m_i \vec{v}_i^{\,2}}{2}$$

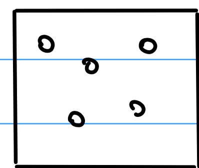
U_{TOT} POTENTIAL ENERGY



$$r(t) = |\vec{r}_1(t) - \vec{r}_2(t)|$$



TEMPERATURE ?



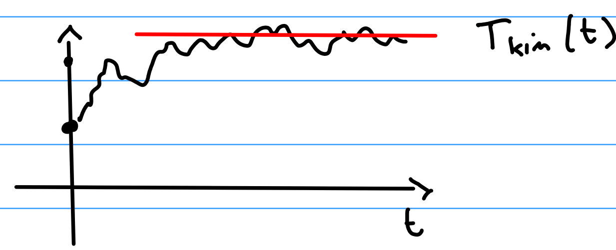
SAY LJ PARTICLES

STAT. MECH. (EQUIPARTITION THEOREM)

$$\left\langle \sum_i \frac{m_i \vec{v}_i^{\,2}}{2} \right\rangle = \frac{3}{2} N k_B T$$

WE CAN USE THIS TO DEFINE A KINETIC TEMPERATURE

$$T_{kin}(t) = \frac{1}{3 N k_B} \sum_i m_i \vec{v}_i^{\,2}(t)$$



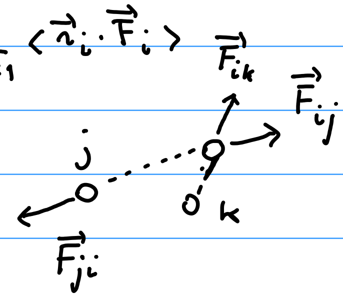
PRESSURE ?

VIRIAL THEOREM
EQ. STAT. MECH.

$$PV = N k_B T + \frac{1}{3} \sum_{i=1}^{N} \langle \vec{r}_i \cdot \vec{F}_i \rangle$$

$$\vec{F}_i = \sum_{j \neq i} \vec{F}_{ji}$$

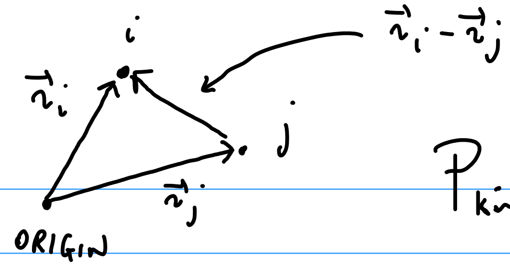
3^{rd} LAW $\boxed{\vec{F}_{ij} = -\vec{F}_{ji}}$



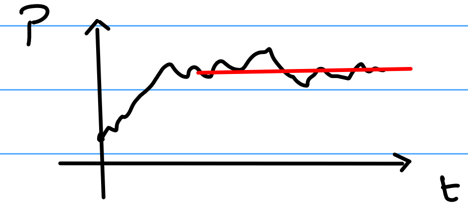
$$P_{kin}(t) = \frac{N k_B}{V} T_{kin}(t) + \frac{1}{3V} \sum_{i=1}^{N} \vec{r}_i(t) \cdot \vec{F}_i(t)$$

$$\sum_i \vec{r}_i \cdot \vec{F}_i = \sum_{ij} \vec{r}_i \cdot \vec{F}_{ij} = \frac{1}{2} \sum_{ij} \left(\vec{r}_i \cdot \vec{F}_{ij} + \vec{r}_j \cdot \underbrace{\vec{F}_{ji}}_{= -\vec{F}_{ij}} \right)$$

$$= \frac{1}{2} \sum_{ij} (\vec{r}_i - \vec{r}_j) \cdot \vec{F}_{ij}$$



$$P_{kin}(t) = \frac{N k_B}{V} T_{kin}(t) - \frac{1}{6} \sum_{i \neq j} \left\langle r_{ij} \frac{dV}{dr_{ij}} \right\rangle$$

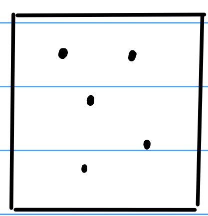


15 October 2025

SIMULATIONS AT CONSTANT TEMPERATURE

NVE ENSEMBLE

OR MICROCANONICAL



N PARTICLES

V VOLUME

E ENERGY

$\left.\begin{array}{l}\vec{r}_i(0)\\ \vec{v}_i(0)\end{array}\right]$ FIXES E

P & T CAN BE DETERMINED FROM FORMULAS FROM LAST PAG.

