

COMPUTATIONAL PHYSICS

outline

numerical methods to study systems of many particles

→ thermodynamic properties: compute free energies

→ dynamics: non-linear problems

transport processes in fluids

Hamiltonian systems (classical)

central tools:

I. Molecular Dynamics simulation

II. Monte Carlo simulation

literature:

- (1) B. Leimkuhler, S. Reich, *Simulating Hamiltonian Dynamics* (Cambridge Univ. Press, 2005)
- (2) D. Frenkel, B. Smit, *Understanding Molecular Simulation* (Academic Press, 2002)
- (3) M.P. Allen, D.J. Tildesley, *Computer Simulation of Liquids* (Clarendon Press, 1991)
- (4) D.P. Landau, K. Binder, *Monte Carlo Simulations in Statistical Physics*, 4th ed. (Cambridge Univ. Press, 2015)

I. Molecular Dynamics simulation

I. 1. Newton's equations of motion

system of N particles with Cartesian coordinates

$$\vec{X} = \{\vec{r}_i\} \quad i = 1, \dots, N$$

$$d \text{ dimensions } \vec{r}_i = (r_1, r_2, \dots, r_d)$$

Newton II : system of $3N$ ordinary differential equations of 2nd order

$$m_i \ddot{\vec{r}}_i = \vec{F}_i \quad i = 1, \dots, N$$

m_i : mass of i 'th particle

$$\ddot{\vec{r}}_i = \frac{d^2 \vec{r}_i}{dt^2}$$

\vec{F}_i : force on i 'th particle, assume existence of conservative potential $U(\vec{r}_1, \dots, \vec{r}_N)$

$$\Rightarrow \vec{F}_i = -\nabla_i U(\vec{r}_1, \dots, \vec{r}_N)$$

- goals:
- find trajectories of particles; i.e. positions, $\{\vec{r}_i\}$, and velocities, $\{\dot{\vec{r}}_i \equiv \vec{v}_i\}$, as function of time t
 - analyse these trajectories in the framework of Statistical Mechanics

remarks:

$$\text{or diffusion eqn. } \frac{\partial f(\vec{r}, t)}{\partial t} = D \nabla^2 f(\vec{r}, t)$$

(i) microscopic equations (in contrast to continuum equations, such as Navier - Stokes equations)
one has to specify potential function

simplest assumption: U pairwise-additive and only function of distance between particles

$$r_{ij} \equiv |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|$$

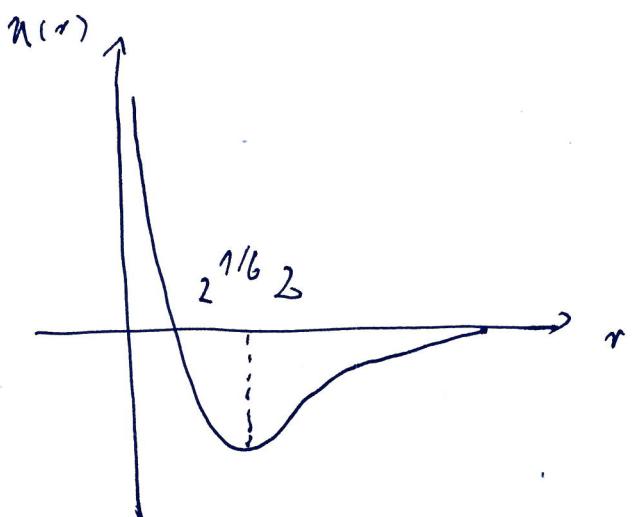
$$\Rightarrow U = \sum_{i=1}^N \sum_{j>i} u(r_{ij})$$

$$\Rightarrow \vec{F}_i = - \sum_{j \neq i} \frac{\partial u(r_{ij})}{\partial \vec{r}_i} = - \sum_{j \neq i} \frac{\partial u}{\partial r_{ij}} \frac{\vec{r}_i - \vec{r}_j}{r_{ij}}$$

example:

Lennard-Jones potential

$$u(r) = 4 \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



→ good model for some metallic systems and rare gases, e.g. fit parameters $\sigma = 3.405 \text{ \AA}$, $\frac{\epsilon}{k_B} = 121 \text{ K}$

→ model system in Statistical Mechanics

(ii) isolated Newtonian system with conservative forces

→ microcanonical ensemble

→ total energy conserved

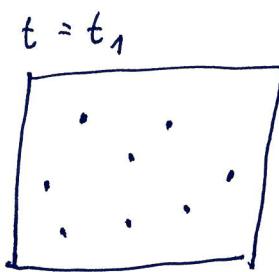
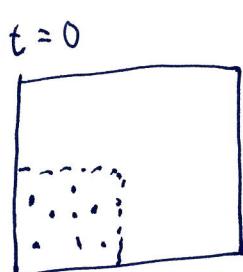
$$E = T + U = \sum_{i=1}^N \frac{m_i}{2} \dot{r}_i^2 + U$$

(iii) (Newton's equations exhibit) symmetries

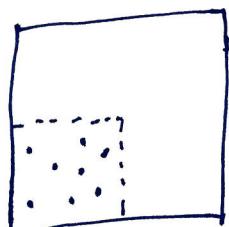
→ conservation laws follow from symmetries
(Noether theorem)

→ phase-space volume conserved

→ time reversibility

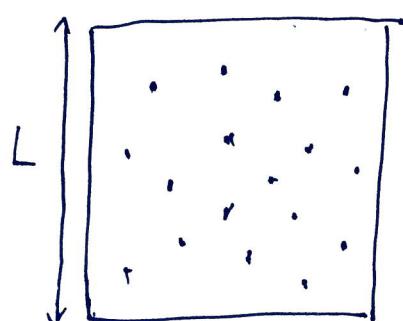


- after time t_1 , particles distributed in the whole volume
- reverse time arrow at time t_1 , \Rightarrow move backward in time $\Rightarrow t = -t_1$



configuration identical to that at $t=0$

(iv) practical issues for simulation, i.e. numerical solution of Newton's equations



put N particles in a box of volume $V = L^d$

→ boundary conditions?

→ computation of $u(r)$ for particle pairs separated by large distance (use cut-off?)

→ numerical solution requires discretization of equations with respect to time



$$t_n \equiv n \delta t$$

task: compute $\vec{r}_i(t_n \equiv n \delta t)$ and $\vec{v}_i(t_n)$
for all $i = 1, \dots, N$

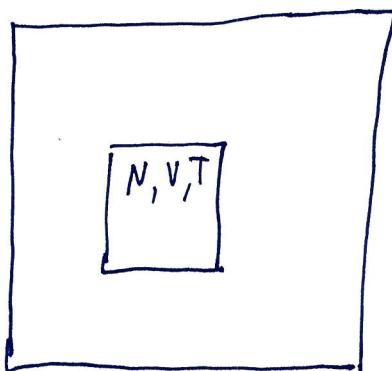
problems:

- discretization error → choice of δt sufficiently small
- E conserved? symmetries such as time reversibility hold?

- does one solve the original problem ; i.e. problem for system with Hamilton function $\mathcal{H} = T + U$?

→ realize statistical ensembles different from the microcanonical one !

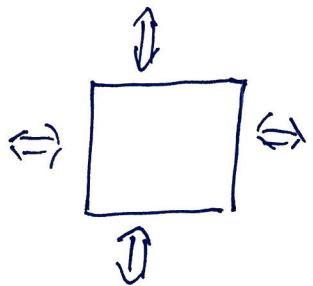
e.g. canonical ensemble



subsystem coupled to heat bath
 \Rightarrow temperature T constant

$N \rho H$ ensemble (H enthalpy)

system coupled to environment via mass piston

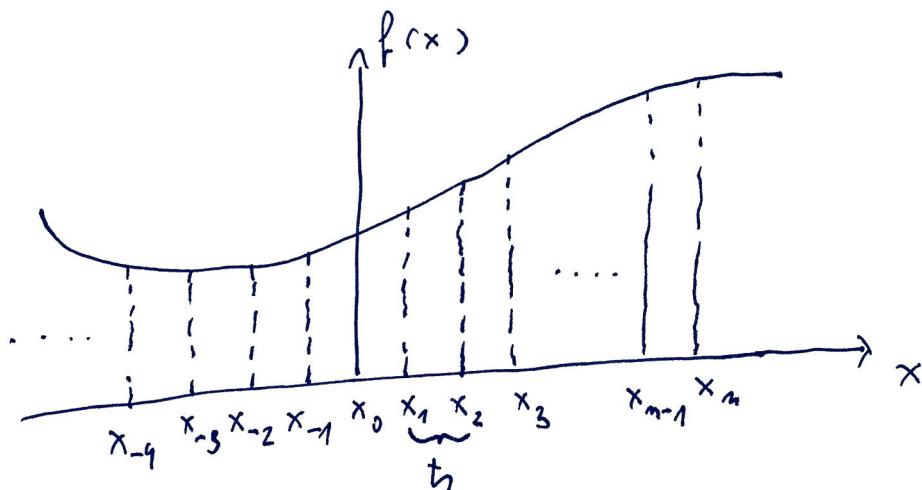


\Leftrightarrow volume fluctuates, pressure p kept constant

→ finite-size effects : properties of system depend on its size : thermodynamic limit ?

I.2. Discrete derivatives and integrals

I.2.1. Derivatives



$f'(x_i)$ at $x = x_i$?

$f(x)$ given on grid (distance between grid points $\approx h$)

$$x_m = nh \quad m = 0, \pm 1, \pm 2, \dots$$

$$f_m \equiv f(x_m)$$

consider $f'(x_0)$

→ Taylor expansion around $x = x_0 = 0$

$$f(x) = f_0 + x f'(0) + \frac{1}{2!} x^2 f''(0) + \frac{1}{3!} x^3 f'''(0) + \dots$$

$$\Rightarrow f_{\pm 1} \equiv f(x = \pm h)$$

$$= f_0 \pm h f'(0) + \frac{1}{2} h^2 f''(0) \pm \frac{h^3}{6} f'''(0) + O(h^4)$$

$$\Rightarrow f_{+1} - f_{-1} = 2h f'(0) + \frac{1}{3} h^3 f'''(0)$$

solve $f'(0)$ ⇒

$$\Rightarrow f'(0) = \frac{f_{+1} - f_{-1}}{2h} + \Theta(h^2)$$

discretization error $\propto h^2$

note : $f'(0) = \frac{f_1 - f_0}{h} + \Theta(h)$ forward differential quotient

$f'(0) = \frac{f_0 - f_{-1}}{h} + \Theta(h)$ backward differential quotient

higher-order scheme : requires $f_{\pm 2}$

$$f_{\pm 2} \equiv f(x = \pm 2h)$$

$$= f_0 \pm 2h f'(0) + 2h^2 f''(0) \pm \frac{4h^3}{3} f'''(0) + \Theta(h^4)$$

$$f_{+1} - f_{-1} - \frac{1}{8} f_{+2} + \frac{1}{8} f_{-2}$$

$$= 2h f'(0) + \frac{1}{3} h^3 f'''(0) - \frac{1}{2} h f'(0) - \frac{h^3}{3} f'''(0) + \Theta(h^4)$$

$$= \frac{3}{2} h f'(0) + \Theta(h^4)$$

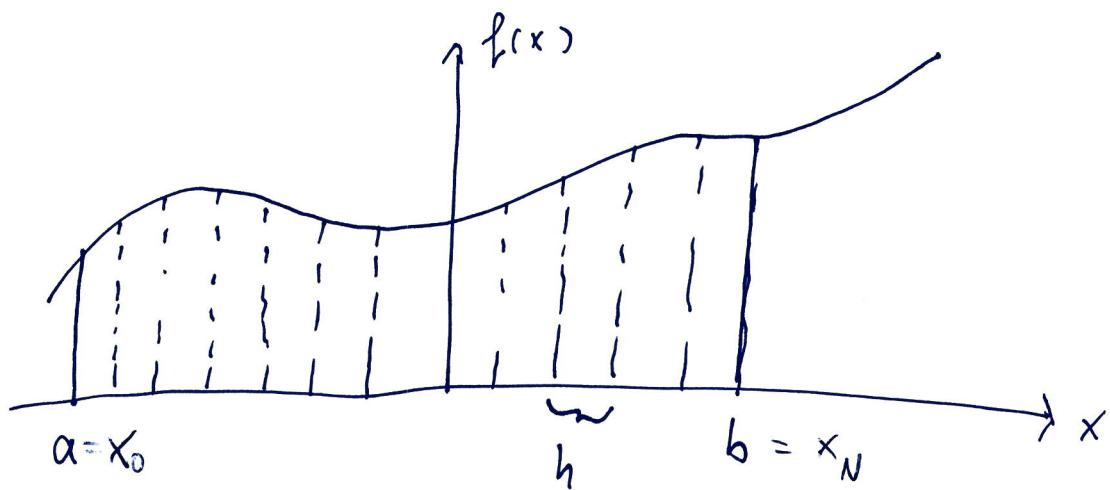
$$\Rightarrow f'(0) = \frac{2}{3h} [f_{+1} - f_{-1} - \frac{1}{8} f_{+2} + \frac{1}{8} f_{-2}] + \Theta(h^3)$$

$$= \frac{1}{12h} [f_{-2} + 8f_{+1} - 8f_{-1} - f_{+2}] + \Theta(h^3)$$

higher derivatives : consider $f_{+1} + f_{-1} = 2f_0 + h^2 f''(0) + \Theta(h^4)$

$$\Rightarrow f''(0) = \frac{f_{+1} - 2f_0 + f_{-1}}{h^2} + \Theta(h^2)$$

I. 2. 2. Quadrature



$$\int_a^b f(x) dx = ?$$

equidistant grid between a and b with distance h between grid points

$f(x)$, given at $N = \frac{b-a}{h}$ values of x

$$h = x_{i+1} - x_i = \frac{b-a}{N}$$

$$x_0 = a, x_i = a + hi, x_N = b, f_i = f(x_i)$$

idea: approximate $f(x)$ in each interval $[x_i, x_{i+1}]$ by function for which integral can be solved exactly

$$\Rightarrow \text{ansatz: } \int_a^b f(x) dx \approx \sum_{i=1}^N w_i f_i$$

weight factors, independent of f_i 's



approximate f by linear
function in $[x_i, x_{i+1}]$

$$f(x) \approx f_i + \frac{f_{i+1} - f_i}{h} (x - x_i) + O((x - x_i)^2)$$

$$\begin{aligned} \int_{x_i}^{x_{i+1}} f(x) dx &\approx \int_{x_i}^{x_{i+1}} dx \left\{ f_i + \frac{f_{i+1} - f_i}{h} (x - x_i) \right\} \\ &= f_i \underbrace{(x_{i+1} - x_i)}_h + \frac{f_{i+1} - f_i}{h} \underbrace{\int_{x_i}^{x_{i+1}} dx}_{=h} (x - x_i) \\ &= \frac{1}{2} h^2 \\ &= \frac{h}{2} (f_i + f_{i+1}) \end{aligned}$$

integral obtained from sum over all intervals \Rightarrow

$$\begin{aligned} \int_a^b f(x) dx &= h \left(\frac{1}{2} f_0 + f_1 + f_2 + \dots + f_{N-1} + \frac{1}{2} f_N \right) \\ &= h \left(\frac{1}{2} (f_0 + f_N) + \sum_{i=1}^{N-1} f_i \right) \end{aligned}$$

trapezoidal rule

\Rightarrow weight factors

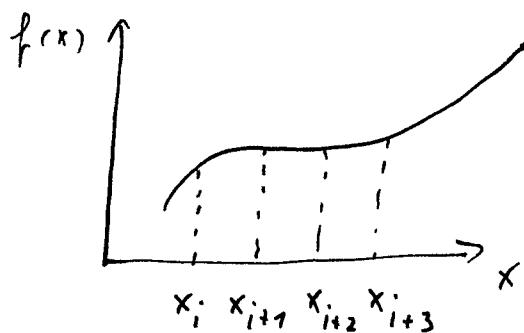
$$w_i = \begin{cases} \frac{1}{2} & i = 0, N \\ 1 & i = 1, 2, \dots, N-1 \end{cases}$$

error estimate

$$\int_{x_i}^{x_{i+1}} \Theta((x - x_i)^2) dx \sim \Theta((x_{i+1} - x_i)^3)$$
$$\sim \Theta(h^3)$$

integral $\int_a^b f(x) dx : \Theta(\underbrace{\sum_{n=0}^{N-1} h^3}_{= Nh^3} = \frac{b-a}{h} h^3 \sim h^2)$

(ii) more systematic approach: polynomial interpolation
(Lagrange method)



approximate function
in interval $[x_i, x_{i+3}]$
by polynomial of degree 3

general approach:

interval $[x_i, x_{i+m}] \rightarrow$ use polynomial

$P_m(x)$ of degree m for which $P_m(x_{i+j}) = f_{i+j}$

at $m+1$ nodes with $j = 0, 1, 2, \dots, m$

• linear interpolation

$$P_1(x) = a_i + (x - x_i) b_i;$$

$$P_1(x_i) = f_i, P_1(x_{i+1}) = f_{i+1}$$

$$\Rightarrow a_i = f_i, b_i = \frac{f_{i+1} - f_i}{x_{i+1} - x_i}$$

$$\Rightarrow P_1(x) = f_i + (x - x_i) \frac{f_{i+1} - f_i}{x_{i+1} - x_i}$$

$$= \frac{x - x_{i+1}}{x_i - x_{i+1}} f_i + \frac{x - x_i}{x_{i+1} - x_i} f_{i+1}$$

• quadratic interpolation

$$P_2(x) = a_i + (x - x_i) b_i + (x - x_i)^2 c_i$$

3 unknowns $a_i, b_i, c_i \Rightarrow f$ at 3 nodes x_i, x_{i+1}, x_{i+2}

$$\Rightarrow P_2(x) = \frac{(x - x_{i+1})(x - x_{i+2})}{(x_i - x_{i+1})(x_i - x_{i+2})} f_i$$

$$+ \frac{(x - x_i)(x - x_{i+2})}{(x_{i+1} - x_i)(x_{i+1} - x_{i+2})} f_{i+1}$$

$$+ \frac{(x - x_i)(x - x_{i+1})}{(x_{i+2} - x_i)(x_{i+2} - x_{i+1})} f_{i+2}$$

• polynomial of n^{th} degree

$$P_n(x) = \sum_{j=0}^n L_{i+j}(x) f_{i+j} \quad (*)$$

with $L_{i+j}^n(x) = \prod_{\substack{k=0 \\ k \neq j}}^n \frac{x - x_{i+k}}{x_{i+j} - x_{i+k}}$

clear: $L_{i+j}^n(x_{i+j}) = 1, L_{i+j}^n(x_{i+k}) = 0 \quad \forall j \neq k$

$$x_{i+k} = x_i + h k$$

$x = x_i + hs$ in interval $[x_i, x_{i+m}]$

$s \in \mathbb{R}$ in interval $[0, m]$

$$\Rightarrow L_{i+j}^n(x) = \prod_{\substack{k=0 \\ k \neq j}}^m \frac{x_i + hs - x_i - hk}{x_i + hk - x_i - hk}$$

$$= \prod_{\substack{k=0 \\ k \neq j}}^m \frac{s-k}{j-k}$$

$$\Rightarrow \int_{x_i}^{x_{i+m}} P_m(x) dx = \sum_{j=0}^m f_{i+j} \int_{x_i}^{x_{i+m}} L_{i+j}^n(x) dx$$

$$= h ds$$

$$= \sum_{j=0}^m f_{i+j} h \underbrace{\int_{x_i}^{x_{i+m}} \prod_{\substack{k=0 \\ k \neq j}}^m \frac{s-k}{j-k} ds}_{= w_{i+j}}$$

$$\Rightarrow \boxed{\int_{x_i}^{x_{i+m}} P_m(x) dx = h \sum_{j=0}^m f_{i+j} w_{i+j}}$$

Newton - Cotes formula

(iii) $n = 1$

$$\int_{x_i}^{x_{i+1}} P_1(x) dx = h (w_i f_i + w_{i+1} f_{i+1})$$

$$w_i = \int_0^1 \frac{s-1}{-1} ds = \frac{1}{2}$$

$$w_{i+1} = \int_0^1 s ds = \frac{1}{2}$$

$$\Rightarrow \boxed{\int_{x_i}^{x_{i+1}} P_1(x) dx = \frac{h}{2} (f_i + f_{i+1})}$$

\Rightarrow trapezoidal rule

(iv) $n = 2$

$$w_i = \int_0^2 \frac{1}{2} (s-1)(s-2) ds = \frac{1}{3}$$

$$w_{i+1} = \int_0^2 \frac{1}{2} s(s-2) ds = \frac{4}{3}$$

$$w_{i+2} = \int_0^2 \frac{1}{2} s(s-1) ds = \frac{1}{3}$$

$$\Rightarrow \boxed{\int_{x_i}^{x_{i+2}} P_2(x) dx = \frac{h}{3} [f_i + 4f_{i+1} + f_{i+2}]}$$

simpson's rule

(v) $n = 3$

$$\int_{x_i}^{x_{i+3}} P_3(x) dx = \frac{3h}{8} [f_i + 3f_{i+1} + 3f_{i+2} + f_{i+3}]$$

Lagrange's $\frac{3}{8}$ rule

(vi) $n = 4$

$$\int_{x_i}^{x_{i+4}} P_4(x) dx = \frac{2h}{45} [7f_i + 32f_{i+1} + 12f_{i+2} + 32f_{i+3} + 7f_{i+4}]$$

Burke's rule

remarks:

• Newton - Cotes method

$$\int_a^b f(x) dx \approx h \sum_{i=0}^{\frac{N}{m}-1} \sum_{j=0}^m f_{im+j} w_{im+j}$$

for $\frac{N}{m} \in N$

• approximation error

$$E = \int_{x_i}^{x_{i+m}} P_m(x) dx - \int_{x_i}^{x_{i+m}} f(x) dx$$

one can show that

$$E = h^{p+1} K \underset{\text{p'th derivative}}{\uparrow} f^{(p)}(\xi) \quad \text{with } \xi \in [x_i, x_{i+m}]$$

$$\text{trapezoidal rule } (n=1) : E = h^3 \frac{1}{12} f''(\xi)$$

$$\text{simpson's rule } (n=2) : E = h^5 \frac{1}{90} f^{(4)}(\xi)$$

$$\text{simpson's } \frac{3}{8} \text{ rule } (n=3) : E = h^5 \frac{3}{80} f^{(4)}(\xi)$$

$$\text{Boole's rule } (n=4) : E = h^7 \frac{8}{945} f^{(6)}(\xi)$$

- Gauß quadrature (remain!)

→ non-equidistant nodes

→ assume interval $[x_s, x_e]$ with N nodes

$$\int_{x_s}^{x_e} f(x) \underbrace{w(x) dx}_{\text{weight function } \geq 0} \simeq \sum_{m=1}^N w_m f_m$$

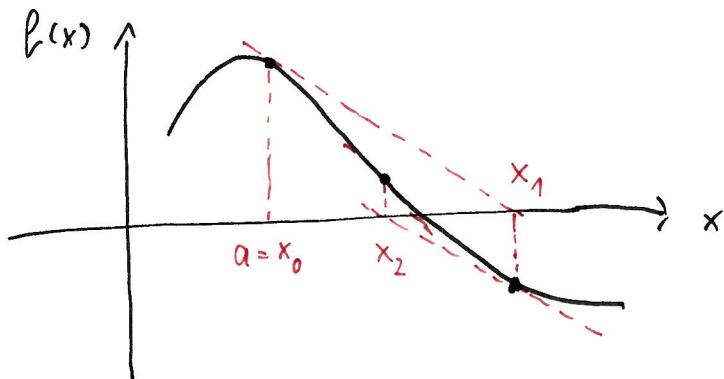
now: $2N$ unknowns, namely N nodes and weight factors w_m

⇒ polynomial of degree $2N-1$

I. 2. 3. Roots

goal : find roots of non-linear function $f(x)$, i.e. values of x for which $f(x) = 0$

(i) Newton - Raphson method



start with

$$f(x) \approx f(x_0) + f'(x_0)(x-x_0)$$

(Taylor expansion around $x=x_0$)

$$f(x_i) = 0 \Rightarrow x_i = x_0 - \frac{f(x_0)}{f'(x_0)}$$

$$\text{iterate } x_{i+1} = x_i - \frac{f(x_i)}{f'(x_i)} \quad (+)$$

error propagation?

$$\text{error at } i\text{'th iteration} \quad \varepsilon_i = x_{ex} - x_i$$

\downarrow exact root

$$\begin{aligned} \text{Eq. (+)} \Rightarrow x_{i+1} - x_{ex} &= x_i - x_{ex} - \frac{f(x_i)}{f'(x_i)} \\ &= -\varepsilon_{i+1} \quad = -\varepsilon_i \end{aligned}$$

$$\Rightarrow \varepsilon_{i+1} = \varepsilon_i + \frac{f(x_i)}{f'(x_i)} \quad (++)$$

expand $f(x)$ around $x = x_i$

$$f(x) = f(x_i) + f'(x_i)(x-x_i) + \frac{1}{2!} f''(x_i)(x-x_i)^2 + \dots$$

$$x = x_m \Rightarrow f(x_m) = 0 = f(x_i) + f'(x_i) \varepsilon_i + f''(x_i) \frac{1}{2} \varepsilon_i^2 + O(\varepsilon_i^3)$$

$$\Rightarrow f(x_i) = -\varepsilon_i f'(x_i) - \frac{1}{2} \varepsilon_i^2 f''(x_i)$$

$$\text{in Eq. (++) } \Rightarrow \varepsilon_{i+1} = \varepsilon_i + \frac{-\varepsilon_i f'(x_i) - \frac{1}{2} \varepsilon_i^2 f''(x_i)}{f'(x_i)} \\ = -\frac{\varepsilon_i^2}{2} \frac{f''(x_i)}{f'(x_i)}$$

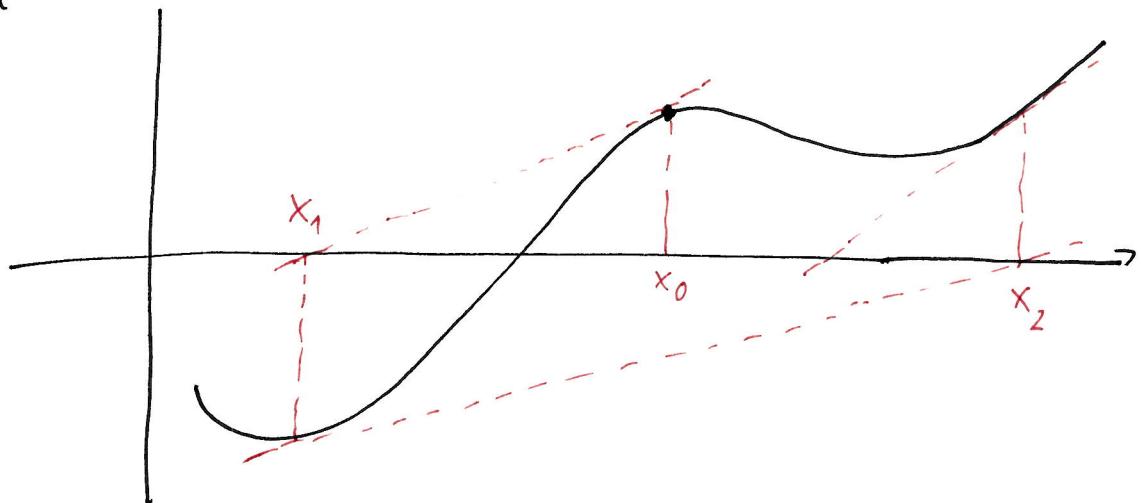
$\rightarrow \frac{f''(x_i)}{f'(x_i)} \approx \text{const. close to root}$

\Rightarrow error \propto square of error from previous iteration step

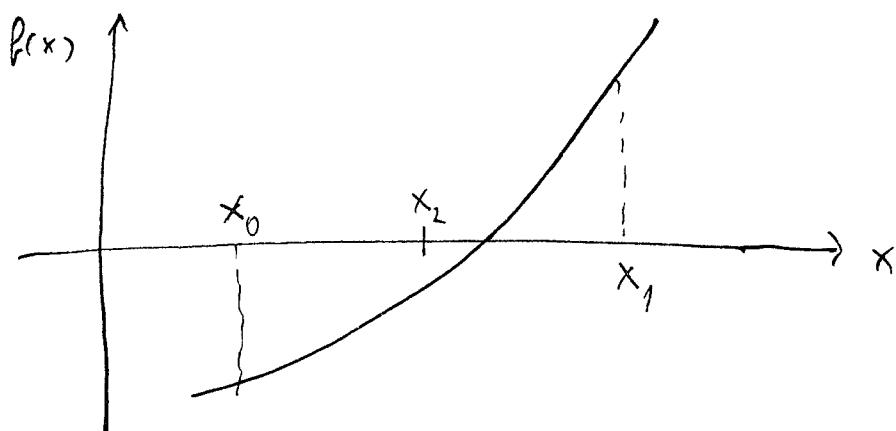
\Rightarrow 1st order Newton-Raphson scheme has quadratic convergence

problem: scheme not necessarily convergent!

example



(ii) different scheme: bisection



identify interval $[x_0, x_1]$ around root

$$x_2 = \frac{x_0 + x_1}{2}$$

$f(x_0)f(x_2) > 0 \Rightarrow$ continue in $[x_2, x_1]$

$f(x_0)f(x_2) < 0 \Rightarrow$ continue in $[x_0, x_2]$

problem: slow convergence

→ bisection can be used in combination with Newton-Raphson

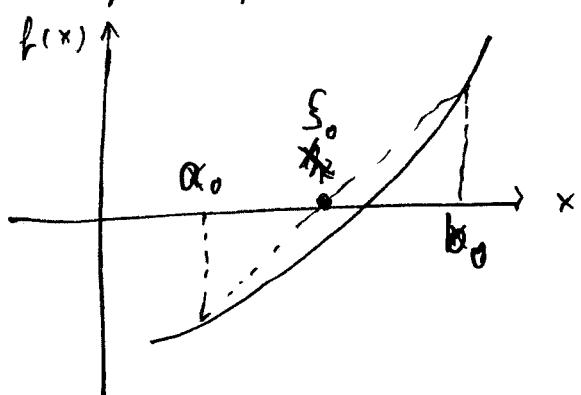
(iii) secant method

discretized version of Newton - Raphson

$$\text{use } f'(x_i) \approx \frac{f(x_i) - f(x_{i-1})}{x_i - x_{i-1}} \Rightarrow x_{i+1} = x_i - \frac{x_i - x_{i-1}}{f(x_i) - f(x_{i-1})} f(x_i)$$

superlinear convergence (not necessarily convergent)

(iv) regula falsi



improves bisection

α_0, β_0 located around root
(to left and right, respectively)

$$0 = f(a_i) + (\xi_i - a_i) \frac{f(a_i) - f(b_i)}{a_i - b_i}$$

$$\Rightarrow \xi_i = a_i - \frac{b_i - a_i}{f(b_i) - f(a_i)} f(a_i)$$

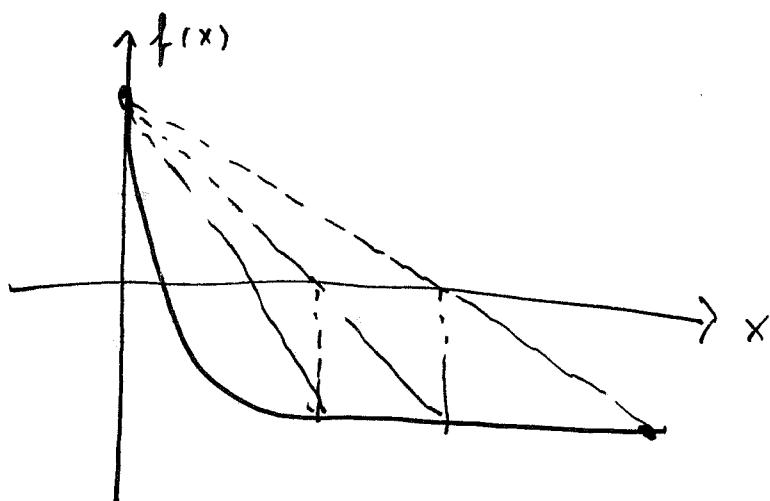
analog to bisection

$$\begin{aligned} f(a_i) f(\xi_i) > 0 &\Rightarrow b_{i+1} = b_i, \quad a_{i+1} = \xi_i \\ f(a_i) f(\xi_i) < 0 &\Rightarrow b_{i+1} = \xi_i, \quad a_{i+1} = a_i \end{aligned}$$

remark:

regula falsi not always better than bisection

example



I.3. Integrators for ordinary differential equations

consider "one-particle" systems

- themes :
- integration error due to discretization
- stability of integrator
- symmetries of Hamiltonian systems

I.3.1. Euler algorithm

$$\dot{x}(t) + f(x, t) = 0 \quad \dot{x} = \frac{dx}{dt} = v \quad (*)$$

$$\Rightarrow x(t) = x(t_0) - \int_{t_0}^t f(x(t'), t') dt' \quad (**)$$

- examples :

decay / relaxation $\dot{x} + \alpha x = 0 \Rightarrow x = x_0 e^{-\alpha t}$
 $\alpha > 0$

harmonic oscillator



k : spring constant

m : mass of particle

$$\frac{dv}{dt} = -\frac{k}{m} x$$

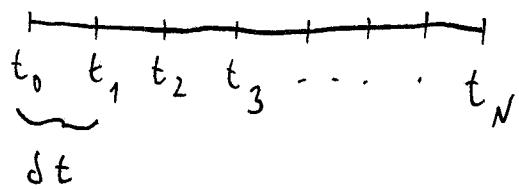
\downarrow displacement with respect to
rest position

$$\frac{dx}{dt} = v$$

differential equation of order n can be converted into n differential equations of 1st order

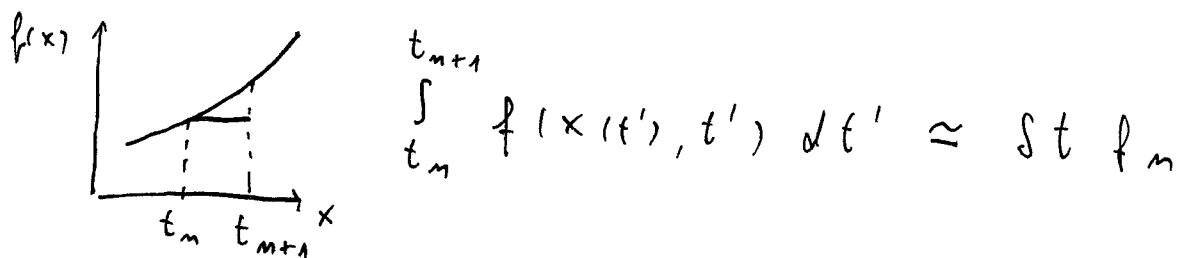
numerical solution of Eq. (*)

→ discrete



$$x_n \equiv x(t_n), \quad t_n = n \delta t, \quad f_n \equiv f(x_n, t_n)$$

→ lowest-order approximation of integral in (**) in each interval



$$\Rightarrow \boxed{x_{m+1} = x_m + \delta t f_m} \quad (***)$$

Euler algorithm

→ or: discrete derivative in Eq. (*)

$$\dot{x}_n \approx \frac{x_{m+1} - x_m}{\delta t} \Rightarrow \text{Euler algorithm}$$

→ or: Taylor expansion around $t = t_m$

$$\begin{aligned} x_{m+1} &= x_m + \delta t \underbrace{\dot{x}_m}_{=} + \frac{1}{2} \delta t^2 \ddot{x}_m + \dots \\ &= -f_m \quad (*) \end{aligned}$$

\Rightarrow accuracy $\Theta(\delta t)$; discretization or integration error $\Theta(\delta t^2)$

• stability

(i) introduce perturbation $\varepsilon_m \equiv \varepsilon(t_m)$ at time t_m

$$\tilde{x}_m = x_m + \varepsilon_m \quad \varepsilon_m \text{ small}$$

propagation of perturbation?

$$\tilde{x}_{m+1} = \tilde{x}_m + -\delta t f(\tilde{x}_m, t_m)$$

$$x_{m+1} + \varepsilon_{m+1} = x_m + \varepsilon_m - \delta t \underbrace{f(x_m + \varepsilon_m, t_m)}_{\approx f_m + \frac{\partial f}{\partial x}|_{t_m} \varepsilon_m}$$

subtract Eq. (***)

$$\Rightarrow \varepsilon_{m+1} = \underbrace{\left(1 - \delta t \frac{\partial f}{\partial x}\Big|_{t_m}\right)}_{=: g} \varepsilon_m$$

stability requires $|g| \leq 1$

$$\text{example: } \dot{x} + \alpha x = 0 \Rightarrow \frac{\partial f}{\partial x} = \alpha > 0$$

$$g = 1 - \delta t \alpha$$

$$|g| \leq 1 \Rightarrow (1 - \delta t \alpha)^2 \leq 1$$

\Rightarrow Euler alg. stable for $\delta t \leq \frac{2}{\alpha}$

$$\text{exact solution } x(t) = x_0 e^{-\alpha t}$$

$\alpha = \frac{1}{T}$, T : characteristic decay time

$$\Rightarrow \delta t \leq 2T$$

Note: δt must be chosen such that $\delta t \ll \tau$

(ii) harmonic oscillator

$$\frac{d v}{dt} = -\frac{k}{m} x \quad \frac{d x}{dt} = v$$

$$\text{set } k=1, m=1 \Rightarrow \frac{d v}{dt} = -x \quad \frac{d x}{dt} = v$$

$$\Rightarrow \text{Euler} \quad v_{n+1} = v_n - \delta t \cdot x_n$$

$$x_{n+1} = x_n + \delta t \cdot v_n$$

in matrix form

$$\vec{u}_n = \begin{pmatrix} x_n \\ v_n \end{pmatrix} \Rightarrow \vec{u}_{n+1} = \underbrace{\begin{pmatrix} 1 & \delta t \\ -\delta t & 1 \end{pmatrix}}_{= A} \vec{u}_n$$

point in phase space

→ consecutive application of \underline{A} gives sequence of phase space points $\vec{u}_0, \vec{u}_1, \vec{u}_2, \dots$

→ $\vec{\epsilon}_i$: discretization error at time t_i :

$$\vec{u}_{n+1} + \vec{\epsilon}_{n+1} = \underline{A} (\vec{u}_n + \vec{\epsilon}_n)$$

$$\underline{A} \text{ linear: } \vec{u}_{n+1} + \vec{\epsilon}_{n+1} = \underline{A} \vec{u}_n + \underline{A} \vec{\epsilon}_n$$

$$\Rightarrow \vec{\epsilon}_{n+1} = \underline{G} \vec{\epsilon}_n = \underline{A} \vec{\epsilon}_n$$

\uparrow
stability matrix

remark: \underline{A} non-linear, then linearize equations of motion

(iii) insert : stability matrix $\underline{\underline{G}}$

algorithm unstable if consecutive application of $\underline{\underline{G}}$ leads to diverging discretization error

$$\underline{\underline{G}} \vec{b} = \lambda \vec{b} \quad \left. \begin{array}{l} \vec{b} \text{ eigen vector} \\ \lambda \text{ eigen value} \end{array} \right\} \text{of } \underline{\underline{G}}$$

apply $\underline{\underline{G}}$ n times \Rightarrow

$$\underline{\underline{G}}^n \vec{b} = \lambda^n \vec{b}$$

$$\Rightarrow |\lambda| < 1 : \underline{\underline{G}}^n \vec{b} = 0 \text{ for } n \rightarrow \infty$$

$$|\lambda| > 1 : \underline{\underline{G}}^n \vec{b} \rightarrow \infty \text{ for } n \rightarrow \infty$$

k linear independent eigen vectors \vec{b}_i of $\underline{\underline{G}}$ and k eigen values λ_i ($i = 1, 2, \dots, k$)

$$\vec{\varepsilon} = \sum_{i=1}^k \alpha_i \vec{b}_i$$

$$\Rightarrow \underline{\underline{G}} \vec{\varepsilon} = \sum_{i=1}^k \alpha_i \underline{\underline{G}} \vec{b}_i = \sum_{i=1}^k \alpha_i \lambda_i \vec{b}_i$$

two cases :

1. $|\lambda_i| < 1 \quad \forall i \Rightarrow \underline{\underline{G}}^n \vec{\varepsilon} = 0 \text{ for } n \rightarrow \infty$

\Rightarrow algorithm stable

2. \exists at least one eigen value with index i for which $|\lambda_i| > 1$

$\Rightarrow \underline{\underline{G}}^n \vec{\varepsilon} \rightarrow \infty \text{ for } n \rightarrow \infty \Rightarrow$ algorithm unstable

definition: spectral radius $\rho(\underline{G}) = \max |\lambda|$;
 $\rho(\underline{G}) > 1 \Rightarrow$ algorithm unstable

(iv) apply to harmonic oscillator

$$\det(\underline{G} - \lambda \underline{I}) = \det \begin{pmatrix} 1-\lambda & \delta t \\ -\delta t & 1-\lambda \end{pmatrix} = 0$$

$$\Rightarrow \lambda^2 - 2\lambda + 1 + \delta t^2 = 0$$

$$\Rightarrow \lambda_{1,2} = 1 \pm \sqrt{-\delta t^2} = 1 \pm i\delta t$$

$$\Rightarrow |\lambda| = \sqrt{1 + \delta t^2} > 1$$

Enter algorithm unstable for any choice $\delta t > 0$

\rightarrow amplitude of oscillations increases as function of time

$$\rightarrow \text{total energy } E = \frac{1}{2} v^2 + \frac{1}{2} x^2$$

$$E_{n+1} = \frac{1}{2} v_{n+1}^2 + \frac{1}{2} x_{n+1}^2$$

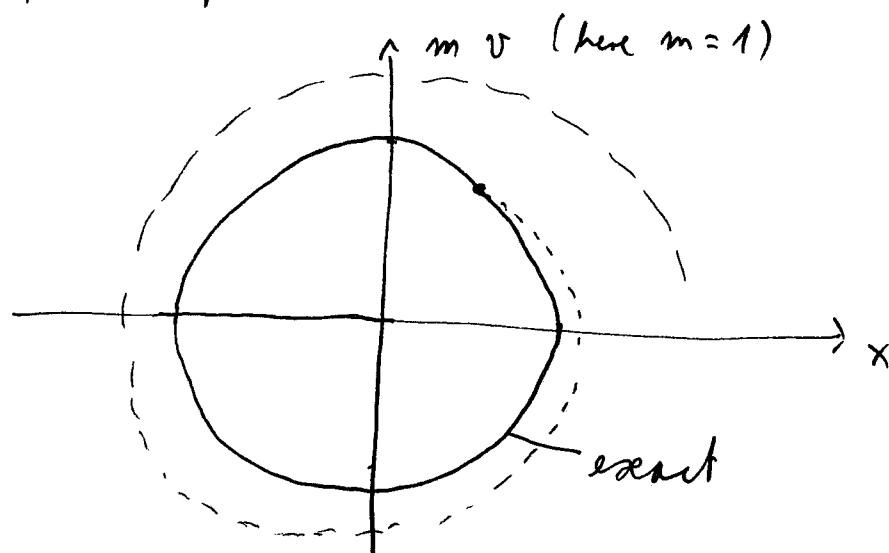
$$= \frac{1}{2} (v_n - \delta t x_n)^2 + \frac{1}{2} (x_n + \delta t v_n)^2$$

$$= \underbrace{\frac{1}{2} v_n^2 + \frac{1}{2} x_n^2}_{= E_n} + \delta t^2 \underbrace{\frac{1}{2} (v_n^2 + x_n^2)}_{= E_n}$$

$$= E_n (1 + \delta t^2)$$

\Rightarrow total energy not conserved, but increasing with time

→ phase space



Euler algorithm drives the system away from exact energy hyper surface (in this case a circle)

(V) simple modification of Euler algorithm for harmonic oscillator

$$\begin{aligned}
 v_{m+1} &= v_m - \delta t x_m \\
 x_{m+1} &= x_m + \underbrace{\delta t v_{m+1}}_{= x_m + \delta t v_m - \delta t^2 x_m}
 \end{aligned}$$

Euler-Cromer
algorithm

stability matrix

$$G = \begin{pmatrix} 1 & \delta t \\ -\delta t & 1 - \delta t^2 \end{pmatrix}$$

$$\det(G - \lambda \mathbb{1}) \neq 0$$

$$\Rightarrow \lambda^2 - \lambda(2 - \delta t^2) + 1 = 0$$

$$\Rightarrow \lambda_{1,2} = \frac{1}{2}(2 - \delta t^2) \pm \frac{1}{2}\delta t\sqrt{\delta t^2 - 4}$$

$\delta t > 2$: $|\lambda_2| > 1 \Rightarrow$ algorithm unstable

$\delta t \leq 2$: $|\lambda| = 1 \Rightarrow$ algorithm stable

define : $\tilde{E} = \frac{1}{2}v^2 + \frac{1}{2}x^2 - \frac{1}{2}\delta t x v$

$$\tilde{E}_{m+1} = \frac{1}{2}v_{m+1}^2 + \frac{1}{2}x_{m+1}^2 - \frac{1}{2}\delta t x_{m+1} v_{m+1}$$

$$= \frac{1}{2}[v_m - \delta t x_m]^2 + \frac{1}{2}[x_m + \delta t v_{m+1}]^2 - \frac{1}{2}\delta t (x_m + \delta t v_{m+1}) v_{m+1}$$

$$= \frac{1}{2}v_m^2 + \frac{1}{2}\delta t^2 x_m^2 - \delta t x_m v_m + \frac{1}{2}x_m^2 + \frac{1}{2}\delta t^2 v_{m+1}^2 + \delta t x_m v_{m+1}$$

$$- \frac{1}{2}\delta t x_m (v_m - \delta t x_m)$$

$$- \frac{1}{2}\delta t^2 \underline{v_{m+1}^2}$$

$$= \frac{1}{2}v_m^2 + \frac{1}{2}x_m^2 + \frac{1}{2}\delta t^2 \underline{x_m^2} - \delta t x_m v_m$$

$$+ \delta t x_m v_m - \underline{\delta t^2 x_m^2} - \frac{1}{2}\delta t x_m v_m$$

$$+ \frac{1}{2}\delta t^2 \underline{x_m^2}$$

$$= \frac{1}{2}v_m^2 + \frac{1}{2}x_m^2 - \frac{1}{2}\delta t x_m v_m = \tilde{E}_m$$

$\Rightarrow \tilde{E}$ conserved

(27)

correction $- \frac{1}{2} \delta t \times v$:

function that oscillates around zero and that vanishes when integrated over one period

I.3.2. Beyond the Euler algorithm

consider $\dot{x}(t) + f(x, t) = 0$

(i) leap frog algorithm

use $\dot{x}_m \approx \frac{x_{m+1} - x_{m-1}}{2 \delta t}$

$$\Rightarrow \boxed{x_{m+1} = x_{m-1} - 2 \delta t f_m}$$

accuracy

expand both sides of equation around $x_m \Rightarrow$

$$\begin{aligned} & x_m + \delta t \dot{x}_m + \frac{1}{2} \delta t^2 \ddot{x}_m + \frac{1}{6} \delta t^2 \dddot{x}_m + \dots \\ &= x_m - \delta t \dot{x}_m + \frac{1}{2} \delta t^2 \ddot{x}_m - \frac{1}{6} \delta t^3 \dddot{x}_m + \dots \\ & \quad - 2 \delta t f_m \\ & \quad \underbrace{}_{= - \ddot{x}_m} \end{aligned}$$

\Rightarrow all terms up to $\Theta(\delta t^2)$ cancel each other

\Rightarrow accuracy $\Theta(\delta t^2)$

stability:

$$\varepsilon_{n+1} = \varepsilon_{n-1} - 2 \delta t \left. \frac{\partial f}{\partial x} \right|_{t_n} \varepsilon_n$$

$$\text{set } \varepsilon_n = g \varepsilon_{n-1} \Rightarrow \varepsilon_{n+1} = g^2 \varepsilon_{n-1}$$

$$\Rightarrow \varepsilon_{n+1} = \varepsilon_{n-1} - 2 \delta t \left. \frac{\partial f}{\partial x} \right|_{t_n} g \varepsilon_{n-1}$$

$$= \underbrace{\left(1 - 2 \delta t \left. \frac{\partial f}{\partial x} \right|_{t_n} g \right)}_{= g^2} \varepsilon_{n-1}$$

$$\Rightarrow g = \delta t \left. \frac{\partial f}{\partial x} \right|_{t_n} \pm \sqrt{\left(\delta t \left. \frac{\partial f}{\partial x} \right|_{t_n} \right)^2 + 1}$$

example:

$$1. \dot{x} + \alpha x = 0 \quad \frac{\partial f}{\partial x} = \alpha > 0$$

$$\Rightarrow g_{\pm} = \delta t \alpha \pm \sqrt{\alpha^2 \delta t^2 + 1}$$

$$\Rightarrow |g| > 1 \text{ algorithm unstable}$$

examples :

1. $\dot{x} + \alpha x = 0 \quad \alpha > 0$
 $\Rightarrow g_{\pm} = \delta t \alpha \pm \sqrt{\alpha^2 \delta t^2 + 1}$

$\Rightarrow |g_+| > 1 \quad \text{algorithm unstable}$

2. complex differential equation with oscillatory solution

$\dot{x} + i\omega x = 0 \quad \frac{\partial f}{\partial x} = i\omega$

$\Rightarrow g_{\pm} = \delta t i\omega \pm \sqrt{1 - \omega^2 \delta t^2}$

two cases :

$\delta t > \frac{1}{\omega} : \quad g_{\pm} = i(\delta t \omega \pm \sqrt{\omega^2 \delta t^2 - 1})$

$\Rightarrow |g_{\pm}| = \delta t \omega \pm \sqrt{\omega^2 \delta t^2 - 1}$

$\Rightarrow |g_+| > 1 \quad \text{algorithm unstable}$

$\delta t \leq \frac{1}{\omega} : \quad \text{time step smaller than period of oscillation}$

$|g_{\pm}|^2 = 1 \quad \text{algorithm stable}$

(ii) implicit method

idea: approximate $\int_{t_n}^{t_{n+1}} f dt'$ by trapezoidal rule

$$\Rightarrow x_{n+1} = x_n - \frac{1}{2} \delta t (f_{n+1} + f_n)$$

problem: f_{n+1} depends on x_{n+1}

apply to $\dot{x} + \alpha x = 0$

$$x_{n+1} = x_n - \frac{1}{2} \delta t (\alpha x_{n+1} + \alpha x_n)$$

now solve for $x_{n+1} \Rightarrow$

$$x_{n+1} = \left(\frac{1 - \frac{1}{2} \delta t \alpha}{1 + \frac{1}{2} \delta t \alpha} \right) x_n$$

→ accuracy $\Theta(\delta t^2)$

→ stable also for oscillator ($\alpha \rightarrow \pm i\omega$)

- problem:
- works only in special cases
 - not applicable in general to non-linear differential equations

(iii) Runge-Kutta algorithms

- 2nd order scheme

idea: combine Euler and leap frog algorithm

→ Euler step for \dot{x} at half time step

→ then x_{m+1} via leap frog

$$\dot{x}_{m+\frac{1}{2}} = -f_{m+\frac{1}{2}} \approx x_m - \frac{1}{2} \delta t f_m$$

$$x_{m+1} = x_m + \delta t f_{m+\frac{1}{2}}$$

can be written as follows

$$K_1 = -f_m = -f(x_m, t_m)$$

$$K_2 = -f_{m+\frac{1}{2}} = -f\left(x_m + \frac{1}{2} \delta t K_1, t_m + \frac{1}{2} \delta t\right)$$

$$x_{m+1} = x_m + \delta t K_2$$

$$\text{now: } g = 1 - \delta t \frac{\partial f}{\partial x} + \frac{1}{2} \left(\delta t \frac{\partial f}{\partial x}\right)^2$$

examples:

$$\dot{x} + \alpha x = 0 \rightarrow \text{stable for } \delta t \leq \frac{2}{\alpha}$$

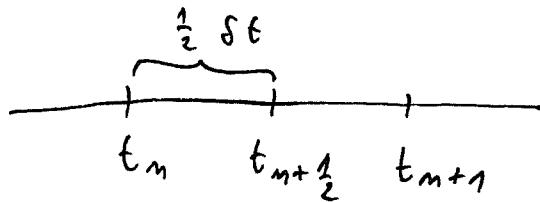
$$\dot{x} + i\omega x = 0 \rightarrow |g| = 1 + \frac{1}{4} \delta t^2 \omega^2 > 1$$

"weakly unstable"

- 3rd order scheme

$$\dot{x}(t) = -f(x, t)$$

integrate over time interval with "middle" node



apply Simpson's rule

$$\int_{t_m}^{t_{m+1}} f(x(t'), t') dt' \approx \frac{\delta t}{2} \frac{1}{3} [f_m + 4f_{m+\frac{1}{2}} + f_{m+1}]$$

$$\Rightarrow x_{m+1} = x_m - \frac{\delta t}{6} [f_m + 4f_{m+\frac{1}{2}} + f_{m+1}] + O(\delta t^5)$$

obtain f's from Euler steps

$$K_1 = -f_m = f(x_m, t_m)$$

$$K_2 = -f(x_m + \frac{1}{2}\delta t K_1, t_m + \frac{1}{2}\delta t)$$

$$= -f_{m+\frac{1}{2}}$$

$$K_3 = -f(x_m - \delta t K_1 + 2\delta t K_2, t_m + \delta t)$$

$$= -f_{m+1}$$

$$\Rightarrow x_{m+1} = x_m + \frac{1}{6} \delta t (K_1 + 4K_2 + K_3) + O(\delta t^4)$$

I. 3.3. Verlet algorithm

Hamilton's equations of motion for a N particle system

$$\dot{\vec{r}}_i \equiv \frac{d\vec{r}_i}{dt} = \vec{v}_i \quad ; = 1, 2, \dots, N$$

$$m_i \ddot{\vec{r}}_i = \vec{F}_i$$

requirements for algorithm:

- accuracy $\Theta(\delta t^2)$
- energy conserved
- time reversibility
- in general: symplectic properties of Hamilton's equations of motion

Taylor expansion forward and backward in time:

$$(i) \vec{r}_i(t + \delta t) = \vec{r}_i(t) + \delta t \vec{v}_i(t) + \frac{\delta t^2}{2m_i} \vec{F}_i(t) + \frac{1}{6} \delta t^3 \ddot{\vec{r}}_i(t) + \Theta(\delta t^4)$$

$$(ii) \vec{r}_i(t - \delta t) = \vec{r}_i(t) - \delta t \vec{v}_i(t) + \frac{\delta t^2}{2m_i} \vec{F}_i(t) - \frac{1}{6} \delta t^3 \ddot{\vec{r}}_i(t) + \Theta(\delta t^4)$$

$$(i) + (ii) : \boxed{\vec{r}_i(t + \delta t) = 2\vec{r}_i(t) - \vec{r}_i(t - \delta t) + \frac{1}{m_i} \delta t^2 \vec{F}_i(t) + \Theta(\delta t^4)}$$

$$(i) - (ii) : \boxed{\vec{v}_i(t) = \frac{1}{2\delta t} [\vec{r}_i(t + \delta t) - \vec{r}_i(t - \delta t)] + \Theta(\delta t^3)}$$

Verlet algorithm

→ time reversible

→ not elegant: update of \vec{r}_i and \vec{v}_i not synchronized

alternative algorithm:

$$(i) \vec{r}_i(t + \delta t) = \vec{r}_i(t) + \delta t \vec{v}_i(t) + \frac{1}{2m_i} \delta t^2 \vec{F}_i(t)$$

$$(ii) \vec{v}_i(t) = \vec{v}_i(t + \delta t) - \delta t \vec{v}_i(t + \delta t) + \frac{1}{2m_i} \delta t^2 \vec{F}_i(t + \delta t)$$

$$(i) + (ii) \Rightarrow$$

$$\vec{v}_i(t + \delta t) = \vec{v}_i(t) + \frac{\delta t}{2m_i} (\vec{F}_i(t) + \vec{F}_i(t + \delta t))$$

$$\Rightarrow \boxed{\begin{aligned} \vec{r}_i(t + \delta t) &= \vec{r}_i(t) + \delta t \vec{v}_i(t) + \frac{1}{2m_i} \delta t^2 \vec{F}_i(t) \\ \vec{v}_i(t + \delta t) &= \vec{v}_i(t) + \frac{\delta t}{2m_i} (\vec{F}_i(t) + \vec{F}_i(t + \delta t)) \end{aligned}}$$

velocity Verlet algorithm

time reversible?