CANONICAL ENSEMBLE

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

$\vec{v} = (v_x, v_y, v_z)$

V, N, T

$$p(\vec{v}) = \dots\; e^{-\frac{\beta m \vec{v}^2}{2}} = \dots\; e^{-\frac{\beta m v_x^2}{2}}\, e^{-\frac{\beta m v_y^2}{2}}\, e^{-\frac{\beta m v_z^2}{2}}$$

N_x, N_y, N_z STAT. INDEP.

$v = |\vec{v}|$

SPEED 3D

$$g(v) = \dots\; v^2 e^{-\frac{\beta m v^2}{2}}$$

$v = |\vec{v}| \geq 0$

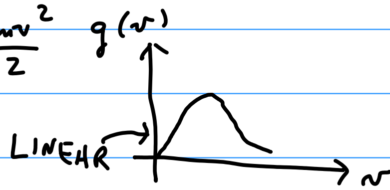
$\langle v_x \rangle = 0$

$\frac{m}{2}\langle v_x^2 \rangle = \frac{k_B T}{2}$

3D: $\frac{m\langle \vec{v}^2 \rangle}{2} = \frac{3}{2} k_B T$

2D

$$g(v) = \dots\; v\, e^{-\frac{\beta m v^2}{2}}$$



$$p(\vec{r}_1, \dots \vec{r}_N, \vec{v}_1 \dots \vec{v}_N) = \dots\; e^{-\beta \sum_i \frac{m_i \vec{v}_i^2}{2}}\, e^{-\beta \Phi(\vec{r}_1 \dots \vec{r}_N)}$$

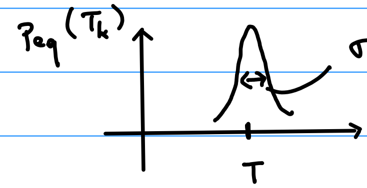
FOR GAUSSIAN $\quad p(x) = A\, e^{-\alpha x^2} \quad \langle \alpha x^2 \rangle = \frac{1}{2}$

KINETIC TEMPERATURE & EQUILIBRIUM STAT. MECH.

$$T_k(t) = \frac{1}{3N k_B} \sum_{i=1}^{N} m_i \vec{v}_i^{\,2}$$

$$\frac{m_i}{2} \langle \vec{v}_i^{\,2} \rangle = \frac{3}{2} k_B T \qquad \text{EQUIPARTITION}$$

$$\langle T_k \rangle = T$$



$$\sigma_{T_k} \sim \frac{1}{\sqrt{N}}$$

VARIANCE $\quad \sigma^2_{T_k} = \langle T_k^2 \rangle - \langle T_k \rangle^2 = \ldots\ldots = \frac{2}{3N} T^2$

USE : VARIANCE OF SUM OF IND. VARIABLES IS THE SUM OF VARIANCES

$$x \longrightarrow \sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2$$
$$y \longrightarrow \sigma_y^2 = \langle y^2 \rangle - \langle y \rangle^2$$

$$\langle xy \rangle \underset{\text{IND.}}{=} \langle x \rangle \langle y \rangle$$

$$\sigma^2_{x+y} = \langle (x+y)^2 \rangle - \langle (x+y) \rangle^2 = \langle x^2 + y^2 + 2xy \rangle - (\langle x \rangle + \langle y \rangle)^2 =$$
$$= \langle x^2 \rangle + \langle y^2 \rangle + 2\langle xy \rangle - \langle x \rangle^2 - \langle y \rangle^2 - 2\langle x \rangle \langle y \rangle$$
$$= \sigma_x^2 + \sigma_y^2 + \cancel{2\langle xy \rangle} - \cancel{2\langle x \rangle \langle y \rangle}$$

THERMOSTATS

* VELOCITY RESCALING

$$T_k(t) = \frac{1}{3N k_B} \sum_{i=1}^{N} m_i \vec{v}_i^{\,2}(t)$$

I WANT TO FIX $T = T_0$

AT TIME STEP t $\quad \vec{v}_i(t) \longrightarrow$ CALCULATE $T_k(t)$ AND $\lambda(t) = \sqrt{\dfrac{T_0}{T_k(t)}}$

$\xrightarrow[\text{RESCALE ALL VELOCITIES}]{}$ $\quad \vec{v}_i^{\,\prime}(t) = \lambda(t)\, \vec{v}_i(t) \longrightarrow$ EVOLVE TO $\vec{v}_i^{\,\prime}(t+\Delta t)$, $\vec{v}_i(t+\Delta t)$

THIS ENSURES $\quad T_k(t) = T_0$

⊕ EASY TO IMPLEMENT

⊖ NOT EXACT

* BERENDSEN THERMOSTAT

SCALE FACTOR $\lambda^2 = 1 + \frac{\Delta t}{\tau} \frac{T_0 - T_K(t)}{T_K(t)}$

TIME STEP OF VELOCITY VERLET

CHARACTERISTIC THERMOSTAT TIME

IF $\tau = \Delta t \Rightarrow \lambda^2 = \frac{T_0}{T_K(t)}$

IF $\tau \to \infty \Rightarrow \lambda^2 = 1$ NOT RESCALING

IF $T_K(t) > T_0$ $\lambda^2 < 1$
$T_K(t) < T_0$ $\lambda^2 > 1$

$\sigma^2_{T_K}$ CAN BE OBTAINED FROM SIMULATION DATA $\neq \frac{2}{3N} T_0^2$

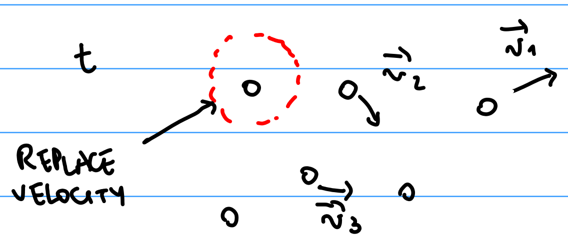
⊕ EQUALLY EASY AS VELOCITY RESCALING
⊕ ALLOWS FOR FLUCTUATIONS IN T_K
⊖ DOES NOT REPRODUCE CANONICAL DISTRIBUTION

* ANDERSEN THERMOSTAT

WE HAVE SEEN THAT IN EQUILIBRIUM VELOCITIES ARE GAUSSIAN DISTRIBUTED

$$p(v_x, v_y, v_z) = \ldots e^{-\beta \frac{m}{2} v_x^2} e^{-\beta \frac{m}{2} v_y^2} e^{-\beta \frac{m}{2} v_z^2}$$

- RUN VELOCITY VERLET
- SELECT SOME RANDOM PARTICLES
- SUBSTITUTE VELOCITIES WITH $\vec{v}$ SELECTED FROM p



IT DOES NOT REPRODUCE CANONICAL FLUCTUATIONS

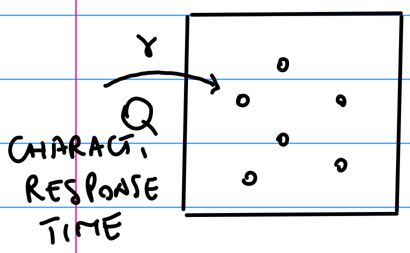
14

* NOSÉ – HOOVER THERMOSTAT

IDEA: COUPLE THE DYNAMICS TO ONE OR MORE ADDITIONAL DEGREES OF FREEDOM

E, N, V FIXED

$$\ddot{\vec{r}}_i = \frac{\vec{F}_i}{m_i} \quad \Longrightarrow \quad \begin{cases} \ddot{\vec{r}}_i = \dfrac{\vec{F}_i}{m_i} - \gamma \dot{\vec{r}}_i \\[2mm] \dot{\gamma} = \dfrac{1}{Q}\Big(\underbrace{\sum_i m_i \dot{\vec{r}}_i^{\,2}}_{2\cdot\text{KINETIC ENERGY}} - 3 N k_B T_0 \Big) \end{cases}$$



γ CAN HAVE BOTH SIGNS

IT CAN BE SHOWN REPRODUCES EXACTLY THE CANONICAL ENSEMBLE

SEE Book FRENKEL & SMIT "UNDERSTANDING MOLECULAR SIMULATIONS"

HERE $\sigma^2_{T_K} = \frac{2}{3N} T_0^2$

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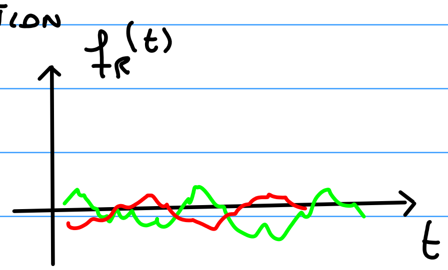
22 October 2025

LANGEVIN DYNAMICS

LARGE PARTICLE IMMERSED IN A "SOLVANT"

$$m\ddot{r} = \underbrace{F}_{\text{DETERMINISTIC FORCE}} - \underbrace{m\gamma\dot{r}}_{\text{FRICTION}} + \underbrace{f_R}_{\text{RANDOM FORCE}}$$