$$t + \delta t \leftrightarrow t \quad \delta t \rightarrow -\delta t$$

$$\vec{r}_i(t) = \vec{r}_i(t + \delta t) - \delta t \vec{v}_i(t + \delta t) + \frac{1}{2m_i} \delta t^2 \vec{F}_i(t + \delta t)$$

$$\vec{v}_i(t) = \vec{v}_i(t + \delta t) - \frac{\delta t}{2m_i} (\vec{F}_i(t + \delta t) + \vec{F}_i(t))$$

$$\Rightarrow \vec{v}_i(t + \delta t) = \vec{v}_i(t) + \frac{\delta t}{2m_i} (\vec{F}_i(t) + \vec{F}_i(t + \delta t)) \checkmark$$

in Eq. for $\vec{r}_i(t)$:

$$\vec{r}_i(t) = \vec{r}_i(t+\delta t) - \delta t \vec{v}_i(t) - \frac{\delta t^2}{2m_i} (\vec{F}_i(t) + \vec{F}_i(t+\delta t)) \\ + \frac{\delta t^2}{2m_i} \vec{F}_i(t+\delta t)$$

then $\vec{r}_i(t) \approx \vec{r}_i(t+\delta t) - \delta t \vec{v}_i(t)$

$$\Rightarrow \vec{r}_i(t+\delta t) = \vec{r}_i(t) + \delta t \vec{v}_i(t) + \frac{\delta t^2}{2m_i} \vec{F}_i(t) \quad \checkmark$$

I. 3.4. Velocity Verlet algorithm for harmonic oscillator
Hamilton function

$$H(x, p) = \frac{p^2}{2m} + \frac{1}{2} m \omega^2 x^2$$

equations of motion

$$\dot{x} = \frac{p}{m} \quad \dot{p} = -m \omega^2 x$$

\Rightarrow velocity Verlet:

$$(i) \quad x(t+\delta t) = x(t) + \delta t \frac{p(t)}{m} - \frac{1}{2} \delta t^2 \omega^2 x(t)$$

$$(ii) \quad p(t+\delta t) = p(t) - \frac{m \omega^2}{2} \delta t (x(t) + x(t+\delta t))$$

conserved quantity associated with these equations?

$$\tilde{H}(x, p, \delta t) = \frac{p^2}{2m(1 - \frac{\omega^2}{4} \delta t^2)} + \frac{1}{2} m \omega^2 x^2$$

remarks :

- \tilde{H} is called shadow Hamilton function.
- \tilde{H} conserved: $\tilde{H}(x(t), p(t); \delta t) = \tilde{H}(x(t+\delta t), p(t+\delta t); \delta t)$
- $\tilde{H}(x(t), p(t); \delta t) \xrightarrow{\delta t \rightarrow 0} H(x, p)$
- algorithm stable for $\delta t < \frac{2}{\omega}$, in practice $\delta t \ll \frac{2}{\omega}$
- leading order correction
 - expand kinetic energy in \tilde{H}
 - $\Rightarrow \tilde{H} = \frac{P^2}{2m} \left[1 + \frac{\omega^2}{4} (\delta t)^2 + O(\delta t^4) \right] + \frac{1}{2} m \omega^2 x^2$
 - correction to exact energy $\propto \delta t^2$
 - can be used to check correct implementation of algorithm

I.4. Hamiltonian dynamics and symplectic algorithms

I.4.1. Canonical transformations

Hamilton function

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U(\vec{q}_1, \vec{q}_2, \dots, \vec{q}_N)$$

$\Rightarrow 2dN$ equations of motion (d : dimension)

$$\dot{\vec{q}}_i = \frac{\partial H}{\partial \vec{p}_i} \equiv \nabla_{\vec{p}_i} H = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{q}_i} \equiv -\nabla_{\vec{q}_i} H = -\frac{\partial U}{\partial \vec{q}_i}$$

in matrix form

$$\dot{\vec{\eta}} = (\underbrace{\vec{q}_1, \dots, \vec{q}_N}_{= \vec{Q}}, \underbrace{\vec{p}_1, \dots, \vec{p}_N}_{= \vec{P}})^T \text{ a transposed vector}$$

$$\dot{\vec{\eta}} = \underline{\underline{\omega}} \frac{\partial H}{\partial \vec{\eta}} = \underline{\underline{\omega}} \nabla_{\vec{\eta}} H$$

with $\underline{\underline{\omega}} = \underbrace{\begin{pmatrix} 0 & \mathbb{1}_{dN} \\ -\mathbb{1}_{dN} & 0 \end{pmatrix}}_{2dN}$

and $\mathbb{1}_{dN} = \begin{pmatrix} 1 & & & \\ & \ddots & & \\ & & 0 & \\ 0 & & & 1 \end{pmatrix}^{2dN}$ $dN \times dN$ unit matrix

transformation of variables:

$$\vec{\gamma} = (\vec{q}_1, \dots, \vec{q}_N, \vec{p}_1, \dots, \vec{p}_N)$$

to new coordinates

$$\vec{\xi} = (\tilde{\vec{q}}_1, \dots, \tilde{\vec{q}}_N, \tilde{\vec{p}}_1, \dots, \tilde{\vec{p}}_N)$$

\Rightarrow map $F: \vec{\gamma} \rightarrow \vec{\xi}$ inverse map $f \equiv F^{-1}: \vec{\xi} \rightarrow \vec{\gamma}$

$$\xi_i = F_i(\vec{\gamma}) \quad \gamma_i = f_i(\vec{\xi})$$

requirements for this map:

F is a diffeomorphism.

$\rightarrow F$ bijective map.

$\rightarrow F$ and f are ^{continuously} differentiable.

\Rightarrow determinant of Jacobi matrix: $\det(\underline{M}) \neq 0$

$$\underline{M} \text{ with elements } M_{ij} = \frac{\partial \xi_i}{\partial \gamma_j}$$

consider total differential of ξ_i :

$$d\xi_i = \frac{\partial \xi_i}{\partial \gamma_1} d\gamma_1 + \frac{\partial \xi_i}{\partial \gamma_2} d\gamma_2 + \dots + \frac{\partial \xi_i}{\partial \gamma_{2dN}} d\gamma_{2dN}$$

\Rightarrow total time derivative

$$\dot{\xi}_i = \frac{d\xi_i}{dt} = \frac{\partial \xi_i}{\partial \eta_1} \dot{\eta}_1 + \dots + \frac{\partial \xi_i}{\partial \eta_{2dN}} \dot{\eta}_{2dN}$$

for all $2dN$ $\xi_i \rightarrow \xi_i \vec{\xi}$

$$\dot{\vec{\xi}} = \underline{M} \vec{\eta} = \underline{M} \underline{w} \frac{\partial H}{\partial \vec{\eta}} \quad (+)$$

transformation of coordinates for Hamilton function
 \rightarrow derivatives

$$\frac{\partial H}{\partial \eta_i} = \sum_{j=1}^{2dN} \frac{\partial H}{\partial \xi_j} \frac{\partial \xi_j}{\partial \eta_i} \quad (++)$$

in matrix form $\frac{\partial H}{\partial \vec{\eta}} = \tilde{M} \frac{\partial H}{\partial \vec{\xi}}$

$$\tilde{M}_{ij} = \frac{\partial \xi_j}{\partial \eta_i} = \left(\frac{\partial \xi_i}{\partial \eta_j} \right)^T = M_{ij}^T$$

M^T transposed matrix of M

(++) in (+) \Rightarrow

$$\dot{\vec{\xi}} = \underline{M} \underline{w} \underline{M}^T \frac{\partial H}{\partial \vec{\xi}} = \underline{M} \underline{w} \underline{M}^T \nabla_{\vec{\xi}} H$$

canonical or symplectic transformation

under this transformation Hamilton's equations of motion maintain their form \Rightarrow

$$\boxed{\underline{M} \quad \underline{W} \quad \underline{M}^T = \underline{W}} \quad (3+)$$

$$\Rightarrow \det(\underline{M} \underline{W} \underline{M}^T) = \det \underline{W}$$

$$= [\det(\underline{M})]^2 \det \underline{W}$$

$$\Rightarrow |\det \underline{M}| = 1 \quad (4+)$$

\underline{M} for which (3+) holds is called symplectic matrix.

remarks:

- the set of all symplectic matrices \underline{M} forms a group, the ^{real} symplectic group $S\mathrm{p}_{2dN}(\mathbb{R})$ on \mathbb{R}^{2dN}
- Eq. (4+) \Rightarrow

$$d\tilde{\vec{q}}_1 \dots d\tilde{\vec{q}}_N d\tilde{\vec{p}}_1 \dots d\tilde{\vec{p}}_N$$

$$= |\det \underline{M}| d\vec{q}_1 \dots d\vec{q}_N d\vec{p}_1 \dots d\vec{p}_N$$

$$\stackrel{!}{=} d\vec{q}_1 \dots d\vec{q}_N d\vec{p}_1 \dots d\vec{p}_N$$

\Rightarrow symplectic transformation conserves phase space volume

I.4.2. Time propagation as symplectic transformation
propagate system over infinitesimal time step δt

$$\begin{aligned}\vec{\xi} &= \vec{\eta}(t + \delta t) \\ &= \underset{\substack{\uparrow \\ \text{Taylor}}}{\vec{\eta}(t)} + \dot{\vec{\eta}}(t) \delta t \\ &\quad \text{expansion}\end{aligned}$$

Jacobi matrix

$$\begin{aligned}\underline{M} &= \frac{\partial \vec{\xi}}{\partial \vec{\eta}} = \underline{1} + \delta t \frac{\partial}{\partial \vec{\eta}} \left(\underline{w} \frac{\partial H}{\partial \vec{\eta}} \right) \\ &= \underline{1} + \delta t \underline{w} \frac{\partial^2 H}{\partial \vec{\eta} \partial \vec{\eta}}\end{aligned}$$

$$\begin{aligned}\underline{M}^T &= \underline{1} + \delta t \frac{\partial^2 H}{\partial \vec{\eta} \partial \vec{\eta}} \underline{w}^T \\ &= -\underline{w}\end{aligned}$$

$$= \underline{1} - \delta t \frac{\partial^2 H}{\partial \vec{\eta} \partial \vec{\eta}} \underline{w}$$

$$\begin{aligned}\Rightarrow \underline{M} \underline{w} \underline{M}^T &= (\underline{1} + \delta t \underline{w} \frac{\partial^2 H}{\partial \vec{\eta} \partial \vec{\eta}}) \underline{w} \\ &\rightarrow (\underline{1} - \delta t \frac{\partial^2 H}{\partial \vec{\eta} \partial \vec{\eta}} \underline{w})\end{aligned}$$

$$= \underline{\underline{W}} + \delta t \underline{\underline{W}} \frac{\partial^2 H}{\partial \vec{q} \cdot \partial \vec{q}} \underline{\underline{W}}$$

$$- \delta t \underline{\underline{W}} \frac{\partial^2 H}{\partial \vec{q} \cdot \partial \vec{q}} \underline{\underline{W}} + O(\delta t^2)$$

$$= \underline{\underline{W}}$$

→ infinitesimal time propagation symplectic

→ arbitrary times by sequential application of infinitesimal time propagator

time evolution in Hamiltonian system:

(1) phase space density

$$f(\vec{q}, t) = f(q_1, \dots, q_N, p_1, \dots, p_N, t)$$

$f(\vec{q}, t) d\vec{q}$: probability to find system in the region $d\vec{q}$ around "point" \vec{q} at time t

total time derivative

$$\begin{aligned} \frac{df(\vec{q}, t)}{dt} &= \frac{\partial f}{\partial t} + \sum_{i=1}^N \left(\underbrace{\frac{\partial f}{\partial q_i} \cdot \dot{q}_i}_{= \frac{\partial H}{\partial p_i}} + \underbrace{\frac{\partial f}{\partial p_i} \cdot \dot{p}_i}_{= -\frac{\partial H}{\partial q_i}} \right) \\ &\equiv \{f, H\} \text{ Poisson bracket} \end{aligned}$$

$$= \frac{\partial f}{\partial t} + \{ f, H \}$$

$$=: \frac{\partial f}{\partial t} + \mathcal{L} f$$

$$\boxed{\mathcal{L} = \sum_{i=1}^N \left(\frac{\partial H}{\partial \vec{p}_i} \cdot \frac{\partial}{\partial \vec{q}_i} - \frac{\partial H}{\partial \vec{q}_i} \cdot \frac{\partial}{\partial \vec{p}_i} \right)}$$

Liouville operator

equilibrium $\frac{df}{dt} = 0$

$$\Rightarrow \frac{\partial f}{\partial t} + \mathcal{L} f = 0$$

formal solution $f(\vec{q}, t) = e^{-\mathcal{L}t} f(\vec{q}, 0)$

This solution describes propagation of system in time
at a fixed phase space point \vec{q}^* .

(2) time evolution of \vec{q}^*

$$\frac{d \vec{q}^*}{dt} = \frac{\partial \vec{q}^*}{\partial t} + \mathcal{L} \vec{q}^*$$

assume that \vec{q}^* not explicitly dependent on time

$$\Rightarrow \frac{\partial \vec{q}^*}{\partial t} = 0$$

$$\Rightarrow \frac{d\vec{\gamma}}{dt} = \mathcal{L} \vec{\gamma}$$

formal solution: $\vec{\gamma}(t) = (\vec{q}_1(t), \dots, \vec{q}_N(t), \vec{p}_1(t), \dots, \vec{p}_N(t))$

$$= e^{\mathcal{L} t} \vec{\gamma}(0)$$

idea: split Liouville operator

$$\begin{aligned} \mathcal{L}_Q &= \sum_{i=1}^N \underbrace{\dot{\vec{q}}_i}_{= \frac{\partial H}{\partial \vec{p}_i}} \cdot \frac{\partial}{\partial \vec{q}_i} & \mathcal{L}_P &= \sum_{i=1}^N \underbrace{\dot{\vec{p}}_i}_{= -\frac{\partial H}{\partial \vec{q}_i}} \cdot \frac{\partial}{\partial \vec{p}_i} \end{aligned}$$

time evolution with respect to \mathcal{L}_Q and \mathcal{L}_P "trivial"

$$e^{\mathcal{L}_Q t} \vec{\gamma}(0) = \sum_{m=0}^{\infty} \sum_{i=1}^N \frac{[\dot{\vec{q}}_i(0) t]^m}{m!} \frac{\partial^m \vec{\gamma}(0)}{\partial \vec{q}_i^m}$$

consider $\vec{q}_1(0) \Rightarrow$

$$\begin{aligned} e^{\mathcal{L}_Q t} \vec{q}_1(0) &= \sum_{m=0}^{\infty} \sum_{i=1}^N \frac{[\dot{\vec{q}}_1(0) t]^m}{m!} \frac{\partial^m \vec{q}_1}{\partial \vec{q}_1^m} \Big|_{t=0} \\ &= \vec{q}_1(0) + \underbrace{\frac{\dot{\vec{q}}_1(0) t}{1} \frac{\partial \vec{q}_1}{\partial \vec{q}_1}}_{= 1} \Big|_{t=0} \\ &= \vec{q}_1(0) + \dot{\vec{q}}_1(0) t \end{aligned}$$

$$e^{\mathcal{L}_Q t} \vec{\gamma}(0) = (\vec{q}_1(0) + \dot{\vec{q}}_1(0) t, \dots, \vec{q}_N(0) + \dot{\vec{q}}_N(0) t, \vec{p}_1(0), \dots, \vec{p}_N(0))^T$$

operator $e^{\mathcal{L}_Q t}$ leads to translation of coordinates

similarly:

$$e^{d_p t} \vec{\eta}(0) = (\vec{q}_1(0), \dots, \vec{q}_N(0), \vec{p}_1(0) + \dot{\vec{p}}_1(0)t, \dots, \vec{p}_N(0) + \dot{\vec{p}}_N(0)t)^T$$

\Rightarrow translation of momenta

$$\text{but: } e^{dt} \neq e^{d_Q t} e^{d_P t}$$

d_Q and d_P do not commute: $d_Q d_P \neq d_P d_Q$

I.4.3. Symplectic algorithms

idea: apply time evolution operators sequentially over infinitesimal time step δt

effect of $e^{d_P \delta t} e^{d_Q \delta t}$?

consider time evolution from $t = 0$ to $t = \delta t$

$$\vec{\eta} = (Q, P)^T$$

$$e^{d_P \delta t} e^{d_Q \delta t} \vec{\eta}(0)$$

$$= e^{d_P \delta t} (Q(0) + \underbrace{\dot{Q}(0) \delta t}_{= \frac{1}{m} P(0)}, P(0))^T$$

$$= Q(\delta t)$$

$$= (Q(\delta t), P(0) + \underbrace{\dot{P}(0) \delta t}_{= -\frac{\partial H}{\partial Q}(Q(\delta t))})^T = (Q(\delta t), P(\delta t))^T$$

$$\Rightarrow \boxed{Q(\delta t) = Q(0) + \frac{P(0)}{m} \delta t}$$

$$P(\delta t) = P(0) - \frac{\partial U(Q(0))}{\partial Q} \delta t$$

symplectic Euler algorithm (A)

remark: this algorithm is not time-reversible

$$\delta t \rightarrow -\delta t \Rightarrow$$

$$Q(0) = Q(\delta t) - \frac{P(\delta t)}{m} \delta t$$

$$P(0) = P(\delta t) + \frac{\partial U(Q(\delta t))}{\partial Q} \delta t$$

$$\Rightarrow \boxed{P(\delta t) = P(0) - \frac{\partial U(Q(0))}{\partial Q} \delta t}$$

$$Q(\delta t) = Q(0) + \frac{P(0)}{m} \delta t$$

symplectic Euler algorithm (B)

$$\text{now: } e^{\mathcal{L}_P \delta t} e^{\mathcal{L}_Q \delta t} \neq e^{(\mathcal{L}_P + \mathcal{L}_Q) \delta t}$$

how is $e^{\mathcal{L}_P \delta t} e^{\mathcal{L}_Q \delta t}$ related to the exact time evolution?

$$\text{ansatz: } e^{\mathcal{L}_P \delta t} e^{\mathcal{L}_Q \delta t} = e^{\mathcal{L}_{\text{app}} \delta t}$$

\mathcal{L}_{app} describes time evolution with respect to modified equation

$$\frac{d\vec{\eta}}{dt} = \mathcal{L}_{\text{app}} \vec{\eta} = \{ \vec{\eta}, H_{\text{app}} \}$$

$\vec{\eta}$ shadow Hamilton function

$$\vec{\eta}^0(0) = (Q(0), P(0)) \rightarrow \vec{\eta}(st) = (Q(st), P(st))$$

$$e^{L_Q st} Q(0) = Q(0) + \dot{Q}(0) st$$

$$e^{L_Q st} P(0) = P(0)$$

$$e^{L_P st} P(0) = P(0) + \dot{P}(0) st$$

$$e^{L_P st} Q(0) = Q(0)$$

$$L_Q = \dot{Q} \cdot \frac{\partial}{\partial Q} = \frac{\partial H}{\partial P} \cdot \frac{\partial}{\partial Q}$$

$$L_P = \dot{P} \cdot \frac{\partial}{\partial P} = - \frac{\partial H}{\partial Q} \cdot \frac{\partial}{\partial P}$$

$$= - \frac{\partial U}{\partial Q}$$

$$e^{L_P st} e^{L_Q st} \vec{\eta}^0(0)$$

$$Q(st) = Q(0) + \frac{1}{m} P(0) st \quad (Q(st), P(0))$$

$$P(st) = P(0) - \frac{\partial U(Q(st))}{\partial Q} \quad (Q(st), P(st))$$

$$e^{L_P st} e^{L_Q st} \neq e^{L st} \quad L = L_P + L_Q$$

sequences of translations of phase space coordinates

relation of $e^{L_P st} e^{L_Q st}$ to exact time evolution?

$$\text{ansatz } e^{L_P st} e^{L_Q st} = e^{L_{app} st}$$

L_{app} describes time evolution with respect to modified equation

$$\text{exact equation: } \frac{d\vec{\eta}}{dt} = L \vec{\eta} = \frac{\partial H}{\partial P} \cdot \frac{\partial \vec{\eta}}{\partial Q} + - \frac{\partial H}{\partial Q} \cdot \frac{\partial \vec{\eta}}{\partial P}$$

$$\frac{\partial \vec{\gamma}}{\partial Q} = \frac{\partial}{\partial Q} \begin{pmatrix} Q \\ P \end{pmatrix} = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \hat{e}_Q$$

$$\frac{\partial \vec{\gamma}}{\partial P} = \frac{\partial}{\partial P} \begin{pmatrix} Q \\ P \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \hat{e}_P$$

$$\Rightarrow \frac{d \vec{\gamma}}{dt} = \mathcal{L} \vec{\gamma} = \{ \vec{\gamma}, H \}$$

$$= \frac{\partial H}{\partial P} \hat{e}_Q - \frac{\partial H}{\partial Q} \hat{e}_P$$

now ansatz:

$$e^{\lambda_P st} e^{\lambda_Q st} = e^{\lambda_{app} st}$$

λ_{app} describes time evolution with respect to modified equations of motion

$$\frac{d \vec{\gamma}}{dt} = \mathcal{L}_{app} \vec{\gamma} = \{ \vec{\gamma}, H_{app} \}$$

↑
shadow Hamilton function

use Baker - Campbell - Hausdorff formula

A, B non-commuting operators, then $e^A e^B = e^C$ with

$$C = A + B + \frac{1}{2} \underbrace{[A, B]}_{AB - BA} + \frac{1}{12} [A, [A, B]]$$

$$- \frac{1}{12} [B, [A, B]] - \frac{1}{24} [B, [A, [A, B]]]$$

- ...

here: $A = \mathcal{L}_P \delta t$, $B = \mathcal{L}_Q \delta t$, $C = \mathcal{L}_{app} \delta t$

$$\Rightarrow \boxed{\begin{aligned} \mathcal{L}_{app} &= \mathcal{L}_P + \mathcal{L}_Q + \frac{1}{2} \delta t [\mathcal{L}_P, \mathcal{L}_Q] \\ &\quad + \frac{1}{12} \delta t^2 [\mathcal{L}_P, [\mathcal{L}_P, \mathcal{L}_Q]] \\ &\quad - \frac{1}{12} \delta t^2 [\mathcal{L}_Q, [\mathcal{L}_P, \mathcal{L}_Q]] + O(\delta t^3) \end{aligned}}$$

H_{app} ?

$$\mathcal{L}_{app} \vec{\gamma} = \{\vec{\gamma}, H_{app}\}$$

$$= \underbrace{\frac{\partial \vec{\gamma}}{\partial Q} \frac{\partial H_{app}}{\partial P}}_{\begin{pmatrix} 1 \\ 0 \end{pmatrix} =: \hat{e}_Q} - \underbrace{\frac{\partial \vec{\gamma}}{\partial P} \frac{\partial H_{app}}{\partial Q}}_{\begin{pmatrix} 0 \\ 1 \end{pmatrix} =: \hat{e}_P}$$

$$= \hat{e}_Q \frac{\partial H_{app}}{\partial P} - \hat{e}_P \frac{\partial H_{app}}{\partial Q} \quad (*)$$

$$\mathcal{L}_{app} \vec{\gamma} = \left(\mathcal{L}_P + \mathcal{L}_Q + \frac{1}{2} \delta t [\mathcal{L}_P, \mathcal{L}_Q] + O(\delta t^2) \right) \begin{pmatrix} Q \\ P \end{pmatrix}$$

$$= \left(-\frac{\partial H}{\partial Q} \frac{\partial}{\partial P} + \frac{\partial H}{\partial P} \frac{\partial}{\partial Q} - \frac{1}{2} \delta t \frac{\partial H}{\partial Q} \frac{\partial}{\partial P} \frac{\partial H}{\partial P} \frac{\partial}{\partial Q} \right. \\ \left. + \frac{1}{2} \delta t \frac{\partial H}{\partial P} \frac{\partial}{\partial Q} \frac{\partial H}{\partial Q} \frac{\partial}{\partial P} + O(\delta t^2) \right) \begin{pmatrix} Q \\ P \end{pmatrix}$$

$$\frac{\partial H}{\partial Q} = \frac{\partial(T+U)}{\partial Q} = \frac{\partial U}{\partial Q}, \quad \frac{\partial H}{\partial P} = \frac{\partial T}{\partial P}$$

$$\Rightarrow \mathcal{L}_{app} \vec{\gamma} = -\frac{\partial U}{\partial Q} \hat{e}_P + \frac{\partial T}{\partial P} \hat{e}_Q - \frac{1}{2} \delta t \frac{\partial U}{\partial Q} \frac{\partial}{\partial P} \frac{\partial T}{\partial P} \hat{e}_Q$$

$$+ \frac{1}{2} \delta t \frac{\partial T}{\partial P} \frac{\partial}{\partial Q} \frac{\partial U}{\partial Q} \hat{e}_P + O(\delta t^2)$$

$$= \hat{e}_Q \frac{\partial}{\partial P} \left(T - \frac{1}{2} \delta t \frac{\partial U}{\partial Q} \frac{\partial T}{\partial P} \right)$$

$$- \hat{e}_P \frac{\partial}{\partial Q} \left(U - \frac{1}{2} \delta t \frac{\partial T}{\partial P} \frac{\partial U}{\partial Q} \right) + O(\delta t^2)$$

\Rightarrow compare to Eq. (*)

$$H_{app} = T + U - \frac{1}{2} \delta t \frac{\partial U}{\partial Q} \frac{\partial T}{\partial P} + O(\delta t^2)$$

$$\{T, U\} = \underbrace{\frac{\partial T}{\partial Q}}_{=0} \underbrace{\frac{\partial U}{\partial P}}_{=0} - \frac{\partial U}{\partial Q} \frac{\partial T}{\partial P} = -\frac{P}{m} \frac{\partial U}{\partial Q}$$

\Rightarrow

$$\boxed{H_{app} = T + U + \frac{1}{2} \delta t \{T, U\} + O(\delta t^2)}$$

shadow Hamilton function up to $O(\delta t)$

remarks:

- shadow Hamilton function with 2nd order term

$$H_{app} = T + U + \frac{1}{2} \delta t \{ T, U \}$$

$$+ \frac{1}{12} \delta t^2 (\{ T, \{ T, U \} \} - \{ U, \{ T, U \} \})$$

+ ...