LANGEVIN EQUATION



→ $\langle f_R(t) \rangle = 0$

→ $\langle f_R(t) f_R(t') \rangle = 2A\,\delta(t-t')$

A: TEMPERATURE DEPENDENT

$$m\ddot{r} = \underset{\substack{\parallel \\ 0}}{F} - m\gamma\dot{r} + f_R$$

$\boxed{F=0}$

<u>LINEAR</u> FIRST SOLVE $\cancel{m}\dot{v} = -\cancel{m}\gamma v \Rightarrow v(t) = C e^{-\gamma t}$

VARIATION OF CONSTANT $v(t) = C(t)e^{-\gamma t}$

$$\dot{v} = -\gamma v + \frac{1}{m} f_R$$

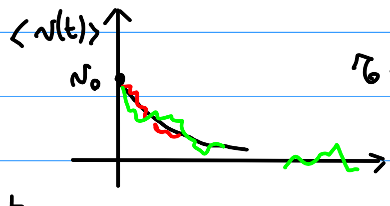
$$\dot{C} e^{-\gamma t} \cancel{-\gamma C e^{-\gamma t}} = \cancel{-\gamma C e^{-\gamma t}} + \frac{1}{m} f_R \qquad \dot{C} = \frac{e^{\gamma t}}{m} f_R$$

$$C(t) = C_0 + \frac{1}{m}\int_0^t e^{\gamma s} f_R(s)\, ds$$

$$\Rightarrow v(t) = v_0 e^{-\gamma t} + \frac{e^{-\gamma t}}{m}\int_0^t e^{\gamma s} f_R(s)\, ds \qquad v(0) = v_0$$

$$\langle v(t) \rangle = v_0 e^{-\gamma t}$$

REALIZATIONS OF f_R



$\tau = 1/\gamma$ RELAXATION TIME

$$\left\langle \left(v(t) - v_0 e^{-\gamma t}\right)^2 \right\rangle = \frac{e^{-2\gamma t}}{m^2}\int_0^t e^{\gamma(s+s')} \underset{\substack{\parallel \\ 2A\,\delta(s-s')}}{\langle f_R(s) f_R(s')\rangle}\, ds\, ds'$$

$$= 2A\frac{e^{-2\gamma t}}{m^2}\int_0^t e^{2\gamma s}\, ds = \cancel{2}A\frac{e^{-2\gamma t}}{m^2}\frac{1}{\cancel{2}\gamma}\left(e^{2\gamma t} - 1\right) = \frac{A}{m^2\gamma}\left(1 - e^{-2\gamma t}\right)$$

AT LONG TIMES $t \gg \frac{1}{\gamma} = \tau$ RELAXATION TIME

$$\langle v^2(t)\rangle = \frac{A}{m^2\gamma}$$

IN EQUILIBRIUM STAT. MECH. EQUIPARTITION HOLDS $\left\langle m\frac{v^2}{2}\right\rangle = \frac{k_B T}{2}$

Equip.

$$= \frac{k_B T}{m}$$

THIS FIXES $A \Rightarrow \boxed{A = m\gamma k_B T}$

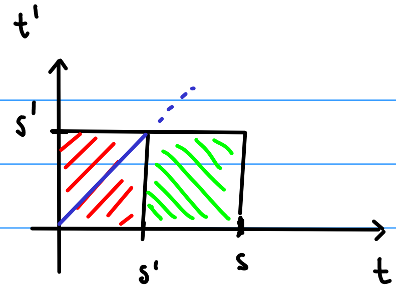
GIVEN $v(t)$ WE GET $x(t) = x_0 + \int_0^t v(s)\, ds$

MEAN SQUARED DISPLACEMENT

$$\left\langle (x(t) - x_0)^2 \right\rangle = \int_0^t \langle v(s) v(s')\rangle\, ds\, ds'$$

$$v(s) = v_0 e^{-\gamma s} + \frac{e^{-\gamma s}}{m}\int_0^s e^{\gamma t} f_R(t)\, dt$$

$$\langle v(s)v(s')\rangle = v_0^2 e^{-\gamma(s+s')} + \frac{e^{-\gamma(s+s')}}{m^2}\int_0^s dt \int_0^{s'} dt'\, e^{\gamma(t+t')} \underbrace{\langle f_R(t) f_R(t')\rangle}_{= 2m\gamma k_BT\,\delta(t-t')}$$

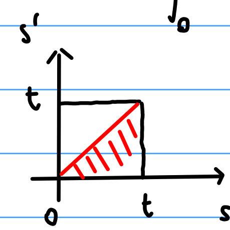


$$= v_0^2 e^{-\gamma(s+s')} + e^{-\gamma(s+s')}\frac{2\gamma k_BT}{m}\int_0^{\min(s,s')} dt\, e^{2\gamma t}$$

$$= v_0^2 e^{-\gamma(s+s')} + \frac{\cancel{2\gamma} k_BT}{m} e^{-\gamma(s+s')}\frac{1}{\cancel{2\gamma}}\left(e^{2\gamma \min(s,s')} - 1\right)$$

$$\langle v(s)v(s')\rangle = \left(v_0^2 - \frac{k_BT}{m}\right)e^{-\gamma(s+s')} + \frac{k_BT}{m}e^{-\gamma|s-s'|} \qquad s+s'-2\min(s,s') = |s-s'|$$

TIP $\int_0^t e^{-\gamma|s-s'|}ds\,ds' = 2\int_0^t ds\int_0^s ds'\, e^{-\gamma(s-s')}$



$$\langle (x(t)-x_0)^2\rangle = \int_0^t \langle v(s)v(s')\rangle\, ds\,ds' = \dots$$

$$= \left(v_0^2 - \frac{k_BT}{m}\right)\left(\frac{1-e^{-\gamma t}}{\gamma}\right)^2 + \frac{2k_BT}{m\gamma}\left[t - \frac{1}{\gamma}\left(1-e^{-\gamma t}\right)\right]$$

TWO LIMITS

$\gamma t \ll 1$ $\quad \langle (x(t)-x_0)^2\rangle \approx v_0^2 t^2$ BALLISTIC

$\gamma t \gg 1$ $\quad \langle (x(t)-x_0)^2\rangle \simeq \frac{1}{\gamma^2}\left(v_0^2 - \frac{k_BT}{m}\right) + \frac{2k_BT}{m\gamma}\left(t - \frac{1}{\gamma}\right) = \dots + \frac{2k_BT}{m\gamma}t$

↑ DOMINATES

DIFFUSIVE BEHAVIOR $\approx 2Dt$

$$\boxed{D = \frac{k_BT}{m\gamma}}$$ EINSTEIN RELATION

OVERDAMPED LIMIT OF LANGEVIN EQUATION

$$\underset{\downarrow\, 0}{\cancel{m\ddot{x}}} = F - m\gamma\dot{x} + f_R$$

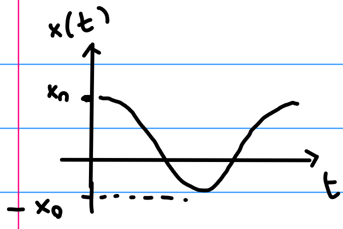
IF $F=0$ $\quad \dot{x} = \frac{1}{m\gamma}f_R \qquad x(t) = x_0 + \frac{1}{m\gamma}\int_0^t f_R(s)\,ds$

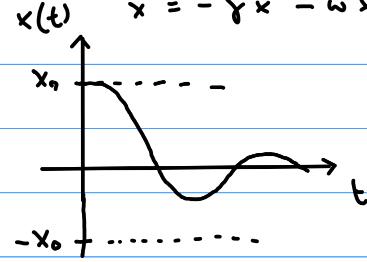
$$\langle (x(t)-x_0)^2\rangle = \frac{1}{m^2\gamma^2}\int_0^t \underbrace{\langle f_R(s) f_R(s')\rangle}_{= 2m\gamma k_BT\,\delta(s-s')} ds\,ds' = \frac{2\cancel{m\gamma}\, k_BT}{(m\gamma)^{\cancel{2}}}t = \frac{2k_BT}{m\gamma}t$$

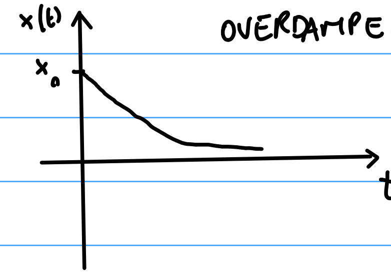
HARMONIC OSCILLATOR + FRICTION

$$m\ddot{x} = -m\omega^2 x \qquad\qquad m\ddot{x} = -m\gamma\dot{x} - m\omega^2 x$$

$$\ddot{x} = -\gamma\dot{x} - \omega^2 x$$







OVERDAMPED

$$y = \dot{x}$$
$$\dot{y} = -\gamma y - \omega^2 x$$

$$\begin{pmatrix} \dot{x} \\ \dot{y} \end{pmatrix} = \begin{pmatrix} 0 & 1 \\ -\omega^2 & -\gamma \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