- symplectic Euler algorithm solves ~~evolutes~~ time evolution of system with respect to modified Hamilton function H_{app}

- problem:
 - algorithm not time-reversible
 - due to symmetry of H_{app} depending on odd powers of δt

- idea: find L_{app} for which the corresponding H_{app} depends only on even powers of δt

→ 2nd order algorithm

→ 2nd order splitting of time evolution operator

$$\text{e.g. } e^{\frac{1}{2} \delta t L_p} e^{\delta t L_A} e^{\frac{1}{2} \delta t L_p}$$

consider time evolution from $t=0$ to $t=\delta t$ for $\vec{\eta} = (Q, P)^T$
exact Hamilton function $H = H(Q, P)$

$$= T(P) + U(Q)$$

ansatz: $e^{\frac{1}{2}\delta t \mathcal{L}_P} e^{\delta t \mathcal{L}_Q} e^{\frac{1}{2}\delta t \mathcal{L}_P}$

(i) $e^{\frac{1}{2}\delta t \mathcal{L}_P} (Q(0), P(0))^T$

$$= (Q(0), \underbrace{P(0) + \frac{\delta t}{2} \dot{P}(0)}_{\text{momentum of particle}})^T$$

at time $\frac{1}{2}\delta t$

$$= (Q(0), P(0) + \frac{\delta t}{2m} \underbrace{F(0)}_{\text{}})^T$$

$$\equiv F(Q(0)) = - \frac{\partial U}{\partial Q}$$

$$= (Q(0), P(\frac{\delta t}{2}))^T$$

(ii) $e^{\delta t \mathcal{L}_Q} (Q(0), P(\frac{\delta t}{2}))^T$

$$= (Q(0) + \frac{\delta t}{m} P(\frac{\delta t}{2}), P(\frac{\delta t}{2}))^T$$

$$= (\underbrace{Q(0) + \frac{\delta t}{m} P(0) + \frac{\delta t^2}{2m} F(0)}_{= Q(\delta t)}, P(0) + \frac{\delta t}{2m} F(0))^T$$

$$= (Q(\delta t), P(\frac{\delta t}{2}))^T$$

$$\begin{aligned}
 \text{(iii)} \quad & e^{\frac{1}{2} \delta t \mathcal{L}_P} (Q(\delta t), P(\frac{\delta t}{2}))^T \\
 &= (Q(\delta t), P(\frac{\delta t}{2}) + \frac{1}{2} \delta t \underbrace{F(Q(\delta t))}_{\equiv F(\delta t)})^T
 \end{aligned}$$

$$\Rightarrow \boxed{
 \begin{aligned}
 Q(\delta t) &= Q(0) + \frac{\delta t}{m} P(0) + \frac{\delta t^2}{2m} F(0) \\
 P(\delta t) &= P(0) + \frac{\delta t}{2m} (F(0) + F(\delta t))
 \end{aligned}
 }$$

velocity Verlet algorithm

\mathcal{L}_{app} and H_{app} ?

$$\text{ansatz } e^{\frac{1}{2} \delta t \mathcal{L}_P} e^{\delta t \mathcal{L}_Q} e^{\frac{1}{2} \delta t \mathcal{L}_P} = e^{\delta t \mathcal{L}_{app}}$$

$$\begin{aligned}
 \mathcal{L}_{app} = & \mathcal{L}_P + \mathcal{L}_Q + \frac{\delta t^2}{24} (2 [\mathcal{L}_Q, [\mathcal{L}_Q, \mathcal{L}_P]] \\
 & - [\mathcal{L}_P, [\mathcal{L}_P, \mathcal{L}_Q]]) \\
 & + \mathcal{O}(\delta t^4)
 \end{aligned}$$

corresponding Hamilton function

$$\begin{aligned}
 H_{app} = & T + U + \frac{\delta t^2}{24} (2 \{U, \{U, T\}\} \\
 & - \{T, \{T, V\}\}) + \mathcal{O}(\delta t^4)
 \end{aligned}$$

remarks:

- velocity Verlet algorithm time-reversible
- leading order term in H_{app} $\mathcal{O}(\delta t^2)$
→ can be used to check algorithm!
- velocity Verlet algorithm can be also written as follows

$$\boxed{\begin{aligned} P\left(\frac{\delta t}{2}\right) &= P(0) + \frac{\delta t}{2m} F(0), \\ Q(\delta t) &= Q(0) + \frac{\delta t}{m} P\left(\frac{\delta t}{2}\right), \\ P(\delta t) &= P\left(\frac{\delta t}{2}\right) + \frac{1}{2} \delta t F(\delta t) \end{aligned}}$$

- consider different ansatz

$$\begin{aligned} & e^{\frac{1}{2}\delta t \mathcal{L}_Q} e^{\delta t \mathcal{L}_P} e^{\frac{1}{2}\delta t \mathcal{L}_Q} (Q(0), P(0))^T \\ &= e^{\frac{1}{2}\delta t \mathcal{L}_Q} e^{\delta t \mathcal{L}_P} \underbrace{(Q(0) + \frac{\delta t}{2m} P(0), P(0))_T}_{= Q\left(\frac{\delta t}{2}\right)} \\ &= e^{\frac{1}{2}\delta t \mathcal{L}_Q} (Q\left(\frac{\delta t}{2}\right), \underbrace{P(0) + \delta t F\left(\frac{\delta t}{2}\right)}_{= P(\delta t)})^T \\ &= (Q\left(\frac{\delta t}{2}\right) + \frac{\delta t}{2m} P(\delta t), P(\delta t))^T \\ &= Q(\delta t) \end{aligned}$$

$$= (Q(\delta t), P(\delta t))$$

\Rightarrow

$$Q\left(\frac{\delta t}{2}\right) = Q(0) + \frac{\delta t}{2m} P(0)$$

$$P(\delta t) = P(0) + \delta t F\left(\frac{\delta t}{2}\right)$$

$$Q(\delta t) = Q\left(\frac{\delta t}{2}\right) + \frac{\delta t}{2m} P(\delta t)$$

I.5. Molecular dynamics simulation at work

I.5.1. Simulation of a two-dimensional fluid

system of N particles: coordinates $\vec{R} = \{\vec{r}_1, \dots, \vec{r}_N\}$
 momenta $\vec{P} = \{\vec{p}_1, \dots, \vec{p}_N\}$

2 dimensions: $d=2$; \vec{r}_i, \vec{p}_i two-dimensional vectors

Hamilton function

$$H = T + U = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U(\vec{R})$$

⇒ equations of motion mass of particle;

$$\dot{\vec{r}}_i = \frac{\partial H}{\partial \vec{p}_i} = \frac{\vec{p}_i}{m_i} \Rightarrow \vec{p}_i = m_i \vec{v}_i$$

$$\dot{\vec{p}}_i = -\frac{\partial H}{\partial \vec{r}_i} = -\frac{\partial U}{\partial \vec{r}_i} = F_i$$

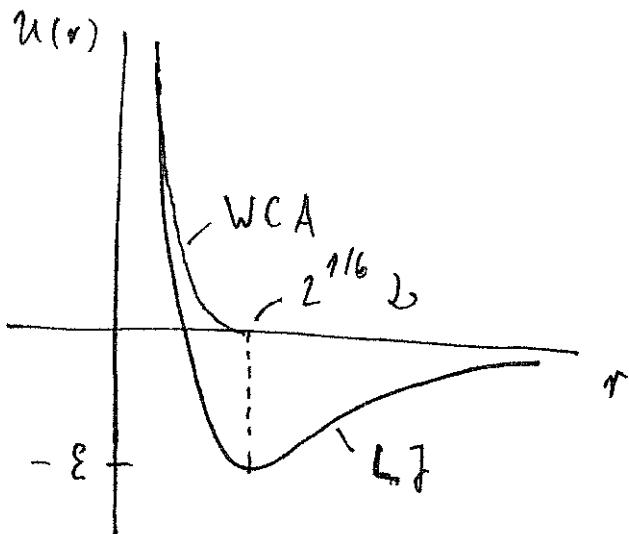
force on particle i

assume pairwise-additive model potential

$$U = \sum_{i=1}^N \sum_{j>i} u(r_{ij})$$

$\underbrace{= |\vec{r}_{ij}| = |\vec{r}_i - \vec{r}_j|}$

choose WCA (Weeks - Chandler - Andersen) potential



"cut off" Lennard-Jones potential at minimum and shift to zero

$$U(r) = \begin{cases} 4\epsilon \left[\left(\frac{b}{r}\right)^{12} - \left(\frac{b}{r}\right)^6 \right] + \epsilon & r \leq 2^{1/6} b \\ 0 & r > 2^{1/6} b \end{cases}$$

"natural units": length b
energy ϵ

same mass for all particles m

time unit $T = \sqrt{\frac{m b^2}{\epsilon}}$

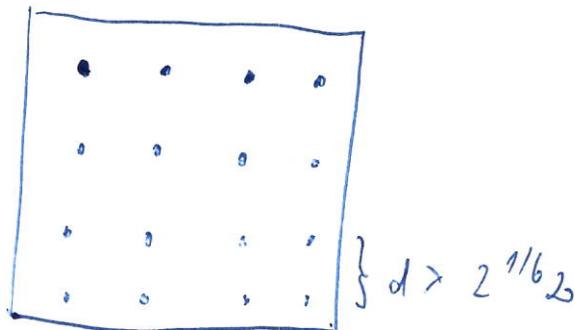
simple example:

$$N = 144 \text{ in } d = 2$$

mass of all particles $m_i = m = 1$

quadratic simulation box with linear dimension $L = 14.0$

(i) initial configuration: particles on square lattice



potential energy

$$U = 0$$

(ii) generate velocities $\{\vec{v}_1, \dots, \vec{v}_N\}$ from Maxwell-Boltzmann distribution

$$\vec{v}_i = (v_{ix}, v_{iy})$$

$$\rightarrow P(v_{i\alpha}) = \exp\left(-\frac{1}{2} v_{i\alpha}^2\right)$$

$$\rightarrow \text{scale total momentum to 0: } v_{i\alpha} \rightarrow v_{i\alpha} - \frac{\sum_m v_{i\alpha}}{m N}$$

\rightarrow scale velocities to desired temperature

$$v_{i\alpha} \rightarrow v_{i\alpha} \sqrt{\frac{2 N k_B T}{\sum_m v_{i\alpha}}}$$

$$\text{set } k_B T = 1$$

(iii) integrate equations of motion

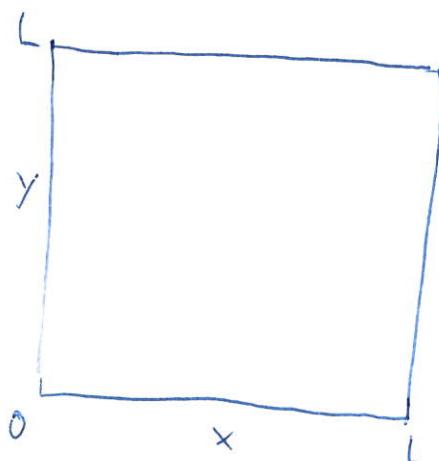
$$\vec{r}_i(t + \Delta t) = \vec{r}_i(t) + \vec{v}_i(t) \Delta t + \frac{1}{2} \frac{\vec{F}_i(t)}{m} \Delta t^2$$

$$\vec{v}_i(t + \Delta t) = \vec{v}_i(t) + \frac{\Delta t}{m} [\vec{F}_i(t) + \vec{F}_i(t + \Delta t)]$$

$$\text{choose } \Delta t = 0.0007 \text{ s}$$

(iv) boundary conditions

→ periodic boundary conditions



```

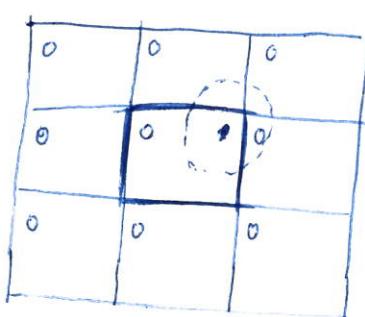
do i=1, 2*N
  if (pos(i).lt.0) then
    pos(i) = pos(i) + lbox
  else
    if (pos(i).gt.lbox) then
      pos(i) = pos(i) - lbox
    endif
  enddo

```

(v) compute forces $\vec{F}_i(t)$

interaction radius $r_{\text{cut}} = 2^{1/6} L$

minimum image convention



- circle with radius r_{cut} around \bullet
- interaction $\bullet \bullet$ (take image \bullet)
- only possible for $r_{\text{cut}} < \frac{L}{2}$

I.5.2. Nosé - Hoover thermostat

goal: MD simulation at constant temperature, i.e. in the canonical ensemble

system of N particles with

$$\vec{P} = (\vec{p}_1, \vec{p}_2, \dots, \vec{p}_N) \text{ momenta } (\vec{p}_i = m_i \vec{v}_i)$$

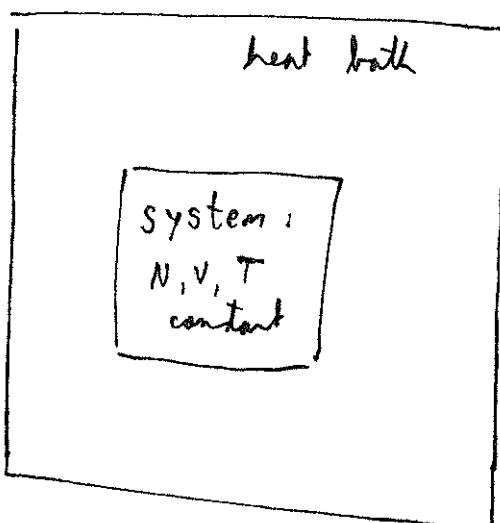
$$\vec{R} = (\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \text{ coordinates}$$

Hamilton function:

$$H = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U(\vec{R})$$

closed system: $H = E = \text{const.}$ (microcanonical ensemble)

now: couple system to a heat bath



consider $d = 3$ dimensions

V volume

T temperature

total energy E fluctuates: $E = E_{\text{kin}} + U$

(59)

thermal energy

$$\begin{aligned} k_B T &= \frac{2}{d} \frac{1}{N} \langle E_{\text{kin}} \rangle \\ &= \frac{2}{d} \frac{1}{N} \left\langle \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} \right\rangle \end{aligned}$$

what is $\langle \dots \rangle$?

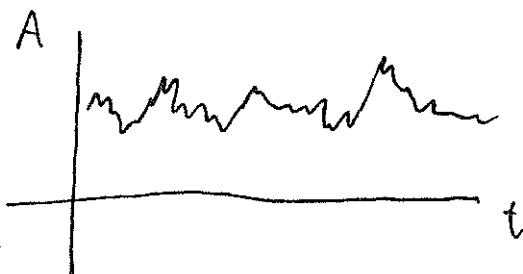
consider observable A , e.g. $A = E_{\text{kin}}$

$\langle A \rangle$ canonical average of A :

$$\langle A \rangle = \frac{\int d\vec{P} \int d\vec{R} A(\vec{R}, \vec{P}) e^{-\beta H(\vec{R}, \vec{P})}}{\int d\vec{P} \int d\vec{R} e^{-\beta H}}$$

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

MD simulation: calculation of time averages



$$\bar{A} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\vec{R}, \vec{P})$$

ergodicity hypothesis $\bar{A} = \langle A \rangle$

(i) 1st approach : simple thermostat
rescale velocities in each time step such that

instantaneous temperature = "desired temperature"

$$T_{\text{inst}} = \frac{2}{3k_B} \frac{1}{N} \sum_{i=1}^N \frac{\tilde{p}_i^2}{2m_i}$$

with $\tilde{p}_i = \alpha \vec{p}_i = m_i \alpha \vec{v}_i$

$$\alpha = \sqrt{\frac{3Nk_B T}{2 \sum_{i=1}^N m_i \vec{v}_i^2}}$$

what is wrong with that?

canonical ensemble : T_{inst} fluctuates

$$\frac{\langle T_{\text{inst}}^2 \rangle - \langle T_{\text{inst}} \rangle^2}{\langle T_{\text{inst}} \rangle^2} = \frac{1}{N} \frac{\langle p^4 \rangle - \langle p^2 \rangle^2}{\langle p^2 \rangle^2}$$

$$\stackrel{(*)}{=} \frac{2}{3N} \rightarrow \text{exercice}$$

$$(*) \quad \langle p^2 \rangle = \int dp \quad p^2 \frac{1}{2\pi m k_B T} e^{-\frac{p^2}{2m k_B T}}$$

$$= 3m k_B T$$

$$\langle p^4 \rangle = \int dp \quad p^4 \frac{1}{2\pi m k_B T} e^{-\frac{p^2}{2m k_B T}}$$

$$= 15(m k_B T)^2$$

(iii) different strategy

- add degree of freedom to system that couples to momenta
- system's degrees of freedom + additional degree of freedom from microcanonical ensemble
- integrate out additional degree of freedom
⇒ canonical ~~average~~ ensemble for system's degrees of freedom obtained

idea: introduce variable s that couples to velocities

$$\frac{d\vec{r}_i}{dt} \rightarrow s \frac{d\vec{r}'_i}{dt'}$$

"condition": coordinates not affected by coupling
 $\Rightarrow \vec{r}_i = \vec{r}'_i$

$\Rightarrow s$ rescales time differential (s dimensionless)

$$dt' = s dt$$

↑ ↑
virtual time real time

\Rightarrow Lagrange function

$$L_{\text{Noi}} = \sum_{i=1}^N \frac{m_i}{2} s^2 \dot{\vec{r}}_i'^2 - U(\{ \vec{r}_i' \}) + \frac{1}{2} Q s^2 - \frac{C}{\beta} f(s)$$

new degree of freedom s associated with kinetic energy ($\frac{1}{2} Q s^2$) and potential energy ($\frac{C}{\beta} f(s)$)

$$\dot{s} = \frac{ds}{dt}$$

Q : effective mass with unit energy \times time²

$f(s)$: "potential", chosen such that sampling in canonical ensemble with temperature T is provided

C : dimensionless parameter (to be specified)

canonical momenta

$$\vec{p}_i' = \frac{\partial \mathcal{L}_{\text{Noi}}}{\partial \dot{r}_i} = m_i s^2 \dot{r}_i'$$

$$p_s = \frac{\partial \mathcal{L}_{\text{Noi}}}{\partial \dot{s}} = Q s$$

\Rightarrow Hamilton function

$$\mathcal{H}_{\text{Noi}} = \sum_{i=1}^N \frac{p_i'^2}{2m_i s^2} + U(\{r_i'\}) + \frac{p_s^2}{2Q} + \frac{C}{\beta} f(s)$$

partition function for microcanonical ensemble $= E_{\text{Noi}} = \text{const.}$

$$S_{\text{Noi}} = \int d\vec{r}_1 \cdots d\vec{r}_N d\vec{p}_1' \cdots d\vec{p}_N ds dp_s \delta(\mathcal{H}_{\text{Noi}} - E_{\text{Noi}})$$

substitute virtual momenta by real ones

$$\vec{p}_i = \frac{1}{s} \vec{p}_i'$$

$$\vec{R} = \{\vec{r}_1, \dots, \vec{r}_N\}, \quad \vec{P} = (\vec{p}_1, \dots, \vec{p}_N)$$

$$\begin{aligned}
 \Rightarrow S_{\text{Nor}} &= \int_{\Gamma} d\vec{R} d\vec{P} ds dp_s s^{3N} \times \\
 &\times \delta \left(\underbrace{\sum_{i=1}^N \frac{p_i^2}{2m_i} + U(\vec{r}_i)}_{H} + \frac{p_s^2}{2Q} + \frac{C}{\beta} f(s) - E_{\text{Nor}} \right) \\
 &=: H(\{\vec{p}_i\}, \{\vec{r}_i\}) \\
 &= \int_{\Gamma} d\vec{R} d\vec{P} ds dp_s s^{3N} \delta \left(H + \frac{p_s^2}{2Q} + \frac{C}{\beta} f(s) - E_{\text{Nor}} \right)
 \end{aligned}$$

what do we need?

$$S(\dots) \rightarrow S(s - A(p_s, E)) \exp(-\beta B(C) H)$$

use

$$S(F(s)) = \frac{1}{F'(s_0)} S(s - s_0)$$

s_0 single root of $F(s)$

$$\text{here: } F(s) = H + \frac{p_s^2}{2Q} + \frac{C}{\beta} f(s) - E_{\text{Nor}}$$

$$F(s_0) \stackrel{!}{=} 0 \Rightarrow \frac{C}{\beta} f(s_0) = E_{\text{Nor}} - H - \frac{p_s^2}{2Q}$$

choose $f(s) = \ln s$

$$\Rightarrow s_0 = \exp \left(\frac{\beta}{C} (E_{\text{Nor}} - H - \frac{p_s^2}{2Q}) \right)$$

$$F'(s_0) = \frac{C}{\beta} f'(s_0) = \frac{C}{\beta} \frac{1}{s_0}$$

$$\begin{aligned}\Rightarrow S_{\text{Nose}} &= \int_{\Gamma} d\vec{R} d\vec{P} ds dp_s s^{3N} \frac{\beta}{C} s_0 \delta(s - s_0) \\ &= \int_{\Gamma} d\vec{R} d\vec{P} dp_s \frac{\beta}{C} s_0^{3N+1} \\ &= \int_{\Gamma} d\vec{R} d\vec{P} dp_s \frac{\beta}{C} \exp \left\{ - (3N+1) \frac{\beta}{C} (H + \right. \\ &\quad \left. + \frac{p_s^2}{2Q} - E_{\text{Nose}}) \right\} \\ &= \frac{\beta}{C} \exp \left\{ - (3N+1) \frac{\beta}{C} E \right\} \times \int dp_s e^{- (3N+1) \frac{\beta}{C} \frac{p_s^2}{2Q}} \\ &\quad \times \int_{\Gamma} d\vec{R} d\vec{P} \exp \left\{ - \beta \frac{3N+1}{C} H \right\}\end{aligned}$$

choose

$$C = 3N + 1$$

$$\Rightarrow S_{\text{Nose}} = \mathcal{N} \int_{\Gamma} d\vec{R} d\vec{P} e^{-\beta H}$$

canonical partition function for system with
momenta \vec{P} and coordinates \vec{R}

Hamilton function

$$H_{\text{Nord}} = \sum_{i=1}^N \frac{\vec{p}_i'^2}{2m_i s^2} + U(\{\vec{r}_i'\}) + \frac{P_s^2}{2Q} + \frac{3N+1}{\beta} \ln s$$

⇒ equations of motion

$$\frac{d\vec{r}_i'}{dt'} = \frac{\partial H_{\text{Nord}}}{\partial \vec{p}_i'} = \frac{\vec{p}_i'}{m_i s^2}$$

$$\frac{d\vec{p}_i'}{dt'} = - \frac{\partial H_{\text{Nord}}}{\partial \vec{r}_i'} = - \frac{\partial U(\{\vec{r}_i'\})}{\partial \vec{r}_i'}$$

$$\frac{ds}{dt'} = \frac{\partial H_{\text{Nord}}}{\partial P_s} = \frac{P_s}{Q}$$

$$\frac{dP_s}{dt'} = - \frac{\partial H_{\text{Nord}}}{\partial s} = \frac{1}{s} \left(\sum_{i=1}^N \frac{\vec{p}_i'^2}{m_i s^2} - \frac{3N+1}{\beta} \right)$$

time averages: sampling in virtual time

$$\bar{A} = \lim_{T' \rightarrow \infty} \frac{1}{T'} \int_0^{T'} dt' A \left(\left\{ \frac{1}{s(t')} \vec{p}_i'(t') \right\}, \left\{ \vec{r}_i(t') \right\} \right)$$

$$= \langle A(\{\vec{p}_i\}, \{\vec{r}_i\}) \rangle_{\text{Nord}}$$

$$= \frac{\int d\vec{P} d\vec{R} A(\{\vec{p}_i\}, \{\vec{r}_i\}) e^{-\beta H}}{\int d\vec{P} d\vec{R} e^{-\beta H}}$$

$$= \langle A(\{\vec{p}_i\}, \{\vec{r}_i\}) \rangle_{N, V, T}$$

not convenient: MD with time steps $\Delta t'$ in virtual time

$$\Rightarrow \Delta t = \frac{1}{s} \Delta t' \text{ fluctuates}$$

↑
real time

convert to real time

$$\tau = \int_0^{\tau'} dt' \frac{1}{s(t')}$$

$$\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A \left(\left\{ \frac{1}{s(t)}, \vec{P}_i(t) \right\}, \left\{ \vec{r}_i(t) \right\} \right)$$

$$\stackrel{\text{subst.}}{=} \lim_{\tau' \rightarrow \infty} \frac{\tau'}{\tau} \frac{1}{\tau'} \int_0^{\tau'} dt' \frac{1}{s(t')} A \left(\left\{ \frac{1}{s(t')}, \vec{P}_i(t') \right\}, \left\{ \vec{r}_i(t') \right\} \right)$$

$$= \underbrace{\lim_{\tau' \rightarrow \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' \frac{1}{s(t')} A \left(\left\{ \frac{1}{s(t')}, \vec{P}_i(t') \right\}, \left\{ \vec{r}_i(t') \right\} \right)}_{\lim_{\tau' \rightarrow \infty} \frac{1}{\tau'} \int_0^{\tau'} dt' \frac{1}{s(t')}}$$

$$= \frac{1}{\langle \frac{1}{s} \rangle} \left\langle A \left(\left\{ \frac{1}{s} \vec{P}_i \right\}, \left\{ \vec{r}_i \right\} \right) \frac{1}{s} \right\rangle$$

$$= \frac{\int d\vec{P} d\vec{R} A \left(\left\{ \vec{P}_i \right\}, \left\{ \vec{r}_i \right\} \right) \exp \left\{ -\beta \frac{3N}{C} H \right\}}{\int d\vec{P} d\vec{R} \exp \left\{ -\beta \frac{3N}{C} H \right\}}$$

$$= \left\langle A \left(\left\{ \vec{P}_i \right\}, \left\{ \vec{r}_i \right\} \right) \right\rangle_{N, V, T} \text{ for } C = 3N$$

$$\frac{d\vec{P}_i}{dt} = s \frac{d\frac{\vec{P}_i}{s}}{dt'} = \frac{d\vec{P}_i'}{dt'} - \vec{P}_i' s \frac{1}{s^2} \frac{ds}{dt'} \\ = \frac{1}{Q} P_s$$

$$= - \frac{\partial U(\{\vec{r}_i\})}{\partial \vec{r}_i} - \vec{P}_i \frac{P_s}{Q}$$

$$P_s^{(n)} = \frac{P_s}{s} \underset{s}{\approx} - \frac{\partial U(\{\vec{r}_i\})}{\partial \vec{r}_i} - \vec{P}_i \frac{s P_s^{(n)}}{Q}$$

$$\frac{1}{s} \frac{ds}{dt} = \frac{s}{s} \frac{ds}{dt'} = \frac{P_s}{Q} = \frac{s P_s^{(n)}}{Q}$$

$$\frac{d\left(\frac{s P_s^{(n)}}{Q}\right)}{dt} = \frac{s}{Q} \frac{d P_s}{d t'} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{\vec{P}_i^2}{m_i} - \frac{C}{\beta} \right)$$

conserved quantity

$$H_{\text{Noé}}^{(\text{real})} = \sum_{i=1}^N \frac{\vec{P}_i^2}{2m_i} + U(\{\vec{r}_i\}) + \frac{s^2 P_s^{(n)2}}{2Q} + C \frac{\ln s}{\beta}$$

$P_s^{(n)}$ is not a canonical momentum

\Rightarrow equations of motion cannot be derived from

$$H_{\text{Noé}}^{(\text{real})}$$

(68)

simplification (Hoover) : $\xi = \frac{s p_s^{(r)}}{Q}$ (unit $\frac{1}{\text{time}}$)

\Rightarrow equations of motion for real variables ($C = 3N$)

$$\dot{\vec{r}}_i = \frac{\vec{p}_i}{m_i}$$

$$\dot{\vec{p}}_i = - \frac{\partial U(\{\vec{r}_i\})}{\partial \vec{r}_i} - \underbrace{\xi \vec{p}_i}_{\text{frictional force}}$$

$$\dot{\xi} = \frac{1}{Q} \left(\sum_{i=1}^N \frac{\vec{p}_i^2}{m_i} - 3N k_B T \right)$$

\rightarrow instantaneous temperature

\rightarrow desired temperature

$$\frac{\dot{\xi}}{\xi} = \frac{d \ln \xi}{dt} = \xi$$

thermostating due to frictional force $- \xi(t) \vec{p}_i$,
 $\xi(t)$ fluctuates around 0

(iii) original references:

S. Nosé, J. Chem. Phys. 81, 511 (1984)

W. G. Hoover, Phys. Rev. A 31, 1495 (1984)

(iv) problems:

→ systems with multiple conserved quantities

→ non-ergodic systems (harmonic oscillator)

solution:

Nosé - Hoover chains

Martyna, Klein, Tuckerman, J. Chem. Phys. 97, 2635 (1992)

(v) dynamics with Nosé - Hoover thermostat not realistic

I.5.3. Algorithms for the Nosé - Hoover thermostat

goal : time-reversible symplectic algorithm

(i) Nosé equations in virtual time

$$\dot{\vec{r}}_i^{(1)} = \frac{\vec{p}_i^{(1)}}{m_i s^2} \quad \dot{s} = \frac{1}{Q} p_s$$

$$\dot{\vec{p}}_i^{(1)} = -\frac{\partial U}{\partial \vec{r}_i}, \quad \dot{p}_s = \frac{1}{s} \left(\sum_{i=1}^N \frac{\vec{p}_i^{(1)2}}{m_i s^2} - \frac{C}{\beta} \right) \text{ with } C = 3N + 1$$