IF $\gamma = 0$ PURELY IMAGINARY EIGENVALUES $\lambda_\pm = \pm i\omega$ $\qquad e^{\lambda_+ t} \quad e^{\lambda_- t}$

IF $\gamma > 0$ (SMALL) $\quad \lambda_\pm = -\rho \pm i\bar{\omega}$

OVERDAMPED LIMIT $\quad \dot{x} = -\frac{\omega^2}{\gamma} x$

NUMERICAL INTEGRATION OF LANGEUIN EQUATION

$$\boxed{m\ddot{x} = F - m\gamma\dot{x} + \sqrt{2m\gamma k_B T}\,\eta} \qquad \langle \eta(t)\rangle = 0 \qquad \langle \eta(t)\eta(t')\rangle = \delta(t-t')$$

$\dot{w} = \eta$

$$w(s) = \int_0^s \eta(t)\,dt \qquad \langle w(s)w(s')\rangle = \min(s,s') \implies \langle w^2(s)\rangle = s$$

$$\langle (w(t+\Delta t) - w(t))^2\rangle = \langle w^2(t+\Delta t)\rangle + \langle w^2(t)\rangle - 2\langle w(t+\Delta t)w(t)\rangle$$
$$= t + \Delta t + t - 2t = \Delta t$$

WE CAN GENERATE $\quad \boxed{w(t+\Delta t) = w(t) + \sqrt{\Delta t}\,\xi} \qquad \xi$ GAUSSIAN RANDOM VARIABLE

$$\langle \xi\rangle = 0 \qquad \langle \xi^2\rangle = 1$$

OVERDAMPED LIMIT ($\ddot{x} \to 0$)

$$\dot{x} = \frac{F}{m\gamma} + \sqrt{\frac{2k_BT}{m\gamma}}\,\underbrace{\eta(t)}_{=\dot{w}}$$

$$\frac{x(t+\Delta t) - x(t)}{\Delta t} = \frac{F(x(t))}{m\gamma} + \sqrt{\frac{2k_BT}{m\gamma}}\,\frac{w(t+\Delta t) - w(t)}{\Delta t}$$

RANDOM VARIABLE

$$x(t+\Delta t) = x(t) + \frac{1}{m\gamma} F(x(t))\,\Delta t + \sqrt{\frac{2k_BT}{m\gamma}}\,\sqrt{\Delta t}\,\xi$$

ASSOCIATED TO STOCHASTIC FORCE

IN LECTURE NOTES WE DERIVE AN INTEGRATOR FOR UNDERDAMPED LANGEVIN DYNAMICS

UPDATING POSITION & VELOCITIES

$\sigma = \sqrt{\frac{2k_BT\gamma}{m}}$

Second order integrator of the Langevin equation

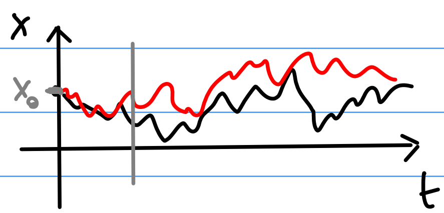
$$\begin{aligned} r(t+\Delta t) &= r(t) + \Delta t v(t) + C(t) \\ v(t+\Delta t) &= v(t) + \frac{\Delta t}{2}[f(r(t+\Delta t)) + f(r(t))] - \Delta t \gamma v(t) \\ &+ \sigma\sqrt{\Delta t}\xi(t) - \gamma C(t) \\ \Longrightarrow C(t) &= \frac{\Delta t^2}{2}[f(r(t)) - \gamma v(t)] + \sigma \Delta t^{3/2}\left(\frac{1}{2}\xi(t) + \frac{1}{2\sqrt{3}}\theta(t)\right) \end{aligned} \tag{98}$$

Note: The integrator reduces to the Velocity Verlet integrator if $\gamma = 0$ and $\sigma = 0$.

LANGEVIN EQUATION $\quad \dot{x} = a_1(x) + \sqrt{a_2(x)}\,\xi(t) \qquad \langle \xi \rangle = 0 \qquad \langle \xi(t)\xi(t')\rangle = \delta(t-t')$

BEFORE $\quad a_1 = 0$ OR $a_1 = -\frac{k}{m\gamma}x$ .... DETERMINISTIC FORCE

$a_2 = \frac{2k_BT}{m\gamma}$



FOKKER-PLANCK EQUATION $\quad \frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[a_1(x)P(x,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[a_2(x)P(x,t)\right] \qquad P(x,t)$ PROB. DISTRIB.