Hoover : convert to equations in real time

$$dt = \frac{1}{s} dt', \quad \vec{P}_i = \frac{1}{s} \vec{p}_i^{(1)}, \quad C = 3N$$

$$\text{variable } \xi = \frac{s p_s^{(1)}}{Q} = \frac{p_s}{Q}$$

$$\Rightarrow \boxed{\begin{aligned} \dot{\vec{r}}_i &= \frac{\vec{P}_i}{m_i} \\ \dot{\vec{P}}_i &= -\frac{\partial U}{\partial \vec{r}_i} - \xi \vec{p}_i \\ \dot{\xi}_s &= \frac{1}{Q} \left(\sum_{i=1}^N \frac{\vec{P}_i^2}{m_i} - 3N k_B T \right) \\ \dot{\frac{s}{s}} &= \frac{d \ln s}{dt} = \xi \end{aligned}} \quad (\text{H1})$$

equation $\frac{d \ln s}{dt} = \xi$ decoupled from those for $\vec{r}_i, \vec{P}_i, \xi$
 → only 1st order equation for ξ

(ii) modify Hoover's approach

$$\frac{ds}{dt'} = \frac{P_s}{Q} \Rightarrow \frac{1}{s} \frac{ds}{dt} = \frac{d \ln s}{dt} = \frac{P_s}{Q}$$

$$\begin{aligned} \frac{dP_s}{dt} &= s \frac{dP_s}{dt'} = \sum_{i=1}^N \frac{\vec{P}_i^{*2}}{m_i s^2} - \frac{3N}{\beta} \\ &= \sum_{i=1}^N \frac{\vec{P}_i^{*2}}{m_i} - \frac{3N}{\beta} \end{aligned}$$

introduce new dynamical variable : $\gamma = \ln s$

$$\Rightarrow \boxed{\begin{aligned} \dot{\vec{r}}_i &= \frac{\vec{P}_i}{m_i} \\ \dot{\vec{P}}_i &= -\frac{\partial U}{\partial \vec{r}_i} - \frac{m}{Q} \frac{\gamma}{\vec{P}_i} \vec{P}_i \\ \dot{\gamma} &= \frac{P_\gamma}{Q} \\ \dot{P}_\gamma &= \sum_{i=1}^N \frac{\vec{P}_i^{*2}}{m_i} - \frac{3N}{\beta} \end{aligned}} \quad P_\gamma = P_s \quad (H2)$$

(iii) generalize velocity Verlet algorithm to solve Eqs. (H1)
propagate system from $t=0$ to $t=\delta t$

$$(\vec{r}_i(0), \vec{P}_i(0) = m_i \dot{\vec{r}}_i(0), \xi(0))$$

$$\rightarrow (\vec{r}_i(\delta t), m_i \dot{\vec{r}}_i(\delta t), \xi(\delta t))$$

$$\vec{r}_i(\delta t) = \vec{r}_i(0) + \delta t \dot{\vec{r}}_i(0) + \frac{\delta t^2}{2} \left[\frac{\vec{F}_i(0)}{m_i} - \xi(0) \dot{\vec{r}}_i(0) \right]$$

$$\dot{\vec{r}}_i(\delta t) = \dot{\vec{r}}_i(0) + \frac{\delta t}{2} \left[\frac{\vec{F}_i(0)}{m_i} - \xi(0) \dot{\vec{r}}_i(0) + \frac{\vec{F}_i(\delta t)}{m_i} \right. \\ \left. - \xi(\delta t) \dot{\vec{r}}_i(\delta t) \right] \quad (*)$$

problem: term $-\xi(\delta t) \dot{\vec{r}}_i(\delta t)$
 ↑ ↑
 only $\xi(0)$ known should be updated

iterative solution:

Fox, Anderson, J. Phys. Chem. 88, 4019 (1989)

$$\tilde{\xi}(\delta t) = \xi(0) + \frac{\delta t}{2} \left[\sum_{i=1}^N m_i \dot{\vec{r}}_i^2(0) - \frac{3N}{\beta} \right]$$

Euler step

$$\tilde{\dot{\vec{r}}}_i(\delta t) = \dot{\vec{r}}_i(0) + \frac{\delta t}{2} \left[\frac{\vec{F}_i(0)}{m_i} - \xi(0) \dot{\vec{r}}_i(0) + \frac{\vec{F}_i(\delta t)}{m_i} \right. \\ \left. - \tilde{\xi}(\delta t) \dot{\vec{r}}_i(0) \right]$$

approximate $-\xi(\delta t) \dot{\vec{r}}_i(\delta t)$ by $\tilde{\xi} \cdot \tilde{\dot{\vec{r}}}_i$ in Eq. (*) \Rightarrow

$$\dot{\vec{r}}_i(\delta t) = \dot{\vec{r}}_i(0) + \frac{\delta t}{2} \left[\frac{\vec{F}_i(0)}{m_i} - \xi(0) \dot{\vec{r}}_i(0) + \frac{\vec{F}_i(\delta t)}{m_i} - \frac{\tilde{\xi}(\delta t)}{2} \right.$$

$$\xi(\delta t) = \xi(0) + \frac{\delta t}{2\alpha} \left[\sum_{i=1}^N m_i (\dot{\vec{r}}_i^2(0) + \dot{\vec{r}}_i^2(\delta t)) - 2 \frac{3N}{\beta} \right]$$

this algorithm is not time-reversible

(v) now time-reversible algorithm for solution of Eqs. (H2)
consider

$$(x^{(0)}, p^{(0)}, \gamma^{(0)}, p_\gamma^{(0)}) \rightarrow (x^{(st)}, p^{(st)}, \gamma^{(st)}, p_\gamma^{(st)})$$

Liouville operator

$$\begin{aligned} \mathcal{L} &= \dot{x} \frac{\partial}{\partial x} + \dot{p} \frac{\partial}{\partial p} + \dot{\gamma} \frac{\partial}{\partial \gamma} + \dot{p}_\gamma \frac{\partial}{\partial p_\gamma} \\ &= \underbrace{\frac{P}{m} \frac{\partial}{\partial x}}_{= \mathcal{L}_x} - \underbrace{\frac{\partial H}{\partial x} \frac{\partial}{\partial p}}_{= \mathcal{L}_{p_1}} - \underbrace{\frac{1}{Q} p_\gamma P \frac{\partial}{\partial p}}_{= \mathcal{L}_{p_2}} + \underbrace{\frac{1}{Q} p_\gamma \frac{\partial}{\partial \gamma}}_{= \mathcal{L}_\gamma} \\ &\quad - \underbrace{\cancel{\dot{p}_\gamma \frac{\partial}{\partial p_\gamma}}}_{= \mathcal{L}_{p_\gamma}} \end{aligned}$$

$$\dot{p}_\gamma = \sum_{i=1}^N \frac{\vec{p}_i^2}{m_i} - \frac{3N}{\beta} \quad \text{for } N\text{-particle system}$$

exact time evolution operator : $G(st) = e^{st \mathcal{L}}$

approximate $G(st)$ by Trotter factorization (see
derivation of velocity Verlet algorithm)

$$\begin{aligned} G(st) &= e^{\frac{st}{2} \mathcal{L}_{p_\gamma}} e^{\frac{st}{2} \mathcal{L}_\gamma} e^{\frac{st}{2} \mathcal{L}_{p_2}} e^{\frac{st}{2} \mathcal{L}_{p_1}} \\ &\approx e^{st \mathcal{L}_x} e^{\frac{st}{2} \mathcal{L}_{p_1}} e^{\frac{st}{2} \mathcal{L}_{p_2}} e^{\frac{st}{2} \mathcal{L}_\gamma} e^{\frac{st}{2} \mathcal{L}_{p_\gamma}} \end{aligned} \tag{4}$$

remarks:

- time reversibility $G(st) G(-st) = 1$
 $\Rightarrow G(st)$ generates reversible dynamics
- most of the exponential operators in Eq. (+) lead to translation of phase space coordinates, e.g.

$$e^{st \mathcal{L}_x} x(0) = x(0) + \frac{p}{m} st$$

- except for $e^{\frac{st}{2} \mathcal{L}_{p_2}}$

$$e^{\frac{st}{2} \mathcal{L}_{p_2}} p(0) = \exp\left(-\frac{st}{2} \frac{p_y}{\Omega} p \frac{\partial}{\partial p}\right) p(0)$$

$$= \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{st}{2} \frac{p_y}{\Omega}\right)^n \underbrace{\left(p \frac{\partial}{\partial p}\right)^n p(0)}_{= p(0)}$$

$$= p(0) \sum_{n=0}^{\infty} \frac{1}{n!} \left(-\frac{st}{2} \frac{p_y}{\Omega}\right)^n$$

$$= p(0) e^{-\frac{st}{2} \frac{1}{\Omega} p_y(0)}$$

now apply $G(st)$, as given by Eq. (+), to phase space point $(x(0), p(0), q(0), p_q(0))$

\Rightarrow sequential application of exponential operators

$$p_\gamma\left(\frac{\delta t}{2}\right) = p_\gamma(0) + \frac{\delta t}{2} \dot{p}_\gamma(0)$$

$$\gamma\left(\frac{\delta t}{2}\right) = \gamma(0) + \frac{\delta t}{2} \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right)$$

$$= \gamma(0) + \frac{\delta t}{2} \frac{1}{Q} p_\gamma(0) + \frac{\delta t^2}{2} \frac{1}{Q} \dot{p}_\gamma(0)$$

$$\tilde{p}(0) = p(0) e^{-\frac{\delta t}{2} \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right)}$$

$$\hat{p}\left(\frac{\delta t}{2}\right) = \tilde{p}(0) + \frac{\delta t}{2} \underbrace{F(0)}_{= -\frac{\partial U(0)}{\partial x}}$$

$$x(\delta t) = x(0) + \delta t \frac{1}{m} p\left(\frac{\delta t}{2}\right)$$

$$= x(0) + \delta t \frac{1}{m} \tilde{p}(0) + \frac{\delta t^2}{2} \frac{1}{m} F(0)$$

$$\hat{p}(\delta t) = \hat{p}\left(\frac{\delta t}{2}\right) + \frac{\delta t}{2} F(\delta t)$$

$$= \tilde{p}(0) + \frac{\delta t}{2} (F(0) + F(\delta t))$$

$$p(\delta t) = \hat{p}(\delta t) e^{-\frac{\delta t}{2} \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right)}$$

$$= p(0) e^{-\delta t \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right)}$$

$$+ \frac{\delta t}{2} e^{-\frac{\delta t}{2} \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right)} [F(0) + F(\delta t)]$$

(26)

$$\begin{aligned}
 \gamma(\delta t) &= \gamma\left(\frac{\delta t}{2}\right) + \frac{\delta t}{2} \frac{1}{Q} p_\gamma\left(\frac{\delta t}{2}\right) \\
 &= \gamma(0) + \delta t \frac{1}{Q} p_\gamma(0) \\
 &= \gamma(0) + \delta t \frac{1}{Q} p_\gamma(0) + \frac{\delta t^2}{2} \frac{1}{Q} \dot{p}_\gamma(0)
 \end{aligned}$$

$$p_\gamma(\delta t) = p_\gamma(0) + \frac{\delta t}{2} [\dot{p}_\gamma(0) + \dot{p}_\gamma(\delta t)]$$

M. Tuckerman, B. J. Berne, G. J. Martyna,
 J. Chem. Phys. 97, 1990 (1992)

(77)

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I.6. MD simulation at constant pressure

IV. 2. Virial equation

I.6.1.

pressure

$$p = - \frac{\partial F}{\partial V} = k_B T \frac{\partial \ln Z}{\partial V} = \frac{k_B T}{Z} \frac{\partial Z}{\partial V}$$

volume V : conjugate variable of p

Helmholtz free energy : $F = F(N, V, T)$

partition function (configurational part)

$$Z = \int d\vec{r}_1 \cdots \int d\vec{r}_N \exp \left\{ -\beta U(\vec{r}_1, \dots, \vec{r}_N) \right\}$$

$$\bar{L} = \frac{1}{k_B T}$$

consider system in cubic box of volume $V = L^d$

$$\frac{\partial Z}{\partial V} \Big|_{\bar{L}}$$

$$\text{scaled coordinates } \vec{s} : = \frac{\vec{r}}{L}$$

$$\vec{s} = \frac{\vec{r}}{L} \Rightarrow d\vec{r}_1 \cdots d\vec{r}_N = V^N d\vec{s}_1 \cdots d\vec{s}_N$$

$$\partial_V U = U(\vec{s}_1, \dots, \vec{s}_N, V)$$

$$= \sum_{i=1}^N \sum_{j>i} \mu_{ij} \underbrace{(L |\vec{s}_i - \vec{s}_j|)}_{= \vec{p}_{ij}}$$

pairwise additive

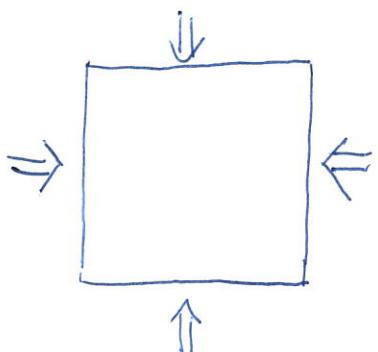
I.6.2. Equations of motion

IV. 4. MD simulation at constant pressure

idea: perform mechanical work on the system to keep pressure p constant

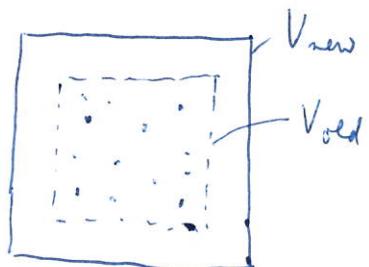
$\rightarrow V$ fluctuating

\rightarrow couple external degree of freedom to system



"isotropic piston" of mass M ,
subject to ~~exp~~ external pressure p_{ext}
 \rightarrow equilibrium $p = p_{ext}$

instantaneous change of volume
 \rightarrow rescale particle coordinates



$$\vec{r}_i = \frac{\vec{r}_i}{V^{1/3}} \quad V = V(t)$$

$$\dot{\vec{r}}_i = \frac{d}{dt} (V^{1/3} \vec{r}_i) = V^{1/3} \vec{v}_i + \frac{1}{3} V^{-\frac{2}{3}} \dot{V} \vec{r}_i$$

"construct" Lagrange function with additional variables
 \dot{V} and V

simplification: $\vec{r}_i = V^{1/3} \vec{r}_i$

(79)

Lagrange function:

$$\mathcal{L} = \sum_{i=1}^N \frac{m_i}{2} V^{2/3} \dot{\vec{r}}_i^2 - U(\{V^{1/3} \vec{r}_i\})$$

$$+ \frac{1}{2} M \dot{V}^2 - \underbrace{P_{ext} V}_{\text{mechanical work}}$$

$$U = \sum_{i=1}^N \sum_{j>i} M(r_{ij})$$

M effective mass

canonical momenta:

$$\vec{\Pi}_i = \frac{\partial \mathcal{L}}{\partial \dot{\vec{r}}_i} = m_i V^{2/3} \dot{\vec{r}}_i$$

$$P_V = \frac{\partial \mathcal{L}}{\partial \dot{V}} = M \dot{V}$$

\Rightarrow Hamilton function:

$$\mathcal{H} = \sum_{i=1}^N \frac{\vec{\Pi}_i^2}{2m_i V^{2/3}} + U(\{V^{1/3} \vec{r}_i\}) + \frac{P_V^2}{2M} + P_{ext} V$$

\Rightarrow equations of motion:

$$(i) \ddot{\vec{r}}_i = \frac{\partial \mathcal{H}}{\partial \vec{\Pi}_i} = \frac{\vec{\Pi}_i}{m_i V^{2/3}}$$

$$(ii) \dot{\vec{\Pi}}_i = - \frac{\partial \mathcal{H}}{\partial \vec{r}_i} = V^{1/3} \vec{F}_i$$

$$(iii) \dot{V} = \frac{\partial \mathcal{H}}{\partial p_v} = \frac{p_v}{M}$$

$$(iv) \dot{p}_v = - \frac{\partial \mathcal{H}}{\partial V}$$

$$= \frac{2}{3} V^{-5/3} \sum_{i=1}^N \frac{\vec{\pi}_i^2}{2m_i} - \sum_i \sum_{j>i} \frac{\partial \mu}{\partial V^{1/3} \vec{r}_{ij}} \frac{s_{ij}}{3V^{2/3}} - p_{ext}$$

$$\Rightarrow M \ddot{V} = \dot{p}_v$$

$$= \frac{2}{3} V^{-5/3} \underbrace{\sum_i \frac{\vec{\pi}_i^2}{2m_i}}_{-} - \sum_i \sum_{j>i} \frac{\partial \mu}{\partial r_{ij}} \frac{r_{ij}}{3V} - p_{ext}$$

$$= \frac{1}{2} m_i V^{4/3} \dot{\vec{r}}_i^2 = \frac{1}{2} m_i V^{2/3} \dot{\vec{r}}_i^2 = V^{2/3} \frac{\dot{\vec{p}}_i^2}{2m_i}$$

$$= \underbrace{\frac{1}{V} \left(\frac{2}{3} \sum_i \frac{\vec{\pi}_i^2}{2m_i} - \frac{1}{3} \sum_i \sum_{j>i} \frac{\partial \mu}{\partial r_{ij}} r_{ij} \right)}_{\text{instantaneous pressure } p(t)} - p_{ext}$$

instantaneous pressure $p(t)$

$$\text{Eq. (i)} \Rightarrow \vec{\pi}_i = m_i V^{1/3} \dot{\vec{r}}_i = V^{1/3} \vec{p}_i$$

$$\Rightarrow \dot{\vec{p}}_i = \vec{\pi}_i \frac{dV^{-1/3}}{dt} + V^{-1/3} \vec{\pi}_i$$

$$= V^{1/3} \vec{p}_i \leftarrow \frac{1}{3} V^{-4/3} \dot{V} + \vec{F}_i$$

$$= \vec{F}_i - \frac{1}{3} \frac{\dot{V}}{V} \vec{p}_i = \vec{F}_i - \frac{1}{3} \frac{d \ln V}{dt} \vec{p}_i$$

(81)

remarks:

- equation $M\ddot{V} = p(t) - p_{ext}$

"restoring force" on volume V when $p(t) \neq p_{ext}$

- $\vec{P}_i = \vec{F}_i - \frac{1}{3} \frac{d \ln V}{dt} \vec{p}_i$

→ frictional force on particle $i \propto \vec{p}_i$

→ friction coefficient $\frac{1}{3} \frac{d \ln V}{dt}$

- conserved quantity

enthalpy

$$H \cancel{\partial} = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m_i} + U + \frac{1}{2} M \dot{V}^2 + p_{ext} V$$

⇒ NpH ensemble

- original reference

H. C. Andersen, J. Chem. Phys. 72, 2384 (1980)

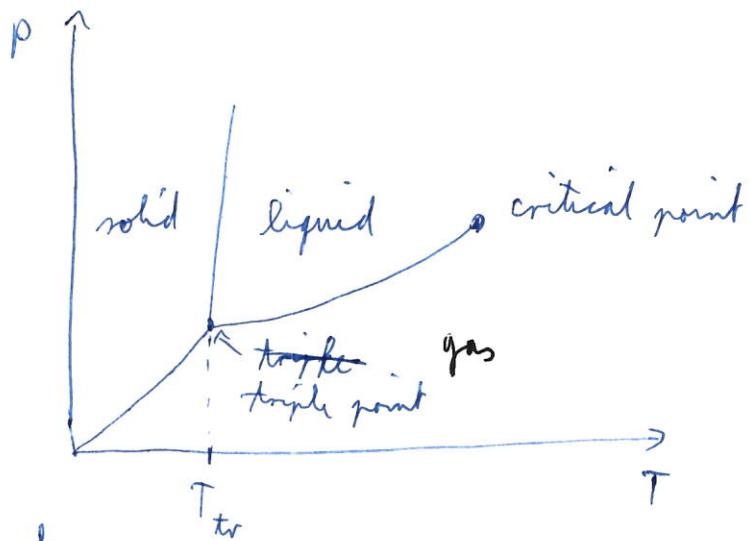
I. 7.

IV. 5. The liquid state

I. 7.1.

IV. 5. 1. Dense liquids

typical phase diagram of one-component system (e.g. Ar)



- dense liquid :
 - vicinity of triple point
 - structure similar to dense hard-sphere packing
 - short-ranged interactions

quantum effects?

$$\text{de Broglie wave-length } \lambda = \left(\frac{2\pi t_1^2}{k_B T m} \right)^{1/2}$$

$$t_1 = \frac{\hbar}{2\pi} = 1.0546 \cdot 10^{-34} \text{ Js}$$

C mass of particle

classical description reasonable for

$$\frac{\lambda}{a} \ll 1$$

a: typical distance between neighboring particles

(83)

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typical values at T_{tr}

$\frac{1}{\alpha}$	H_2	Ne	CH_4	N_2	Xe
0.97	0.26	0.12	0.11	0.083	

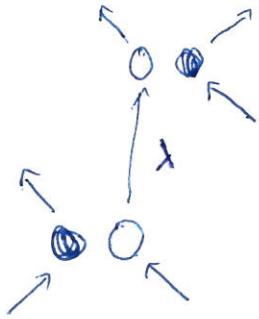
theoretical description of liquids difficult

- no small parameter for perturbation theory
- no minimal model (gas: ideal gas, solid: harmonic crystal)

dynamics of fluids:

- gas at low densities

dynamics controlled by uncorrelated, binary collisions



$$\lambda \text{ mean free path} \approx \lambda \approx \frac{1}{\rho \sigma}$$

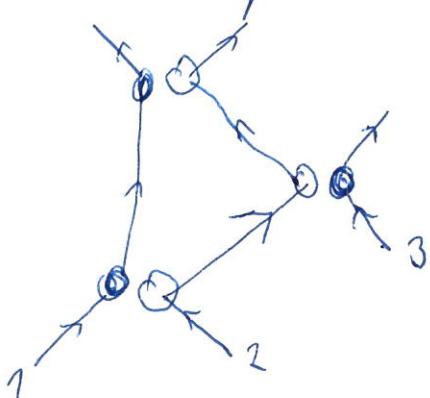
(σ) sphere with diameter d

$$\rho = \frac{N}{V} \text{ number density}$$

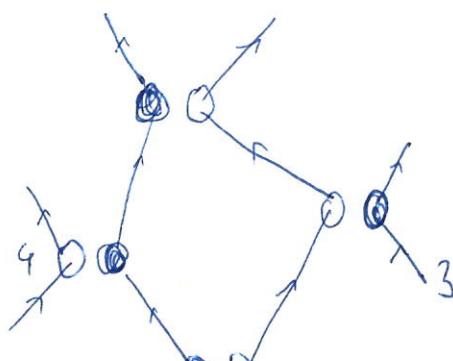
$\sigma = \pi d^2$ cross section for collision
of 2 particles

- gas at higher densities: collisions correlated

→ ring collisions



3-body event



4-body event

- dense liquid

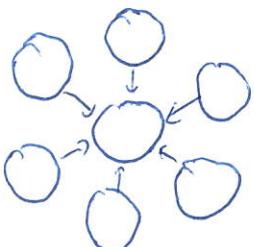


→ particle in cage, formed by surrounding particles

→ dynamics controlled by dense packing of particles

interaction models:

- hard-core interactions most important for structure of dense liquid



attractive interactions cancel to first approximation

- large distances between atoms

multipole interactions due to fluctuations of charge distribution around atoms

$$\text{dipole-dipole} \propto r^{-6}$$

$$\text{dipole-quadrupole} \propto r^{-8}$$

- simplest model: hard spheres $U(r) = \begin{cases} \infty & r < d \\ 0 & r > d \end{cases}$



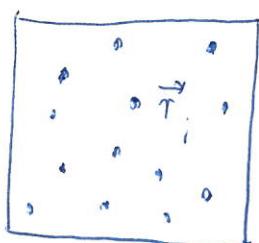
no attractive interactions: no gas-liquid transition

- Lennard-Jones potential $U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$

parameters $\frac{\epsilon}{k_B} = 119.8 \text{ K}$, $\sigma = 3.405 \text{ \AA}$

I. 7.2.

IV. 5.2. Fluid structure: radial distribution function
define microscopic density variable



N particles in volume V

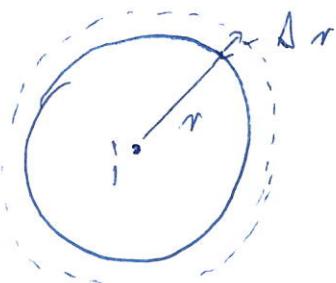
$$\rho(\vec{r}) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i)$$

thermal equilibrium $\Rightarrow \langle \rho(\vec{r}) \rangle = \rho = \frac{N}{V}$
structural correlations?

spatial fluctuations of density?

reference: ideal gas $\hat{=} \text{system with no structural correlations}$

$g(r) = \frac{\text{average particle density at distance } r \text{ from atom}}{\text{same for ideal gas at same density}}$



$n_p(r) = \text{number of pairs } (i, j)$
with $r_{ij} = |\vec{r}_i - \vec{r}_j|$
 $\in [r, r + \Delta r]$

ideal gas: $\langle n_p(r) \rangle = \frac{N}{2} \rho \frac{4\pi}{3} [(r + \Delta r)^3 - r^3]$

$$\langle n_p(r) \rangle = \frac{N(N-1)}{2} \frac{1}{V_{\text{shell}}} V_{\text{shell}} \underset{\Delta r \text{ small}}{\approx} \frac{N}{2} \rho 4\pi r^2 \Delta r$$

correlations: $\langle n_p(r) \rangle = \frac{N}{2} \rho 4\pi r^2 \Delta r g(r)$

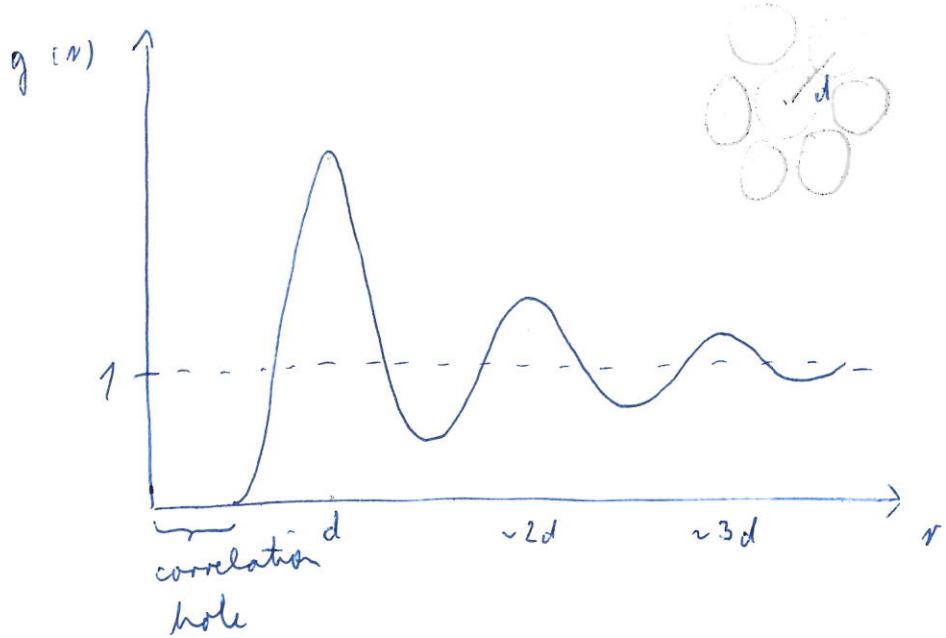
(86)

19.12.13

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typical $g(r^n)$ of liquid



IV. 5.3. Correlation functions

consider dynamical variable $A(\vec{r}, t)$

examples:

$$\rho(\vec{r}, t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t)) \quad \text{density}$$

$$\rho(\vec{q}, t) = \sum_{i=1}^N e^{i\vec{q} \cdot \vec{r}_i(t)} \quad \begin{matrix} \text{Fourier transform} \\ \text{of } \rho(\vec{r}, t) \end{matrix}$$

↑
wave vector

$$\rho_s(\vec{r}, t) = \underbrace{\delta(\vec{r} - \vec{r}_s(t))}_{\text{coordinate of tagged particle}} \quad \begin{matrix} \text{one-particle} \\ \text{density} \end{matrix}$$

$$\rho_s(\vec{q}, t) = e^{i\vec{q} \cdot \vec{r}_s(t)} \quad \begin{matrix} \text{Fourier transform} \\ \text{of } \rho_s(\vec{r}, t) \end{matrix}$$

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$$p = k_B T \frac{1}{Z} \frac{\partial Z}{\partial V}$$

$$= k_B T \frac{\int d\vec{p}_1 \dots \int d\vec{p}_N (N V^{N-1} - V^N \cdot \beta \frac{\partial U}{\partial V}) e^{-\beta U}}{V^N \int d\vec{p}_1 \dots \int d\vec{p}_N e^{-\beta U}}$$

$$= k_B T \frac{N}{V} - \langle \frac{\partial U}{\partial V} \rangle$$

$$\frac{\partial U}{\partial V} ?$$

$$\begin{aligned} \frac{\partial U}{\partial V} &= \sum_i \sum_{j>i} \underbrace{\frac{\partial m_{ij} (L \rho_{ij})}{\partial V}}_{= \frac{\partial m_{ij} (L \rho_{ij})}{\partial L \rho_{ij}} \frac{\partial L \rho_{ij}}{\partial V}} \\ &= \frac{\partial m_{ij} (r_{ij})}{\partial r_{ij}} \frac{1}{L} \frac{\partial V}{\partial V} \\ &= \sum_i \sum_{j>i} \frac{\partial m_{ij} (r_{ij})}{\partial r_{ij}} \frac{r_{ij}}{L} \frac{1}{d} \underbrace{V^{\frac{1}{d}-1}}_{= \frac{L}{V}} \\ &= - \frac{1}{dV} \sum_i \sum_{j>i} \vec{F}_{ij}^\infty \cdot \vec{r}_{ij}^\infty \end{aligned}$$

$$\Rightarrow \boxed{p = k_B T \frac{N}{V} + \frac{1}{dV} \left\langle \sum_{i=1}^N \sum_{j>i} \vec{F}_{ij}^\infty \cdot \vec{r}_{ij}^\infty \right\rangle}$$

(88)

I. 2. 3.

IV. 5. 3. Correlation functions

consider dynamical variables $A(\vec{r}, t)$, $B(\vec{r}, t)$, ...

examples:

$$\rho(\vec{r}, t) = \sum_{i=1}^N \delta(\vec{r} - \vec{r}_i(t)) \quad \text{density}$$

$$\rho_{\vec{q}}(t) = \sum_{i=1}^N e^{i\vec{q} \cdot \vec{r}_i(t)} \quad \text{Fourier transform of } \rho(\vec{r}, t)$$

$$\rho_s(\vec{r}, t) = \underbrace{\delta(\vec{r} - \vec{r}_s(t))}_{\substack{\text{coordinate of} \\ \text{tagged particle}}} \quad \text{one-particle density}$$

$$\rho_{s\vec{q}}(t) = e^{i\vec{q} \cdot \vec{r}_s(t)} \quad \text{Fourier transform of } \rho_s(\vec{r}, t)$$

correlation function of two variables

$$C_{AB}(t) = \langle A(t+t') B^*(t') \rangle$$

$$= \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T A(t+t') B^*(t') dt'$$

ergodicity hypothesis

properties:

(i) equilibrium:

$$C_{AB}(t) \text{ not dependent on } t'$$

(89)

$$\begin{aligned}
&\Rightarrow \frac{d}{dt'} \langle A(t+t') B^*(t') \rangle \\
&= \langle \dot{A}(t+t') B^*(t') \rangle + \langle A(t+t') \dot{B}^*(t') \rangle \\
&\stackrel{!}{=} 0 \\
&\Rightarrow \langle \dot{A}(t) B^*(0) \rangle = - \langle A(t) \dot{B}^*(0) \rangle
\end{aligned}$$

$$A = B \Rightarrow \langle \dot{A}(0) A(0) \rangle = 0$$

$\dot{A}(0)$ orthogonal on $A(0)$.

$$(\ddot{\mu}) \lim_{t \rightarrow \infty} \langle A(t+t') B^*(t') \rangle = \langle A \rangle \langle B^* \rangle$$

$$\begin{aligned}
&\Rightarrow \tilde{C}_{AB}(t) = \langle [A(t) - \langle A \rangle] [B^*(0) - \langle B^* \rangle] \rangle \\
&= \underbrace{\langle A(t) B^*(0) \rangle - \langle A \rangle \langle B^* \rangle}_{\substack{t \rightarrow \infty \\ \longrightarrow 0}}
\end{aligned}$$

density correlations:

- static density correlation function

$$\begin{aligned}
G(\vec{r}', \vec{r}'') &= \langle [s(\vec{r}') - \underbrace{\langle s \rangle}_{=\frac{N}{V} = \bar{s}}] [s(\vec{r}'') - \langle s \rangle] \rangle \\
&\quad \underbrace{\qquad\qquad\qquad}_{\text{density fluctuation}}
\end{aligned}$$

$$= \langle s(\vec{r}') s(\vec{r}'') \rangle - \bar{s}^2$$

$$= \langle \sum_{k=1}^N \sum_{l=1}^N \delta(\vec{r}' - \vec{r}_k) \delta(\vec{r}'' - \vec{r}_l) \rangle - \bar{s}^2$$

(90)

$G(\vec{r}^1, \vec{r}^4) \sim$ probability to find a particle at position \vec{r}^1 while a different particle is located at \vec{r}^4

assume: homogeneous system \rightarrow translation invariance

$$G(\vec{r}^1, \vec{r}^4) \rightarrow G(\vec{r}^1 - \vec{r}^4, \vec{r}^4)$$

now integrate over \vec{r}^4 :

$$\frac{1}{V} \int d\vec{r}^4 G(\vec{r}^1 - \vec{r}^4, \vec{r}^4)$$

$$= \frac{1}{V} \int d\vec{r}^4 \left\{ \left\langle \sum_{n,e} \delta(\vec{r}^1 - \vec{r}_n) \delta(\vec{r}^4 - \vec{r}_e) \right\rangle - \rho^2 \right\}$$

$$= \frac{1}{V} \int d\vec{r}^4 \left\{ \left\langle \sum_{n,e} \delta(\vec{r} + \vec{r}^4 - \vec{r}_n) \delta(\vec{r}^4 - \vec{r}_e) \right\rangle - \rho^2 \right\}$$

subst.
 $\vec{r} = \vec{r}^1 - \vec{r}^4$

$$= \frac{1}{V} \left\langle \sum_{n,e} \delta(\vec{r} - (\vec{r}_n - \vec{r}_e)) \right\rangle - \rho^2$$

$$= \frac{1}{V} \delta(\vec{r}) + \frac{1}{V} \left\langle \sum_k \sum_{e \neq k} \delta(\vec{r} - (\vec{r}_k - \vec{r}_e)) \right\rangle - \rho^2$$

"non-trivial" part $= \rho^2 g(\vec{r})$

$g(\vec{r})$: pair correlation function

$$\Rightarrow G(\vec{r}) = \frac{1}{V} \delta(\vec{r}) + \rho^2 g(\vec{r}) - \rho^2$$

(9)

$$\frac{1}{V} = \frac{1}{N} \frac{\rho^2}{\rho^2} = \rho^2 \frac{1}{\rho} \frac{1}{N}$$

$$\Rightarrow \rho g(\vec{r}) = \frac{1}{N} \left\langle \sum_k \sum_{l \neq k} \delta(\vec{r} - (\vec{r}_k - \vec{r}_l)) \right\rangle$$

isotropic fluid \Rightarrow definition of radial distribution function $g(r)$

$$\boxed{\rho 4\pi r^2 g(r) = \frac{1}{N} \left\langle \sum_k \sum_{l \neq k} \delta(r - |\vec{r}_{kl}|) \right\rangle}$$

$$\text{with } |\vec{r}_{kl}| \equiv |\vec{r}_k - \vec{r}_l| \equiv r_{kl}$$

- dynamic one-particle correlation function
self part of van Hove correlation function

$$G_s(\vec{r}, t) = \left\langle \delta(\vec{r} - (\vec{r}_s(t) - \vec{r}_s(0))) \right\rangle$$

= probability that a tagged particle is displaced by \vec{r} in a time interval t

here assumption: correlations not dependent on time origin

$$\underline{t=0}: G_s(\vec{r}, t=0) = \delta(\vec{r})$$

(92)

FT with respect to \vec{r} :

$$F_s(\vec{q}, t) = \int d\vec{r} G_s(\vec{r}, t) e^{-i\vec{q} \cdot \vec{r}}$$
$$= \langle \exp(i\vec{q} \cdot (\vec{r}_s(0) - \vec{r}_s(t))) \rangle$$

incoherent intermediate scattering function

FT with respect to t :

$$S_s(\vec{q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{i\omega t} F_s(\vec{q}, t)$$

frequency

self part of dynamic structure factor

homogeneous fluids \rightarrow properties:

(i)' $G_s(\vec{r}, t) = G_s(r, t)$

$$F_s(\vec{q}, t) = F_s(q, t)$$

$$S_s(\vec{q}, \omega) = S_s(q, \omega)$$

(ii)' $S_s(q, \omega)$ real function, describes scattering intensity

$$\Rightarrow S_s(q, \omega) = S_s(q, -\omega) \text{ even function}$$

(iii)' mean-squared displacement

$$\langle r^2(t) \rangle = \langle (\vec{r}_s(t) - \vec{r}_s(0))^2 \rangle$$
$$= \int d\vec{r} r^2 G_s(r, t)$$

(93)

I.7.4

IV. 5.4. Short time expansion

Taylor expansion of $F_s(q, t)$ around $t = 0$

$$F_s(q, t) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n F_s(q, t)}{dt^n} \right|_{t=0} t^n$$

stati coefficients!

$$\begin{aligned} \left. \frac{d^n F_s(q, t)}{dt^n} \right|_{t=0} &= \frac{d}{dt^n} \left\{ \int_{-\infty}^{\infty} dw e^{-iwt} S_s(q, w) \Big|_{t=0} \right\} \\ &= i^n \int_{-\infty}^{\infty} dw w^n S_s(q, w) \\ &=: i^n \langle w_q^n \rangle_s \end{aligned}$$

$S_s(q, w)$ even function \Rightarrow odd moments vanish

$$\Rightarrow F_s(q, t) = \overbrace{\langle w_q^0 \rangle_s}^{=1} - \frac{1}{2!} \langle w_q^2 \rangle_s t^2 + \frac{1}{4!} \langle w_q^4 \rangle_s t^4 - \dots$$

$$\begin{aligned} \langle w_q^2 \rangle_s &= - \left. \frac{d^2 F_s(q, t)}{dt^2} \right|_{t=0} \\ &= - \left[\frac{d^2}{dt^2} \langle S_s^*(\vec{q}, 0) \underbrace{S_s(\vec{q}, t)}_{e^{i\vec{q} \cdot \vec{r}_s(t)}} \rangle \right]_{t=0} \\ &= - \left[\cancel{\frac{d^2}{dt^2}} \langle \ddot{S}_s(\vec{q}, t) S_s^*(\vec{q}, 0) \rangle \right]_{t=0} \end{aligned}$$

(94)

$$= - \left[\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \dot{\rho}_s(\vec{q}, t+t') \rho_s^*(\vec{q}, t') dt' \right]_{t=0}$$

partial
integration

$$\frac{d}{dt} \rightarrow \frac{d}{dt'}$$

$$= - \cancel{\left[\lim_{T \rightarrow \infty} \frac{1}{T} \left(\dot{\rho}_s(\vec{q}, t+t') \rho_s^*(\vec{q}, t') \right) \Big|_0^T \right]}$$

$$\cancel{\left[\lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \dot{\rho}_s(\vec{q}, t+t') \dot{\rho}_s^*(\vec{q}, t') dt' \right]}_{t=0}$$

$$= - \cancel{\left[\lim_{T \rightarrow \infty} \frac{1}{T} \left(\dot{\rho}_s(\vec{q}, t+T) \rho_s^*(\vec{q}, T) - \dot{\rho}_s(\vec{q}, t) \rho_s^*(\vec{q}, 0) \right) \right]}_{t=0} = 0$$

$$+ \left[\lim_{t \rightarrow 0} \langle \dot{\rho}_s(\vec{q}, t) \dot{\rho}_s^*(\vec{q}, 0) \rangle \right]_{t=0}$$

$$= \underbrace{\langle \dot{\rho}_s(\vec{q}, 0) \dot{\rho}_s^*(\vec{q}, 0) \rangle}$$

$$= i \vec{q} \cdot \underbrace{\frac{d \vec{r}_s(t)}{dt}}_{= \vec{v}_s} e^{i \vec{q} \cdot \vec{r}_s(t)}$$

$$= \langle (\vec{q} \cdot \vec{v}_s)^2 \rangle$$

$$= \sum_{\alpha, \beta=1}^3 q_\alpha q_\beta \underbrace{\langle v_{s,\alpha} v_{s,\beta} \rangle}_{=0}$$

$$= \begin{cases} \langle v_{s,\alpha} \rangle \langle v_{s,\beta} \rangle = 0 & \alpha \neq \beta \\ \langle v_{s,\alpha} \rangle^2 = \frac{k_\alpha T}{m} & \alpha = \beta \end{cases}$$

$$= \sum_{\alpha=1}^3 q_{\alpha}^2 \frac{k_B T}{m} \quad \frac{k_B T}{m} = (\text{thermal velocity})^2$$

$$= \frac{k_B T}{m} q^2$$

$$\Rightarrow \boxed{\langle w_q^2 \rangle_s = \frac{k_B T}{m} q^2}$$

- $\langle w_q^2 \rangle_s$ describes ballistic motion of tagged particle
 (no dependence on interaction with other particles)

$$\langle w_q^4 \rangle_s = \frac{d^4 F_s(q, t)}{dt^4} \Big|_{t=0}$$

$$= \left\langle [\ddot{s}_s(\vec{q}, t)]_{t=0} [\dot{s}_s^*(\vec{q}, t)]_{t=0} \right\rangle$$

$$\ddot{s}_s(\vec{q}, t) = i\vec{q} \cdot \vec{v}_s e^{i\vec{q} \cdot \vec{r}_s(t)} - (\vec{q} \cdot \vec{v}_s)^2 e^{i\vec{q} \cdot \vec{r}_s(t)}$$

$$\langle (\vec{q} \cdot \vec{v}_s) (\vec{q} \cdot \vec{v}_s)^2 \rangle = 0 \quad \text{follows from}$$

$$\langle A(t) B^* \rangle = - \langle A(t) B^* \rangle$$

$$\Rightarrow \langle w_q^4 \rangle_s = \langle (\vec{q} \cdot \vec{v}_s)^4 \rangle + \langle (\vec{q} \cdot \vec{v}_s)^2 \rangle$$

(96)

short time expansion

$$F_s(q, t) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n F_s(q, t)}{dt^n} \right|_{t=0} t^n$$

$$= 1 - \frac{1}{2!} \langle w_q^2 \rangle_s t^2 + \frac{1}{4!} \langle w_q^4 \rangle_s t^4 - \dots$$

$$\underbrace{\frac{d^{2n} F_s(q, t)}{dt^{2n}}}_{\text{---}} \Big|_{t=0} = i^{2n} \underbrace{\int_{-\infty}^{\infty} dw w^{2n} S_s(q, w)}_{\text{---}}$$

$$= \langle w_q^{2n} \rangle_s$$

$$\langle w_q^2 \rangle_s = \frac{k_B T}{m} q^2 \rightarrow \text{ballistic motion}$$

$$\langle w_q^4 \rangle_s = \left. \frac{d^4 F_s(q, t)}{dt^4} \right|_{t=0}$$

$$= \left\langle [\ddot{S}_s(\vec{q}, t)]_{t=0} [\ddot{S}_s^*(\vec{q}, t)]_{t=0} \right\rangle$$

$$\ddot{S}_s(\vec{q}, t) = i \vec{q} \cdot \dot{\vec{v}}_s e^{i \vec{q} \cdot \vec{r}_s(t)} - (\vec{q} \cdot \vec{v}_s)^2 e^{i \vec{q} \cdot \vec{r}_s(t)}$$

$$\langle (\vec{q} \cdot \dot{\vec{v}}_s) (\vec{q} \cdot \vec{v}_s)^2 \rangle = 0 \quad \text{follows from}$$

$$\langle \dot{A}(t) B^* \rangle = - \langle A(t) \dot{B} \rangle$$

$$\Rightarrow \langle w_q^4 \rangle_s = \langle (\vec{q} \cdot \vec{v}_s)^4 \rangle + \langle (\vec{q} \cdot \dot{\vec{v}}_s)^2 \rangle$$

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$$\langle (\vec{q} \cdot \vec{v}_s)^4 \rangle = \dots = 3 \left(\frac{k_B T}{m} \right)^2 q^4$$

$$\langle (\vec{q} \cdot \vec{v}_s)^2 \rangle = \langle (\vec{q} \cdot (-\frac{1}{m} \frac{\partial U}{\partial \vec{r}_s}))^2 \rangle$$

↑
force on tagged particle

→ assume isotropic homogeneous system

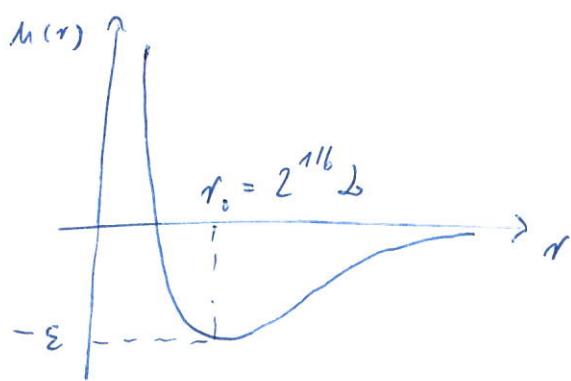
→ pairwise-additive interactions $U = \frac{1}{2} \sum_{i=1}^N \sum_{j>i} \mu(r_{ij})$

then, one can show that

$$\langle (\vec{q} \cdot \vec{v}_s)^2 \rangle = \frac{g k_B T}{3m^2} q^2 \int d\vec{r} \nabla^2 \mu(r) g(r)$$

$$\Rightarrow \boxed{\begin{aligned} \langle w_q^4 \rangle_s &= \frac{k_B T}{m} q^2 [3 \left(\frac{k_B T}{m} \right) q^2 + J_0^2] \\ J_0^2 &= \frac{g}{3m} \int d\vec{r} \nabla^2 \mu(r) g(r) \end{aligned}}$$

example : LJ system



$$\Phi^u(r_0) \approx 52.1 \frac{\epsilon}{\sigma^2}$$

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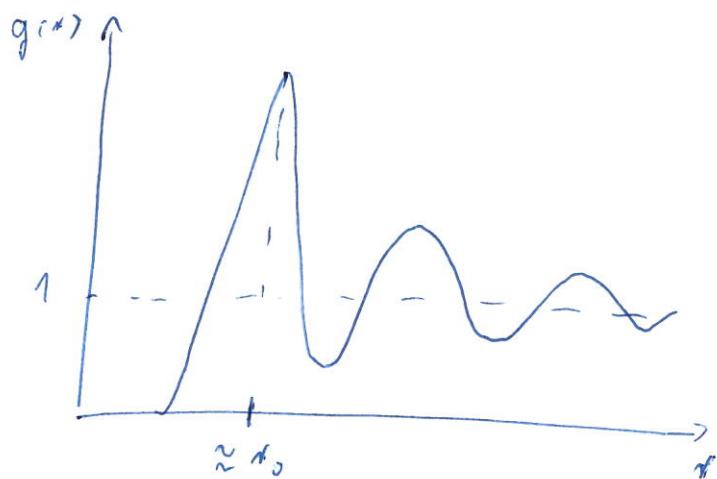
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V2P

$\frac{2}{\pi}$

main contribution in \mathcal{L}_0 for $r \approx r_0$

here $g(r)$ also large



$$\nabla^2 u(r) = u''(r) + 2 \frac{u'(r)}{r}$$

radial part of
Laplace operator

$$r = r_0 : \nabla^2 u(r) = u''(r_0)$$

$$\omega - \omega_0 \Rightarrow \mathcal{L}_0 \approx 3.5 \text{ T Hz}$$

short-time expansion for mean-squared displacement:

$$\begin{aligned} \langle r^2(t) \rangle &= \langle (\vec{r}_s(t) - \vec{r}_s(0))^2 \rangle \\ &= \int d\vec{r} r^2 G_s(r, t) \\ &= \int d\vec{r} r^2 \frac{1}{(2\pi)^3} \int d\vec{q} F_s(q, t) e^{i\vec{q} \cdot \vec{r}} \\ &\approx \int d\vec{r} r^2 \frac{1}{(2\pi)^3} \int d\vec{q} [1 - \langle w_q^2 \rangle_s \frac{t^2}{2} \\ &\quad + \langle w_q^4 \rangle_s \frac{t^4}{4!} - \dots] e^{i\vec{q} \cdot \vec{r}} \end{aligned}$$

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$$(i) \int d\vec{r} r^2 \underbrace{\frac{1}{(2\pi)^3} \int d\vec{q} e^{i\vec{q} \cdot \vec{r}}}_{= \delta(\vec{r})} = \int d\vec{r} r^2 \delta(\vec{r}) = 0$$

$$\begin{aligned} (ii) - \int d\vec{r} r^2 \frac{1}{(2\pi)^3} \int d\vec{q} < w_q^2 >_S \frac{t^2}{2} e^{i\vec{q} \cdot \vec{r}} \\ &= - \int d\vec{r} r^2 \frac{1}{(2\pi)^3} \int d\vec{q} \underbrace{\frac{k_B T}{m} q^2 e^{i\vec{q} \cdot \vec{r}} \frac{t^2}{2}}_{= -\nabla^2 e^{i\vec{q} \cdot \vec{r}}} \\ &= + \int d\vec{r} \frac{k_B T}{m} \frac{t^2}{2} r^2 \nabla^2 \delta(\vec{r}) \end{aligned}$$

$\xrightarrow{2 \text{ partial integrations}}$

$$\begin{aligned} &= \int d\vec{r} \cancel{k_B T} \frac{k_B T}{m} \frac{t^2}{2} \int d\vec{r} \delta(\vec{r}) \underbrace{\nabla^2 r^2}_{= 6} \\ &= \frac{3 k_B T}{m} t^2 \end{aligned}$$

$$(iii) \int d\vec{r} r^2 \frac{1}{(2\pi)^3} \int d\vec{q} \frac{t^4}{4!} \left[3 \left(\frac{k_B T}{m} \right)^2 q^4 + \frac{k_B T}{m} q^2 \mathcal{J}_0^2 \right] e^{i\vec{q} \cdot \vec{r}}$$

$$\begin{aligned} &= \int d\vec{r} r^2 \frac{t^4}{4!} \underbrace{3 \left(\frac{k_B T}{m} \right)^2 \frac{\partial^4}{\partial \vec{r}^4} \delta(\vec{r})}_{= 0} \\ &= 0 \end{aligned}$$

$$= \frac{k_B T}{m} \mathcal{J}_0^2 \frac{t^4}{24} 6$$

$$= - \frac{k_B T}{4m} \mathcal{J}_0^2 t^4$$

$$\Rightarrow \boxed{<r^2(t)> = \frac{3 k_B T}{m} t^2 - \frac{k_B T}{4m} \mathcal{J}_0^2 t^4}$$

oscillatory motion at high frequencies
V27

IV. 5.5. Self diffusion

hydrodynamic limit

- wave-vector $\vec{q} \rightarrow 0 \stackrel{!}{=} \text{large length scales}$
- frequency $\omega \rightarrow 0 \stackrel{!}{=} \text{long times}$
- microscopic details not relevant
- dynamics controlled by slow variables on macroscopic scales: conserved quantities

one-particle dynamics $\rho_s(\vec{r}, t)$ conserved

\Rightarrow continuity equation

$$\frac{\partial \rho_s(\vec{r}, t)}{\partial t} + \nabla \cdot \underbrace{\vec{j}_s(\vec{r}, t)}_{\text{one-particle current}} = 0$$

constitutive equation:

$$\vec{j}_s = -D \nabla \rho_s$$

↑
self-diffusion coefficient

$$\Rightarrow \left[\frac{\partial \rho_s(\vec{r}, t)}{\partial t} = D \nabla^2 \rho_s(\vec{r}, t) \right] \text{diffusion equation}$$

$$\text{FT: } \frac{\partial \rho_s(\vec{q}, t)}{\partial t} = -D q^2 \rho_s(\vec{q}, t)$$

$$\Rightarrow \rho_s(\vec{q}, t) = \rho_s(\vec{q}, 0) e^{-D q^2 t} \quad | \cdot \rho_s(-\vec{q}, 0) \text{ and } \langle \dots \rangle$$

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$$\Rightarrow \underbrace{\langle S_s(\vec{q}, t) S_s(-\vec{q}, 0) \rangle}_{= F_s(q, t)} = e^{-Dq^2 t}$$

→ relaxation time $\tau_q = \frac{1}{Dq^2} \xrightarrow{q \rightarrow 0} \infty$
 "hydrodynamic slowing down"

$$\rightarrow \langle \frac{dS_s(\vec{q}, 0)}{dt} S_s(-\vec{q}, 0) \rangle = -Dq^2 \downarrow$$

$$\langle \vec{A}(0) \vec{A}(0) \rangle = 0 !$$

diffusion equation not valid at short times (at short times ballistic motion and not $\dot{s}_s \propto \nabla S_s$!)

$$\rightarrow G_s(r, t) = \frac{1}{(4\pi D t)^{d/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

d dimensions

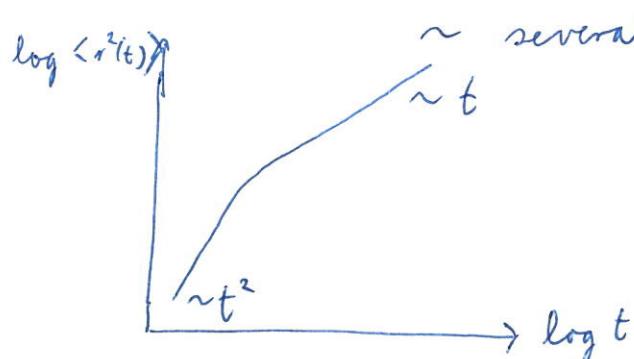
$$\Rightarrow \langle r^2(t) \rangle = \int d\vec{r} r^2 G_s(r, t) = 2dDt$$

$$\Rightarrow \boxed{D = \lim_{t \rightarrow \infty} \frac{\langle r^2(t) \rangle}{2d t}} \quad \text{for } t \rightarrow \infty$$

Einstein relation

→ $t \rightarrow \infty$? for simple dense fluid (\neq near T_{tr})

$\log \langle r^2(t) \rangle \sim$ several ps



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remarks:

(i) glassforming liquids

drastic slowing down of dynamics with decreasing temperature

→ undercooled liquids: crystallization avoided due to slow kinetics

→ occurs typically in multicomponent liquids,
e.g. binary A B mixture

→ example: binary Lennard-Jones mixture
(Kob-Anderson mixture)

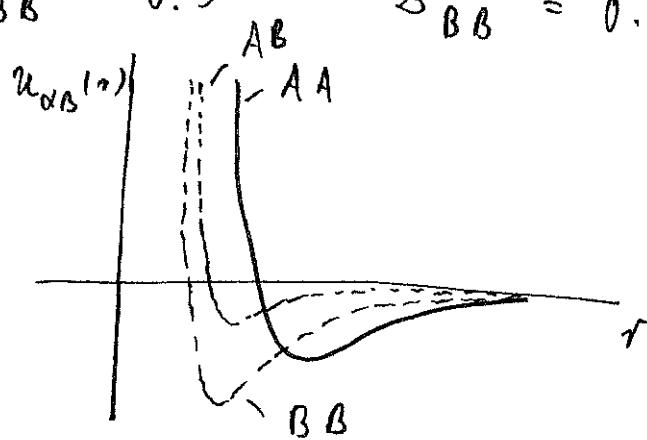
$$u_{\alpha\beta}(r) = 4 \epsilon_{\alpha\beta} \left[\left(\frac{\sigma_{\alpha\beta}}{r} \right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r} \right)^6 \right]$$

$\alpha\beta = AA, AB, BB$

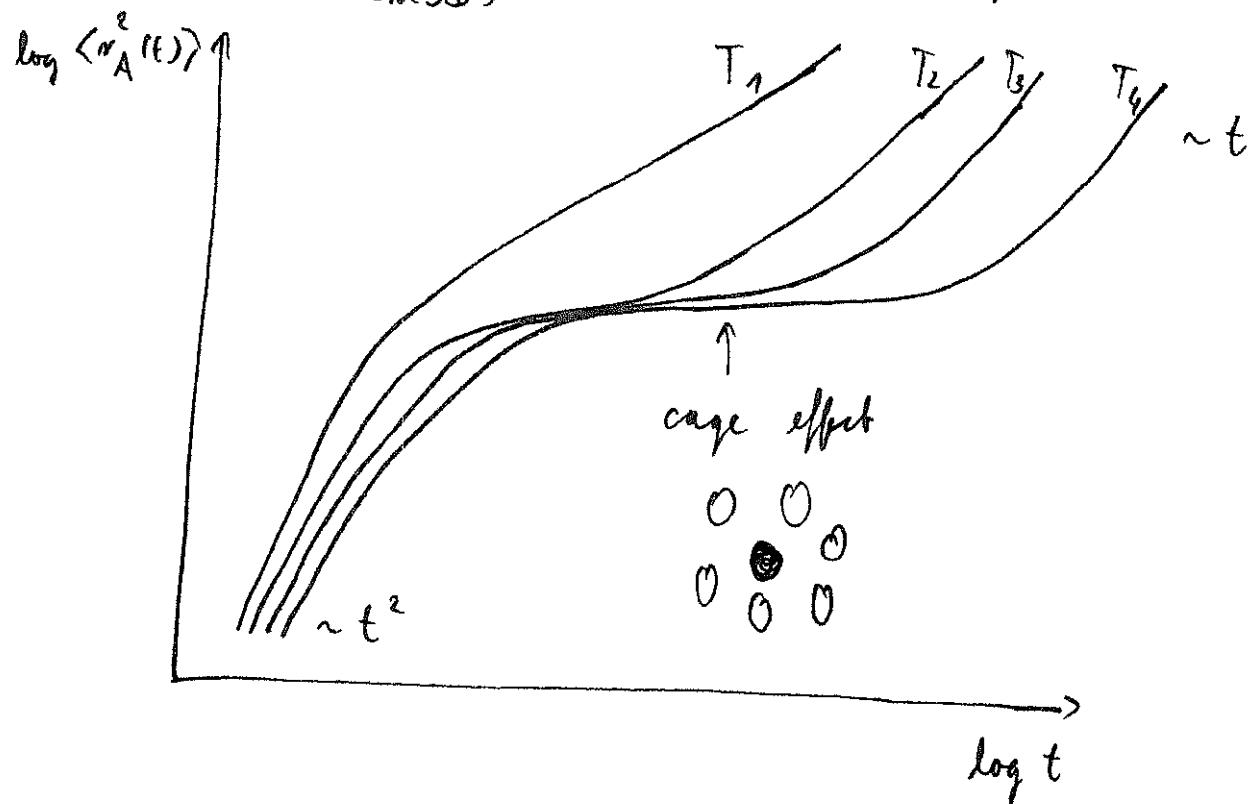
$$\epsilon_{AA} = 1.0 \quad \sigma_{AA} = 1.0$$

$$\epsilon_{AB} = 1.5 \quad \sigma_{AB} = 0.8$$

$$\epsilon_{BB} = 0.5 \quad \sigma_{BB} = 0.88$$



mean-squared displacement, e.g. of A particles
(MSD)



$$T_1 > T_2 > T_3 > T_4$$

$$\text{diffusion coefficient } D_A = \lim_{t \rightarrow \infty} \frac{\langle r_A^2(t) \rangle}{6t}$$

decreases by orders of magnitude in a relatively small temperature window

(ii) how does one determine diffusion coefficient from MSD?