ALSO CALLED SMOLUCHOWSKI EQUATION

AT EQUILIBRIUM $t \to \infty \qquad P(x,t) \xrightarrow[t\to\infty]{} P_{eq}(x) = \dots e^{-\beta V(x)}$

IN OUR CASE $\quad a_1 = \frac{F(x)}{m\gamma} \qquad a_2 = \frac{2k_BT}{m\gamma} = 2D$

$$\frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} - \frac{\partial}{\partial x}\left[\frac{F(x)}{m\gamma}P(x,t)\right]$$

* IF $F=0 \qquad \frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2}$ DIFFUSION EQUATION

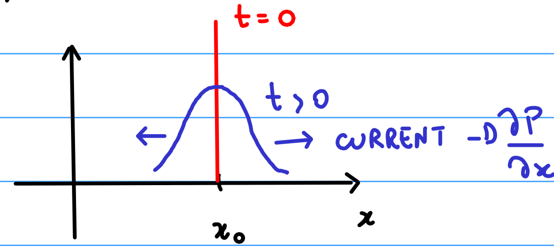
* $\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}\left[-D\frac{\partial P}{\partial x} + \frac{F}{m\gamma}P\right] = -\frac{\partial}{\partial x}j$ CONTINUITY EQUATION

CONTINUITY EQ. $\Rightarrow$ CONSERVED QUANTITY $\int_{-\infty}^{+\infty} P(x,t)\,dx =$ CONSTANT (TIME INDEP.)

$$j = -D\frac{\partial P}{\partial x} + \frac{F}{m\gamma}P = \underbrace{-D\frac{\partial P}{\partial x}}_{\text{DIFFUSION}} \underbrace{- \frac{1}{m\gamma}\frac{dV}{dx}P}_{\text{DRIFT}} \qquad F = -\frac{dV}{dx}$$

SOLUTION OF DIFFUSION EQUATION $(F=0)$ WITH $P(x,0) = \delta(x-x_0)$

$$P(x,t|x_0,0) = \frac{1}{\sqrt{4\pi D t}}\, e^{-\frac{(x-x_0)^2}{4Dt}}$$



REWRITE TOTAL CURRENT AS $\left(D = \frac{k_BT}{m\gamma}\right.$ EINSTEIN RELATION$\left.\right)$

$$j = -D\frac{\partial P}{\partial x} - \beta D\frac{dV}{dx}P = -D\,e^{-\beta V(x)}\frac{\partial}{\partial x}\left[e^{\beta V(x)}P(x,t)\right]$$

<u>NOTE</u>: IN EQUILIBRIUM $P_{eq}(x) = \dots\, e^{-\beta V(x)} \Rightarrow j_{eq} = 0$ AS EXPECTED

SEE (NEW) PROBLEM 13.7

13.7 Overdamped harmonic oscillator

The solution of the Fokker-Planck equation for an overdamped harmonic oscillator with potential energy $V(x) = kx^2/2$

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P(x,t)}{\partial x^2} + \frac{\partial}{\partial x}\left[\frac{kx}{\gamma}P(x,t)\right]$$

$\hookrightarrow$ NOTE SOMETIMES WE USE $m\gamma$

with initial condition $P(x,0) = \delta(x - x_0)$ is

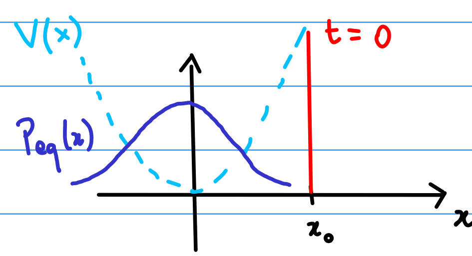
$$P(x,t) = \left(\frac{\Omega e^{\Omega t}}{4\pi D\,\mathrm{sh}\Omega t}\right)^{1/2} \exp\left[-\frac{\Omega}{4D}\frac{\left(xe^{\Omega t/2} - x_0e^{-\Omega t/2}\right)^2}{\mathrm{sh}\Omega t}\right]$$

where we defined $\Omega \equiv Dk/k_BT$.