→ plot $\frac{\langle r_A^2(t) \rangle}{6t}$ as function of t and read off constant at long times

better: plot $\frac{1}{6} \frac{d \langle r^2(t) \rangle}{dt}$ as function of t (numerical derivative)

why? simple model of MSD in glassy regime:
plateau + diffusion

$$\langle r^2(t) \rangle = C + 6Dt \quad (d=3!)$$

$$\Rightarrow \frac{\langle r^2(t) \rangle}{6t} = \frac{C}{6t} + D$$

"correction", vanishes when using numerical derivative

(iii) diffusion coefficient can be also determined from
Green-Kubo relation

$$D = \frac{1}{3} \overbrace{\int_0^\infty dt}^{\text{of dimensions: } \frac{1}{d}} \underbrace{\langle \vec{v}_s(t) \cdot \vec{v}_s(0) \rangle}_{\text{velocity autocorrelation function}}$$

$\vec{v}_s(t)$: velocity of tagged particle at time t (VACF)

VACF equal to 2nd time derivative of $\langle r^2(t) \rangle$

(iv) seminal result of

Hlder, Wainwright,

for long-time behavior of VACF

$$\langle \vec{v}_s(t) \cdot \vec{v}_s(0) \rangle \sim t^{-d/2}$$

→ due to conservation of transverse momentum

$$d=2$$

$$D \sim \frac{1}{2} \int_0^\infty dt \frac{1}{t} \sim [\log t]_0^\infty = \infty$$

⇒ diffusion coefficient in $d=2$ does not exist!

II

IV. Monte Carlo simulation

II.1. IV.1. Introductory remarks

MD: correlation functions, transport coefficients, thermodynamic properties etc. from time averages

now: ensemble averages

consider N particles in canonical ensemble

observable $A(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$
 $\underbrace{\qquad\qquad\qquad}_{= \vec{r}^{(N)}}$

\Rightarrow expectation value

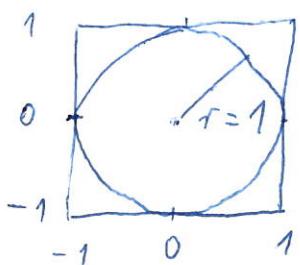
$$\langle A(\vec{r}^{(N)}) \rangle = \frac{\int d\vec{r}^{(N)} A(\vec{r}^{(N)}) e^{-\beta U(\vec{r}^{(N)})}}{\int d\vec{r}^{(N)} e^{-\beta U(\vec{r}^{(N)})}}$$

$U(\vec{r}^{(N)})$ potential energy, $\beta = \frac{1}{k_B T}$

problem: direct calculation of high-dimensional integral over $3N$ variables ($d=3$) in general impossible

idea: use random numbers to compute $\langle A(\vec{r}^{(N)}) \rangle$

simple example: calculation of π

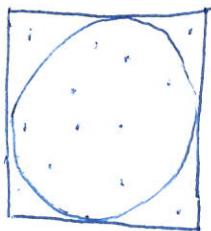


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$$\frac{\text{area of circle}}{\text{area of square}} = \frac{\pi}{4}$$

function $\text{ran}(-1, 1)$: uniformly distributed random numbers on interval $(-1, 1)$

- algorithm:
- N random numbers from $\text{ran}(-1, 1)$
 - compute $N_{\text{hit}} = \text{number of random numbers in the circle}$



$$N \rightarrow \infty : \frac{\pi}{4} = \frac{N_{\text{hit}}}{N}$$

"program":

```

 $N_{\text{hit}} = 0$ 
do  $i = 1, N$ 
     $x = \text{ran}(-1, 1)$ 
     $y = \text{ran}(-1, 1)$ 
    if ( $x^2 + y^2 < 1$ )  $N_{\text{hit}} = N_{\text{hit}} + 1$ 
end do

```

interpretation as ensemble average:

$$\frac{N_{\text{hit}}}{N} = \underbrace{\frac{1}{N} \sum_{i=1}^N A_i}_{\text{sampling}} \stackrel{\text{observable}}{\approx} \langle A \rangle = \frac{\int_{-1}^1 dx \int_{-1}^1 dy f(x,y) A(x,y)}{\int_{-1}^1 dx \int_{-1}^1 dy f(x,y)}$$

integration over probability density $f(x,y)$

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94.7 14

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$$f(x, y) = \begin{cases} 1 & \text{within the square} \\ 0 & \text{otherwise} \end{cases}$$

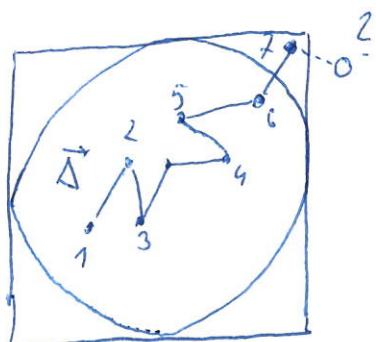
$$A = \begin{cases} 1 & \text{within circle} \\ 0 & \text{otherwise} \end{cases}$$

observable

- here :
- direct sampling of $f(x, y)$
 - all points in square visited with equal probability (provided by uniform random numbers)

different strategy : Markov chains

idea : generate random walk through the square



$$\frac{N_{\text{hit}}}{N} = \frac{\pi}{4} \quad \text{for } N \rightarrow \infty$$

algorithm :

- initial point in square via random number
- random displacement $\vec{r}_2 = \vec{r}_1 + \vec{\Delta}$ $\vec{\Delta} = (\Delta_x, \Delta_y)$
 $\Delta_x = \text{ran}(-\delta, \delta)$, $\Delta_y = \text{ran}(-\delta, \delta)$
- further displacements $\vec{r}_{i+1} = \vec{r}_i + \vec{\Delta}$
→ Markov chain: \vec{r}_{i+1} only depends on \vec{r}_i (no memory)

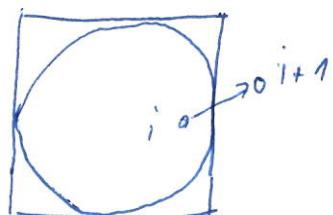
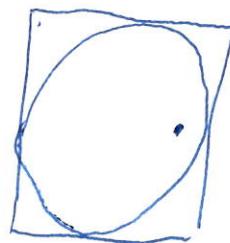
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V22

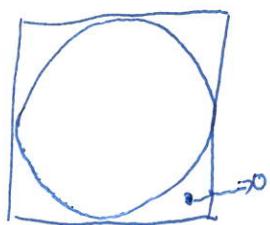
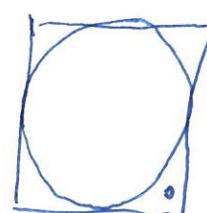
- 3 -

- choice of δ ? not too small and not too large
here $\delta = 0.3$ good choice
- \vec{r}_{i+1} not inside the square?
 → reject move to \vec{r}_{i+1} and stay at \vec{r}_i
 → new attempt at \vec{r}_i


 \Rightarrow


$$N \rightarrow N + 1$$

$$N_{\text{hit}} \rightarrow N_{\text{hit}} + 1$$


 \Rightarrow


$$N \rightarrow N + 1$$

$$N_{\text{hit}} \rightarrow N_{\text{hit}}$$

state at \vec{r}_i counted again?

- code:


```

Nhit = 0
x = ran (-1, 1)
y = ran (-1, 1)
do i = 1, N
  Ax = ran (-δ, δ)
  Ay = ran (-δ, δ)
  if (|x + Ax| < 1. and. |y + Ay| < 1) then
    x = x + Ax
    y = y + Ay
  endif
  if (x2 + y2 < 1) Nhit = Nhit + 1
enddo
      
```

(MO)

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V22

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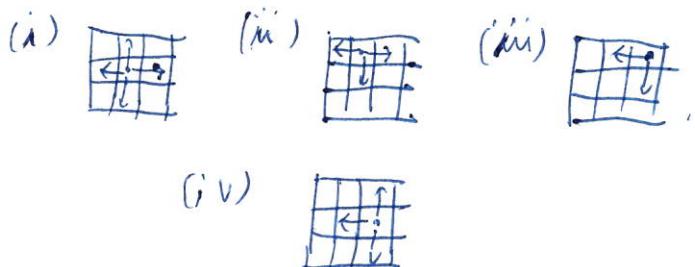
IV.2. Analysis of the Markov chain

requirement: visit all points in square with equal probability

consider simplified system with 9 cells:

i	b	c
h	a	d
g	f	e

moves to neighboring cells possible



$f(a)$: stationary probability to find system in state a

$$f(a) = f(b) = \dots = f(i) = \frac{1}{9}$$

$p(a \rightarrow b)$: transition probability, that system moves from a to b

$$\begin{aligned} \text{normalization: } p(a \rightarrow a) + p(a \rightarrow b) + p(a \rightarrow d) + \\ + p(a \rightarrow f) + p(a \rightarrow h) = 1 \end{aligned}$$

$$\text{similarly: } p(c \rightarrow c) + p(c \rightarrow b) + p(c \rightarrow d) = 1$$

consider case (iii):

$$\begin{aligned} f(c) = f(b) p(b \rightarrow c) + f(d) p(d \rightarrow c) \\ + f(c) p(c \rightarrow c) \end{aligned}$$

$$\Rightarrow f(c) \underbrace{[1 - p(c \rightarrow c)]}_{= p(c \rightarrow b) + p(c \rightarrow d)} = f(b) p(b \rightarrow c) + f(d) p(d \rightarrow c)$$

(111)

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$$\Rightarrow f(c) p(c \rightarrow b) + f(c) p(c \rightarrow d) \\ = f(b) p(b \rightarrow c) + f(d) p(d \rightarrow c)$$

this equation can be fulfilled by

$$f(c) p(c \rightarrow b) = f(b) p(b \rightarrow c)$$

$$f(c) p(c \rightarrow d) = f(d) p(d \rightarrow c)$$

or in general

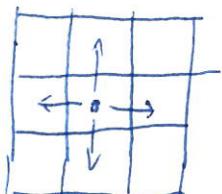
$$f(\text{old}) p(\text{old} \rightarrow \text{new}) = f(\text{new}) p(\text{new} \rightarrow \text{old})$$

detailed balance

$$\text{in our example } f(\text{old}) = f(\text{new})$$

\Rightarrow possible choice of transition probabilities

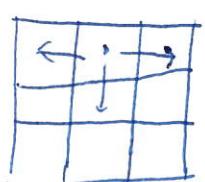
(i)



$$p(a \rightarrow \text{new}) = \frac{1}{4}$$

$$p(a \rightarrow a) = 0$$

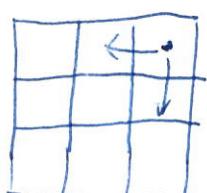
(ii)



$$p(b \rightarrow a) = p(b \rightarrow c) = p(b \rightarrow i) = \frac{1}{4}$$

$$p(b \rightarrow b) = \frac{1}{4}$$

(iii)



$$p(c \rightarrow b) = p(c \rightarrow d) = \frac{1}{4}$$

$$p(c \rightarrow c) = \frac{1}{2}$$

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V22

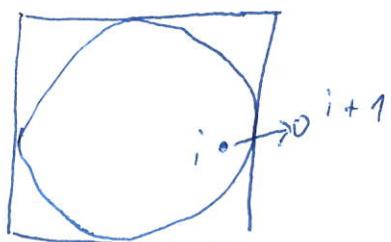
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$$\text{or } p(\text{old} \rightarrow \text{new}) = \frac{1}{4} \quad \text{for old} \neq \text{new}$$

$$p(\text{old} \rightarrow \text{old}) = 1 - \sum_{\text{new} \neq \text{old}} p(\text{old} \rightarrow \text{new})$$

\Rightarrow detailed balance holds

back to original problem:



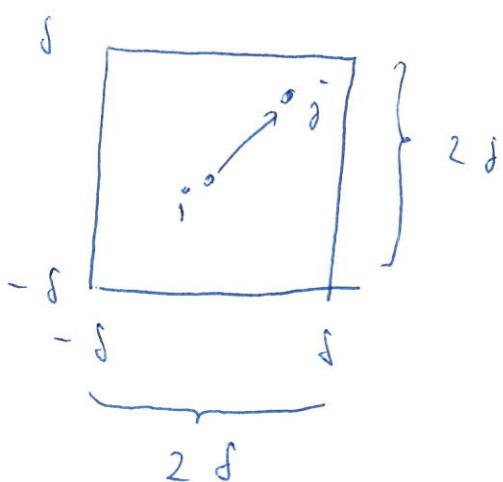
\rightarrow reject $i+1$

\rightarrow count state at i one more

* transition old \rightarrow new accepted or rejected?

acc (old \rightarrow new) : acceptance probability

$$p(\text{old} \rightarrow \text{new}) = \underbrace{\alpha(\text{old} \rightarrow \text{new})}_{\text{a priori probability}} \text{acc}(\text{old} \rightarrow \text{new})$$



$$\Delta x = \text{ran}(-\delta, \delta)$$

$$\Delta y = \text{ran}(-\delta, \delta)$$

$$\Rightarrow \alpha(i \rightarrow j) = \alpha(j \rightarrow i)$$

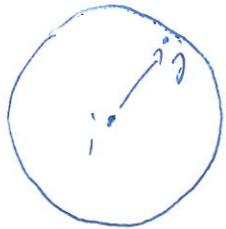
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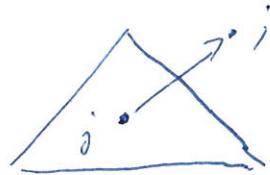
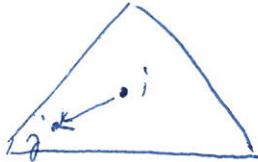
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other possibilities:



$$\alpha(i \rightarrow j) = \alpha(j \rightarrow i)$$

asymmetric α :



$$\alpha(i \rightarrow j) \neq \alpha(j \rightarrow i)$$

in the following: symmetric α

- detailed balance

$$f(\text{old}) p(\text{old} \rightarrow \text{new}) = f(\text{new}) p(\text{new} \rightarrow \text{old})$$

$$\Rightarrow f(\text{old}) \alpha(\text{old} \rightarrow \text{new}) \text{acc}(\text{old} \rightarrow \text{new})$$

$$= f(\text{new}) \underbrace{\alpha(\text{new} \rightarrow \text{old})}_{\text{acc}(\text{new} \rightarrow \text{old})}$$

$$= \alpha(\text{old} \rightarrow \text{new})$$

$$\Rightarrow \frac{\text{acc}(\text{old} \rightarrow \text{new})}{\text{acc}(\text{new} \rightarrow \text{old})} = \frac{f(\text{new})}{f(\text{old})}$$

possible choice for $\text{acc}(\text{old} \rightarrow \text{new})$:

$$\text{acc}(\text{old} \rightarrow \text{new}) = \begin{cases} \frac{f(\text{new})}{f(\text{old})} & \text{for } f(\text{new}) < f(\text{old}) \\ 1 & \text{for } f(\text{new}) \geq f(\text{old}) \end{cases}$$

can be also written as follows

$$\text{acc}(\text{old} \rightarrow \text{new}) = \min\left(1, \frac{f(\text{new})}{f(\text{old})}\right)$$

Metropolis criterion

, does this criterion make sense?

$$\text{acc}(\text{old} \rightarrow \text{new}) \in [0, 1]$$

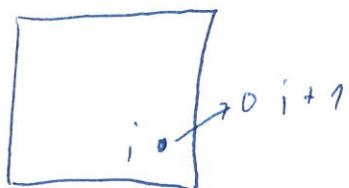
$$\underline{f(\text{new}) < f(\text{old})} : \underbrace{\text{acc}(\text{old} \rightarrow \text{new})}_{= \frac{f(\text{new})}{f(\text{old})}} = \frac{f(\text{new})}{f(\text{old})} \text{acc}(\text{new} \rightarrow \text{old})$$

$$\Rightarrow \text{acc}(\text{new} \rightarrow \text{old}) = 1 \quad \checkmark$$

$$\underline{f(\text{new}) \geq f(\text{old})} : 1 = \frac{f(\text{new})}{f(\text{old})} \text{acc}(\text{new} \rightarrow \text{old})$$

$$\Rightarrow \text{acc}(\text{new} \rightarrow \text{old}) = \frac{f(\text{old})}{f(\text{new})} \quad \checkmark$$

our example:



$$f(i+1) = 0, f(i) = 1$$

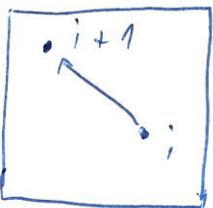
$$\Rightarrow \text{acc}(i \rightarrow i+1) = 0$$

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14. 1. 14

✓ 22

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$$f(i) = 1, \quad f(i+1) = 1 \\ \Rightarrow \text{acc}(i \rightarrow i+1) = 1$$

summary:

two sampling methods

→ direct sampling of f

→ Markov chain sampling:

sample states with probability f , only
knowledge of $\frac{f(\text{new})}{f(\text{old})}$ required

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V22

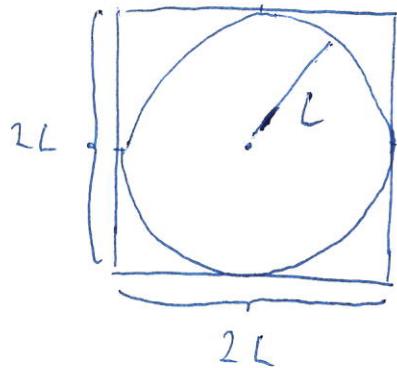
- 10 -

IV. 3. Metropolis algorithm for the sampling in the canonical ensemble

goal: calculation of

$$\langle A(\vec{r}^{(n)}) \rangle = \frac{\int d\vec{r}^{(n)} e^{-\beta U(\vec{r}^{(n)})} A(\vec{r}^{(n)})}{\int d\vec{r}^{(n)} e^{-\beta U(\vec{r}^{(n)})}}$$

what do we learn from our simple problem of calculating π ?



circle defined by all points for which

$$x^2 + y^2 = L^2$$

$$\frac{\pi}{4} = \frac{\text{area of circle}}{\text{area of square}}$$

observable $A(x,y) = \begin{cases} 1 & (x,y) \in \text{circle} \\ 0 & \text{otherwise} \end{cases}$

"ensemble average" $\langle A \rangle = \frac{\int_0^L dx \int_0^L dy f(x,y) A(x,y)}{\int_0^L dx \int_0^L dy f(x,y)}$

probability for point obtaining point (x,y) during sampling with uniform random numbers:

$$\frac{f(x,y)}{\int dx \int dy f(x,y)} = \frac{1}{L^2} \quad \text{where} \quad f(x,y) = \begin{cases} 1 & (x,y) \in \text{square} \\ 0 & \text{otherwise} \end{cases}$$

(117)

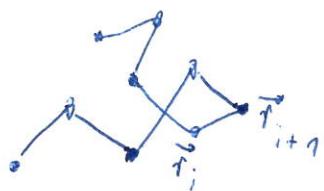
16. 1. 14

(*)

V23

- 1 -

Markov chain sampling : → random walk on square
 → visit all points with prob. (*)



accept move from $\vec{r}_i = (x_i, y_i)$ to
 $\vec{r}_{i+1} = (x_{i+1}, y_{i+1})$?

⇒ detailed balance condition

$$f(\vec{r}_i) p(\vec{r}_i \rightarrow \vec{r}_{i+1}) = f(\vec{r}_{i+1}) p(\vec{r}_{i+1} \rightarrow \vec{r}_i)$$

remember: transition probability

$$p(\vec{r}_i \rightarrow \vec{r}_{i+1}) = \underbrace{\alpha(\vec{r}_i \rightarrow \vec{r}_{i+1})}_{\text{a priori prob.}} \underbrace{\text{acc}(\vec{r}_i \rightarrow \vec{r}_{i+1})}_{\text{acceptance prob.}}$$

$$\text{assume: } \alpha(\vec{r}_i \rightarrow \vec{r}_{i+1}) = \alpha(\vec{r}_{i+1} \rightarrow \vec{r}_i)$$

⇒ accept move with prob.

$$\begin{aligned} \text{acc}(\vec{r}_i \rightarrow \vec{r}_{i+1}) &= \min \left(1, \frac{f(\vec{r}_{i+1})}{f(\vec{r}_i)} \right) \\ &= \begin{cases} \frac{f(\vec{r}_{i+1})}{f(\vec{r}_i)} & f(\vec{r}_{i+1}) < f(\vec{r}_i) \\ 1 & f(\vec{r}_{i+1}) \geq f(\vec{r}_i) \end{cases} \end{aligned}$$

Metropolis criterion

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use all this for canonical ensemble:

- prob. to find system in configuration $\vec{r}^{(N)}$ (at given $N, V, \beta = \frac{1}{k_B T}$) $\propto \frac{e^{-\beta U(\vec{r}^{(N)})}}{\int d\vec{r}^{(N)} e^{-\beta U(\vec{r}^{(N)})}}$
- $\Rightarrow \frac{f(\vec{r}_{i+1}^{(N)})}{f(\vec{r}_i^{(N)})} = e^{-\beta [\Delta U(\vec{r}_{i+1}^{(N)}) - U(\vec{r}_i^{(N)})]}$
 $= e^{-\beta \Delta U}$
 ΔU : difference between potential energies of new and old configuration

- ~~Metropolis criterion~~ detailed balance

$$\frac{p(\vec{r}_i^{(N)} \rightarrow \vec{r}_{i+1}^{(N)})}{p(\vec{r}_{i+1}^{(N)} \rightarrow \vec{r}_i^{(N)})} = e^{-\beta \Delta U}$$

- ~~Metropolis criterion~~ (also assume $\alpha(\vec{r}_i^{(N)} \rightarrow \vec{r}_{i+1}^{(N)}) = \alpha(\vec{r}_{i+1}^{(N)} \rightarrow \vec{r}_i^{(N)})$)

$$\alpha(\vec{r}_i^{(N)} \rightarrow \vec{r}_{i+1}^{(N)}) = \min(1, e^{-\beta \Delta U})$$

$$= \begin{cases} e^{-\beta \Delta U} & \Delta U > 0 \\ 1 & \text{otherwise} \end{cases}$$

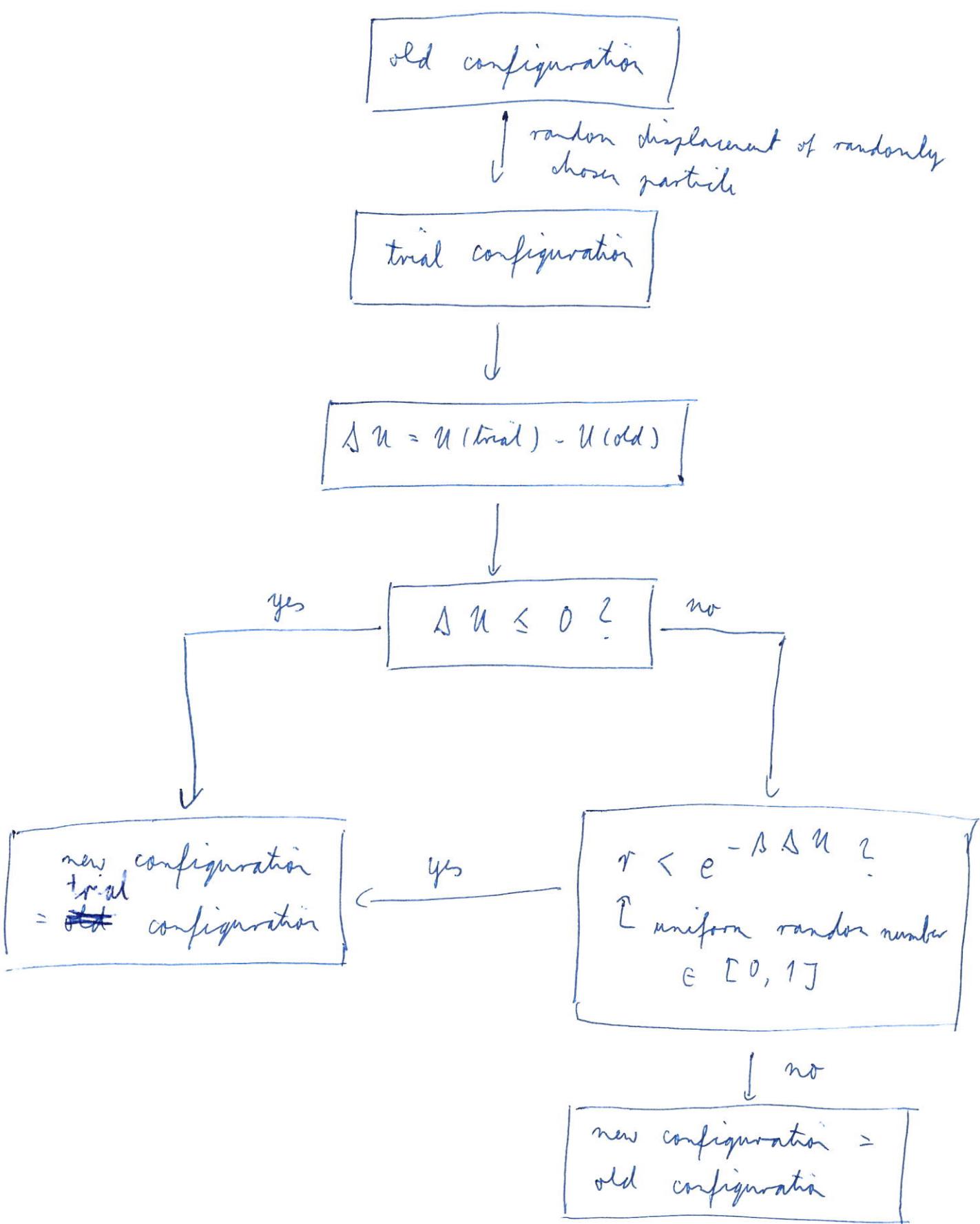
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schematic algorithm :