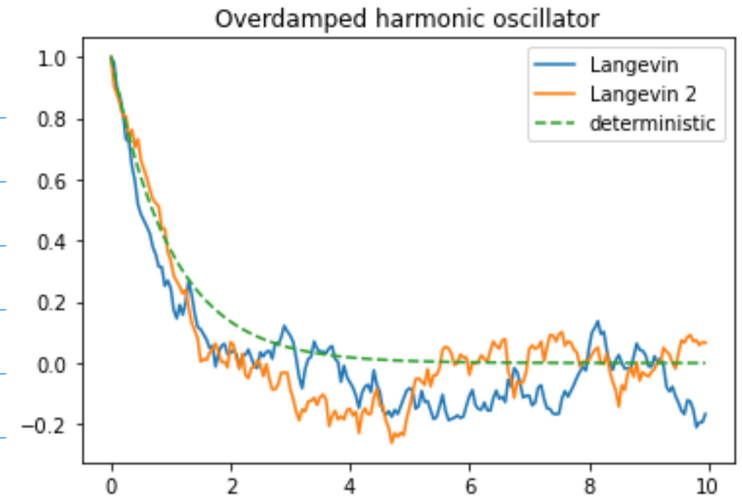
RECALL $\Omega t \ll 1$ $\quad e^{\pm\Omega t} \approx 1 \pm \Omega t \quad \mathrm{sh}\,\Omega t \approx \Omega t$

INDEED $P(x,t) \rightarrow \delta(x-x_0)$

$\Omega t \gg 1$ $\quad P(x,t) \rightarrow P_{eq}(x)$

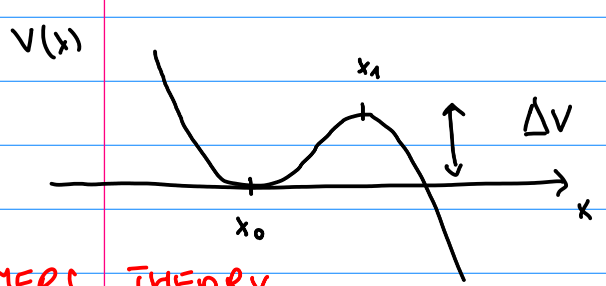


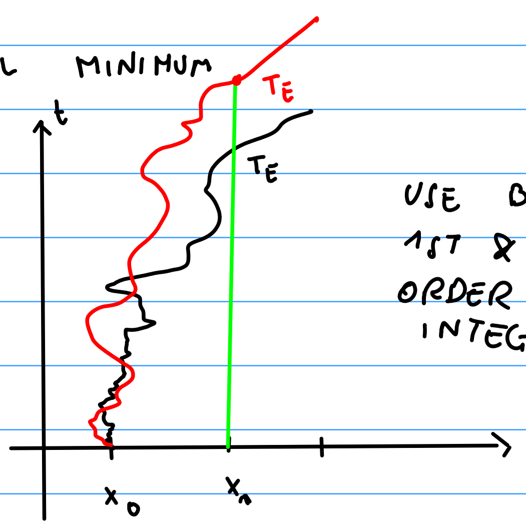
```python
# Langevin dynamics: overdamped harmonic oscillator
import numpy as np
import scipy.special as spc
import scipy.optimize as opt
import scipy.integrate as integrate
import matplotlib.pyplot as plt
from scipy.integrate import quad
import cmath

nsteps=20000
# Temperature & timesteps
T=0.1; dt=0.05;sqdt=np.sqrt(T*dt)
plt.title("Overdamped harmonic oscillator")

x=np.zeros(nsteps)
rdd=np.random.randn(nsteps)
x[0]=1;

for i in range(nsteps-1):
    x[i+1]=x[i]-x[i]*dt+sqdt*rdd[i]

tmn=np.array(range(nsteps))*dt
plt.plot(tmn,x,label='Langevin')

rdd=np.random.randn(nsteps)
for i in range(nsteps-1):
    x[i+1]=x[i]-x[i]*dt+sqdt*rdd[i]
plt.plot(tmn,x,label='Langevin 2')
plt.plot(tmn,x[0]*np.exp(-tmn),'--',label='deterministic')

plt.legend()
plt.show()

plt.hist(x[100:],30)
y=np.linspace(-1,1,200)
plt.plot(y,2000*np.exp(-y**2/T))
plt.show()
```



USE THIS TO COMPUTE $P(x,t)$ FOR A FEW TIMES $t_1 < t_2 < \dots$

PROBLEM 13.6 : ESCAPE FROM POTENTIAL MINIMUM





USE BOTH 1ST & 2ND ORDER INTEGRATORS

KRAMERS THEORY

ESCAPE RATE $\quad K = \frac{1}{N}\sum_m \frac{1}{T_E(m)} = \frac{\omega_W \omega_T}{2\pi\gamma} e^{-\beta\Delta V}$

$$V(x) \underset{x\approx x_0}{\approx} V(x_0) + \frac{\omega_W^2}{2}(x-x_0)^2$$

$$V(x) \underset{x\approx x_1}{\approx} V(x_1) - \frac{\omega_T^2}{2}(x-x_1)^2$$