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remarks:

- Monte-Carlo cycle (or sweep): N trial moves of randomly chosen particles " $\hat{=}$ " time step in MD simulation
- dynamic interpretation

$f(\vec{r}^{(N)}, t)$: prob. to find configuration $\vec{r}^{(N)}$ at time t
 $(t \hat{=}$ number of MC cycles)

$$\frac{df(\vec{r}^{(N)}, t)}{dt} = - \sum_{\vec{r}^{(N)1}} f(\vec{r}^{(N)}, t) p(\vec{r}^{(N)} \rightarrow \vec{r}^{(N)1}) \quad \text{loss}$$

$$+ \sum_{\vec{r}^{(N)1}} f(\vec{r}^{(N)1}, t) p(\vec{r}^{(N)1} \rightarrow \vec{r}^{(N)}) \quad \text{gain}$$

master equation

$$\underline{t \rightarrow \infty}: \quad \frac{df}{dt} = 0 \Rightarrow f(\vec{r}^{(N)}, t) = f_{eq}(\vec{r}^{(N)})$$

\uparrow
stationary distribution

$$\Rightarrow \sum_{\vec{r}^{(N)1}} f_{eq}(\vec{r}^{(N)}) p(\vec{r}^{(N)} \rightarrow \vec{r}^{(N)1})$$

$$= \sum_{\vec{r}^{(N)1}} f_{eq}(\vec{r}^{(N)1}) p(\vec{r}^{(N)1} \rightarrow \vec{r}^{(N)})$$

one possibility to fulfil this equation

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V23

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$$\frac{p(\vec{r}^{(N)} \rightarrow \vec{r}^{(N+1)})}{p(\vec{r}^{(N+1)} \rightarrow \vec{r}^{(N)})} = \frac{f_{eq}(\vec{r}^{(N+1)})}{f_{eq}(\vec{r}^{(N)})} \quad \text{detailed balance}$$

- in practice:

relaxation required until f_{eq} is reached, then calculation of observables

- original publication

N. Metropolis, A.W. Rosenbluth, M.N. Rosenbluth,
 A.H. Teller, E. Teller, J. Chem. Phys. 21, 1087 (1953)

(122)

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II. 4. Monte Carlo simulation in other ensembles

"natural" MC ensemble: canonical ensemble
 N, V, T constant

now consider ensembles where N or V may fluctuate

idea: big system in canonical ensemble decomposed
into physical system and reservoir



- phys. system: coupled to reservoir such that extensive variable (N or V) fluctuates
- reservoir:
 - ideal gas: thermodynamic properties can be computed analytically
 - reservoir much larger than physical system, therefore fluctuations of extensive variables can be neglected

II. 4. 1. Ideal gas properties

Hamilton function of a classical ideal gas consisting of N particles

$$H(\vec{r}^{(N)}, \vec{p}^{(N)}) = \sum_{\ell=1}^N \frac{\vec{p}_\ell^2}{2m_\ell}$$

positions $\vec{r}^{(N)} = (\vec{r}_1, \dots, \vec{r}_N)$

momenta $\vec{p}^{(N)} = (\vec{p}_1, \dots, \vec{p}_N)$

assume that masses for all particles equal:

$$m_1 = m_2 = \dots = m_N = m$$

partition function in canonical ensemble

$$Z(N, V, T) = N! \int d\vec{r}^{(N)} d\vec{p}^{(N)} e^{-\beta H}$$

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

normalization $\mathcal{N} = \frac{1}{N! h^{3N}}$ why?

- prefactor $\frac{1}{h^{3N}}$? h^{3N} elementary volume in phase space ($h = 6.626 \cdot 10^{-34} \text{ Js}$)

• prefactor $\frac{1}{N!}$?

accounts for the fact that for a given configuration
 $N!$ permutations of N particles lead to the same
macrostate

$$Z(N, V, T) = \frac{1}{N! h^{3N}} V^N \int d\vec{p}^{(N)} \exp\left(-\beta \sum_{i=1}^N \frac{\vec{p}_i^2}{2m}\right)$$

$$= \int d\vec{r}^{(N)}$$

$$= \frac{V^N}{N! h^{3N}} \left(\int_{-\infty}^{\infty} dp \exp\left(-\beta \frac{p^2}{2m}\right) \right)^{3N}$$

substitution $x^2 = \frac{p^2}{2m k_B T}$

$$\Rightarrow Z(N, V, T) = \frac{V^N}{N! h^{3N}} \underbrace{\left(\int_{-\infty}^{\infty} dx e^{-x^2} \right)^{3N}}_{= \sqrt{\pi}^3} (2m k_B T)^{3N/2}$$

$$= \frac{V^N}{N!} \left[\frac{(2m k_B T \pi)^{1/2}}{h} \right]^{3N}$$

$$= \frac{V^N}{N! \lambda^{3N}}$$

with $\lambda = \frac{h}{(2\pi m k_B T)^{1/2}}$ de Broglie wavelength

free energy :

$$F(N, V, T) = -k_B T \ln Z(N, V, T)$$

$$= -k_B T \left(-\ln N! + N \ln \frac{V}{\lambda^3} \right)$$

N large \Rightarrow use stirling formula $\ln(N!) \approx N \ln N - N$

$$\Rightarrow N! \approx e^{N \ln N - N}$$

$$\Rightarrow F(N, V, T) = -k_B T \left(-N \ln N + N + N \ln \frac{V}{\lambda^3} \right)$$

$$= -k_B T N \left[1 + \ln \frac{V}{N \lambda^3} \right]$$

pressure : $p = -\frac{\partial F}{\partial V} \Big|_{T, N} = \frac{N k_B T}{V}$

equation of state for an ideal gas

entropy : $S = -\frac{\partial F}{\partial T} \Big|_{V, N} = N k_B \left[\frac{5}{2} + \ln \left(\frac{V}{N \lambda^3} \right) \right]$

chemical potential :

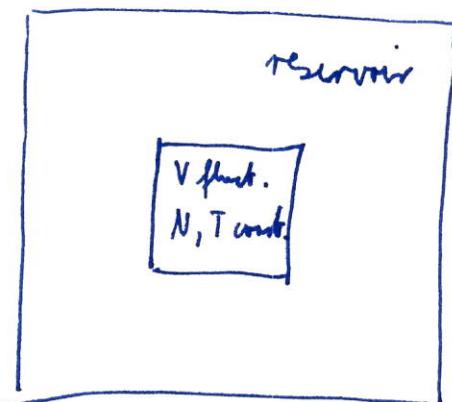
$$\mu = \frac{\partial F}{\partial N} \Big|_{T, V} = -k_B T \ln \left(\frac{V}{N \lambda^3} \right)$$

internal energy : $E = F + TS = \frac{3}{2} N k_B T$

II. 9.2. Monte Carlo simulation at constant pressure

consider N particles at constant T and $p \rightarrow V$ fluctuates

idea: couple system to ideal gas via piston



total volume $V_0 = \text{const.}$

$V_0 - V \gg V = L^3$

total number of particles $M = \text{const.}$

$M - N \gg N$

canonical partition function of complete system
(physical system + reservoir)

=

product of partition functions of subsystems

(i) physical system

$$Z_{\text{phys.}}(N, V, T) = \frac{1}{N! \lambda^{3N}} \int \dots \int d\vec{r}_1 \dots d\vec{r}_N e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)}$$

substitute $\vec{r}_i = L \vec{s}_i$, \vec{s}_i : scaled particle coordinates

$$\Rightarrow Z_{\text{phys.}}(N, V, T) = \frac{V^N}{N! \lambda^{3N}} \underbrace{\int_0^1 \dots \int_0^1}_{3N \text{ integrals}} d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U(\vec{s}_1, \dots, \vec{s}_N, L)}$$

\Rightarrow free energy

$$F_{\text{phys}}(N, V, T) = -k_B T \ln Z_{\text{phys.}}(N, V, T)$$

$$= -k_B T \ln \left(\frac{V^N}{N! \lambda^{3N}} \right) - k_B T \ln \left[\int_0^1 \dots \int_0^1 d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U} \right]$$

(ii) reservoir

$$Z_{\text{res.}}(M-N, V_0-V, T)$$

$$= \frac{1}{(M-N)! \lambda^{3(M-N)}} \int_{V_0-V}^1 \dots \int_{V_0-V}^1 d\vec{r}_1 \dots d\vec{r}_{M-N}$$

$$= \frac{(V_0 - V)^{M-N}}{\lambda^{3(M-N)} (M-N)!}$$

\Rightarrow complete system

$$Z(N, M-N, V, V_0-V, T) = Z_{\text{res.}} \cdot Z_{\text{phys.}}$$

\sim number of possible states for a given volume V
where each state is weighted by the appropriate
Boltzmann factor $e^{-\beta U}$

\Rightarrow probability density $g(V)$ to find physical
system in volume V

$$g(V) = \frac{Z(N, M-N, V, V_0 - V, T)}{\int_0^{V_0} dV' Z(N, M-N, V', V_0 - V', T)}$$

$$= \frac{V^N (V_0 - V)^{M-N} \int_0^1 \dots \int_0^1 d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U}}{\int_0^{V_0} dV' V'^N (V_0 - V')^{M-N} \int_0^1 \dots \int_0^1 d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U}}$$

thermodynamic limit

$$V_0 \rightarrow \infty, M \rightarrow \infty, \beta = \frac{M-N}{V_0} = \text{const}$$

$$\Rightarrow (V_0 - V)^{M-N} = V_0^{M-N} \left[1 - \frac{V}{V_0} \right]^{M-N}$$

$$\boxed{\begin{array}{l} V_0 \gg V \\ M \gg N \end{array}} \approx V_0^{M-N} \exp \left\{ - \frac{(M-N)V}{V_0} \right\}$$

$$= V_0^{M-N} e^{-\beta V}$$

$$\boxed{\begin{array}{l} \beta = \frac{p}{k_B T} \\ = \beta p \end{array}} \approx V_0^{M-N} e^{-\beta p V}$$

\Rightarrow partition function of physical system

$$Y(N, p, T) \propto \int dV' V'^N e^{-\beta p V'} \int_0^1 \dots \int_0^1 d\vec{s}_1 \dots d\vec{s}_N \times$$

$$\times e^{-\beta U(\vec{s}_1, \dots, \vec{s}_N, L)}$$

corresponding thermodynamic potential

$$G(N, p, T) = -k_B T \ln Y(N, p, T)$$

Gibbs free energy

probability density to find physical system in configuration $\vec{s}^{(N)}$ and volume V

$$g(\vec{s}_1, \dots, \vec{s}_N, V) \propto \exp[-\beta(U(\vec{s}^{(N)}, L) + pV - Nk_B T \ln V)] \\ \propto \exp[-\beta H_{\text{eff}}]$$

$$\text{with } H_{\text{eff}} = U(\vec{s}^{(N)}, L) + pV - Nk_B T \ln V$$

[generalized Hamilton function

Monte Carlo algorithm:

perform random walk for volume variable

\Rightarrow volume moves in addition to particle displacements

(i) choose randomly new volume $V' = V + \Delta V$

ΔV : uniform random number

$$\text{ran}(-\Delta V_{\max}, \Delta V_{\max})$$

(ii) accept or reject move according to Metropolis criterion :

$$\text{acc} (V \rightarrow V') =$$

$$\min \left\{ 1, \exp [\beta (U(\vec{s}^{(N)}, L') - U(\vec{s}^{(N)}, L) + p(V' - V) - N k_B T \ln \frac{V'}{V})] \right\}$$

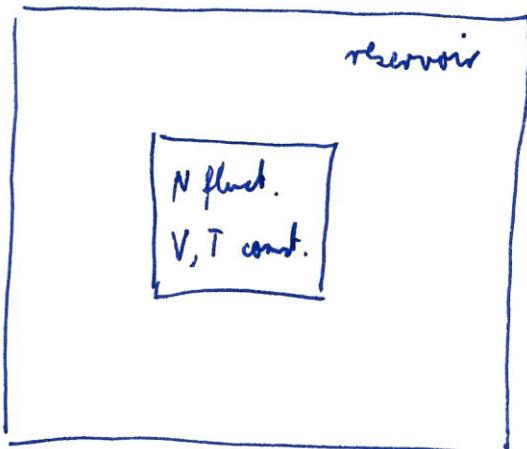
II. 4. 3. Grandcanonical MC simulation

now: system coupled to particle reservoir

→ N fluctuates

→ chemical potential μ constant $\Rightarrow \mu V T$ ensemble

→ reservoir: ideal gas



reservoir:

volume $V_0 - V \gg V = L^3$

particle number $M - N \gg N$

analog to $N_p T$ case:

- partition function of complete system in canonical ensemble

= product of partition functions of subsystems

for given $N, M-N, V, V_0 - V, T$

$$Z(N, M-N, V, V_0 - V, T) = Z_{\text{res.}} \cdot Z_{\text{phys.}}$$

$$= \underbrace{\frac{(V_0 - V)^{M-N}}{\lambda^{3(M-N)} (M-N)!}}_{= Z_{\text{res.}}} \cdot \underbrace{\frac{V^N}{N! \lambda^{3N}} \int_0^1 \dots \int_0^1 d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U}}_{= Z_{\text{phys.}}}$$

$$\lambda = \frac{h}{(2\pi m k_B T)^{1/2}} \quad \text{de Broglie wavelength}$$

- number of particles, N , in physical system fluctuates \Rightarrow

$$Z(M, V, V_0, T)$$

$$= \sum_{N=0}^M \frac{V^N (V_0 - V)^{M-N}}{\lambda^{3(M-N)} (M-N)! N!} \int_0^V \dots \int_0^V d\vec{s}_1 \dots d\vec{s}_N e^{-\beta U}$$

\Rightarrow probability to find $M-N$ particles in volume

$V' = V_0 - V$ and N particles of physical system
in volume V at positions $\vec{s}^{(N)} = (\vec{s}_1, \dots, \vec{s}_N)$

$$N(\vec{s}^{(N)}, N) = \frac{1}{Z(M, V, V_0, T)} \frac{V^N V'^{M-N}}{\lambda^{3(M-N)} (M-N)! N! \lambda^{3N}} e^{-\beta U}$$

- use:

(i) reservoir \gg physical system

thermodynamic limit:

$$M \rightarrow \infty, V' = V_0 - V \rightarrow \infty, \frac{M-N}{V'} = \rho = \text{const} (!)$$

(ii) reservoir: relation between chemical potential μ ,
temperature T , and density ρ

$$\mu = k_B T \ln (\lambda^3 \rho) \Rightarrow \lambda^3 \rho = e^{\beta \mu}$$

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

$$(iii) \text{ consider } \frac{V^{M-N}}{\lambda^{3(M-N)} (M-N)!}$$

stirling $\ln n! \approx n \ln n - n$ (n large)

$$\begin{aligned} \Rightarrow \frac{1}{(M-N)!} &\approx \exp \left\{ -(M-N) \ln (M-N) + (M-N) \right\} \\ &= (M-N)^{-(M-N)} \underbrace{\exp(M)}_{\approx 1} \underbrace{\exp(-N)}_{\approx 1} \\ &\approx (M-N)^{-(M-N)} e^M \end{aligned}$$

$$\begin{aligned} \Rightarrow \frac{V^{M-N}}{\lambda^{3(M-N)} (M-N)!} &\approx \left[\frac{V}{\lambda^3 (M-N)} \right]^{M-N} e^M \\ &= \left[\frac{1}{\lambda^3 \beta} \right]^{M-N} e^M \\ (ii) &= e^{-\beta \mu (M-N)} e^M \\ &= e^{\beta \mu N} f(M) \end{aligned}$$

$f(M)$: function that only depends on M (not on N)

• grandcanonical partition function of physical system

$$S(\mu, V, T) \propto \sum_{N=0}^{\infty} \frac{e^{\beta\mu N} V^N}{\lambda^{3N} N!} \int d\vec{s}^{(N)} e^{-\beta U(\vec{s}^{(N)}, L)}$$

- probability density

$$\mathcal{N}_{\mu, V, T} (\vec{s}^{(N)}, N) \propto \frac{V^N}{\lambda^{3N} N!} e^{\beta\mu N} e^{-\beta U(\vec{s}^{(N)}, N, L)} \\ \propto e^{-\beta H_{\text{eff}}}$$

with $H_{\text{eff}} = U(\vec{s}^{(N)}, N, L) - \mu N - k_B T \ln \frac{V^N}{\lambda^{3N} N!}$

- grandcanonical MC simulation

introduce in addition to particle displacements trial moves where a particle is inserted or removed from the simulation box

\Rightarrow trial move: $N \rightarrow N + 1$

$N \rightarrow N - 1$

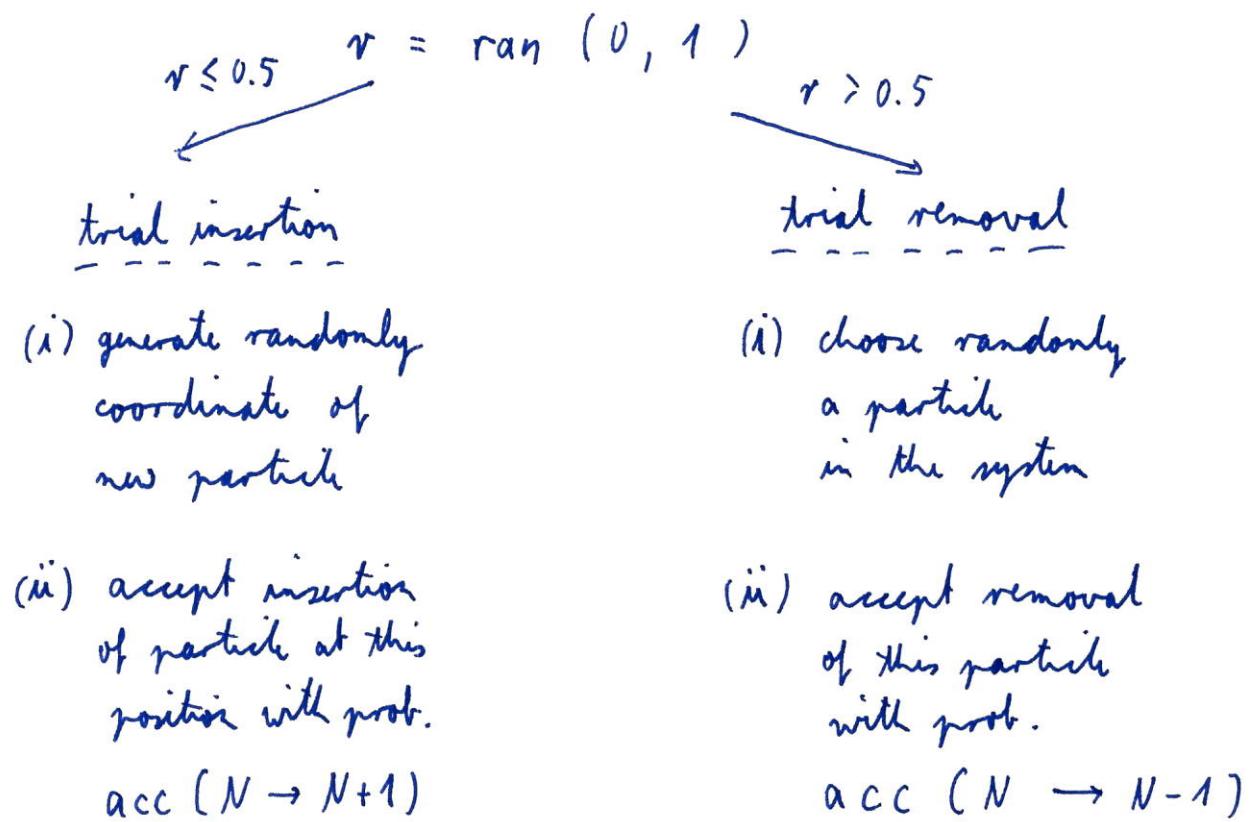
acceptance prob. according to Metropolis criterion.

e.g. $N \rightarrow N + 1$ requires calculation of prob. ratios,

e.g. $N \rightarrow N + 1$:

$$\frac{\mathcal{N}_{\mu, V, T} (\vec{s}^{(N+1)}, N+1)}{\mathcal{N}_{\mu, V, T} (\vec{s}^{(N)}, N)} = \frac{V}{\lambda^3 (N+1)} e^{-\beta (U(N+1) - U(N))}$$

algorithm :



$$\text{acc } (N \rightarrow N+1) = \min \left[1, \frac{V}{\lambda^3(N+1)} e^{\beta(\mu - U(N+1) + U(N))} \right]$$

$$\text{acc } (N \rightarrow N-1) = \min \left[1, \frac{\lambda^3 N}{V} e^{-\beta(\mu + U(N-1) - U(N))} \right]$$

detailed balance?

it holds if

$$\text{flow from } N \rightarrow N+1 = \text{flow from } N+1 \rightarrow N$$

$$N(N) \propto (N \rightarrow N+1) \text{ acc } (N \rightarrow N+1)$$

$$= N(N+1) \propto (N+1 \rightarrow N) \text{ acc } (N+1 \rightarrow N)$$

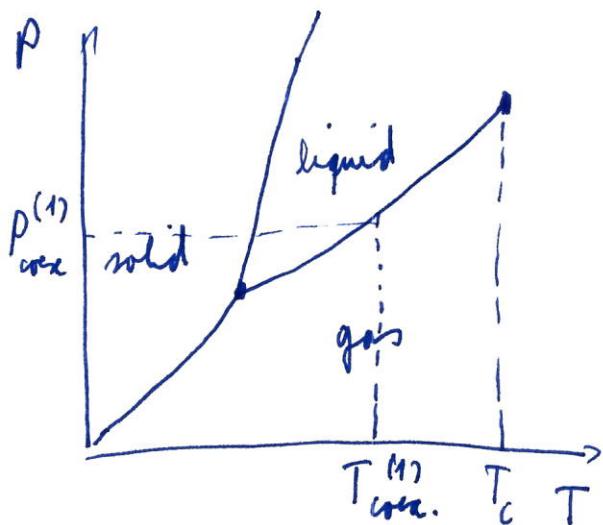
a priori probability symmetric

$$\mathcal{L}(N \rightarrow N+1) = \mathcal{L}(N+1 \rightarrow N)$$

$$\Rightarrow \frac{\text{acc } (N \rightarrow N+1)}{\text{acc } (N+1 \rightarrow N)} = \frac{N(N+1)}{N(N)} \quad \checkmark$$

application of grandcanonical MC: gas - liquid phase transition

phase diagram: p-T plane (p: pressure)



liquid-gas line:
line of 1st order transitions
ending in a critical point

liquid-gas coexistence: $\mu V T$ ensemble

• volume V constant \Rightarrow

$$P_{\text{gas}}^{(1)} = \frac{N_{\text{gas}}^{(1)}}{V} \rightarrow N_{\text{gas}}^{(1)} \text{ particles}$$

$$P_{\text{liq.}}^{(1)} = \frac{N_{\text{liq.}}^{(1)}}{V} \rightarrow N_{\text{liq.}}^{(1)} \text{ particles}$$

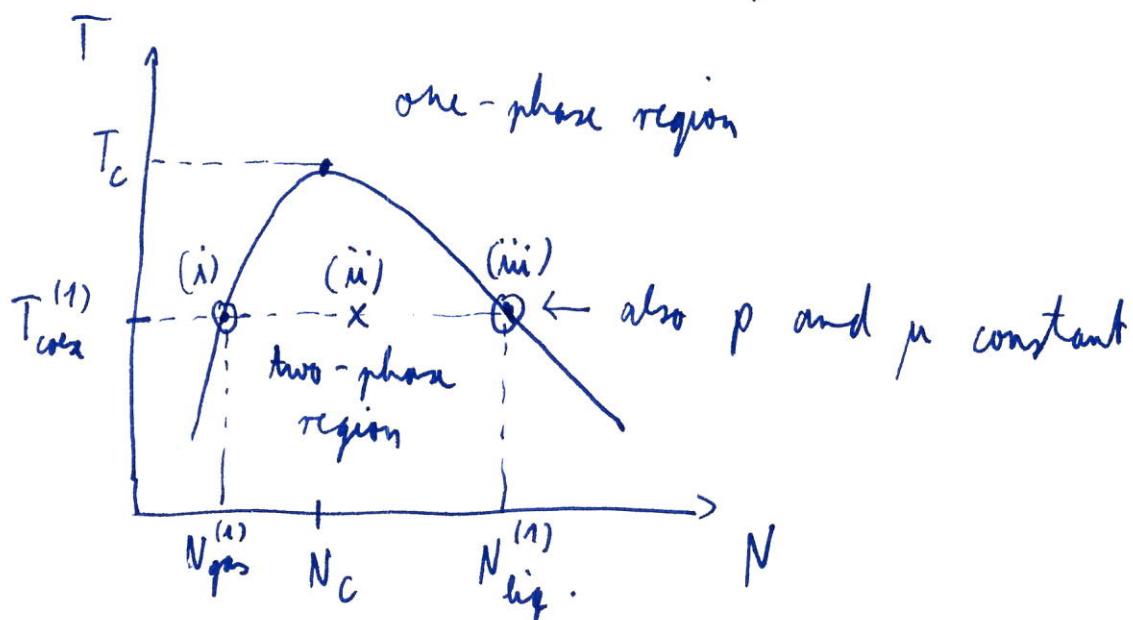
at coexistence

$$T_{\text{coex}}^{(1)} = T_{\text{gas}}^{(1)} = T_{\text{liq.}}^{(1)}$$

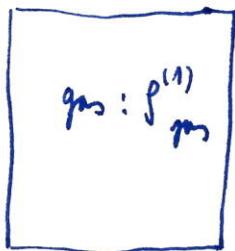
$$p_{\text{coex.}}^{(1)} = p_{\text{gas}}^{(1)} = p_{\text{liq.}}^{(1)}$$

$$\mu_{\text{coex}}^{(1)} = \mu_{\text{coex gas}}^{(1)} = \mu_{\text{liq.}}^{(1)}$$

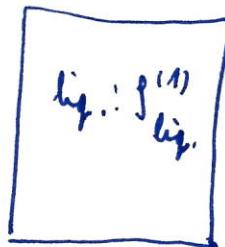
\Rightarrow phase diagram in $T - N$ plane



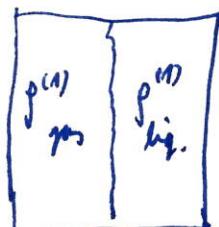
(i)



(iii)



(ii)



questions:

- determination of chemical potential at coexistence?
- phase diagram in T - N plane from grand-canonical MC?

II. 4. 4. Chemical potential

II. 4. 4. 1. Widom method

B. Widom, J. Chem. Phys. 39, 2808 (1963)

F_N : Helmholtz free energy of N -particle system

chemical potential:

$$\mu = \left. \frac{\partial F_N}{\partial N} \right|_{V, T} \underset{N \rightarrow \infty}{\approx} F_{N+1} - F_N$$

$$= -k_B T \ln \left\{ \frac{Z(N+1)}{Z(N)} \right\}$$

$$\boxed{\begin{array}{l} \cancel{\lambda^N} \\ \lambda(\vec{s}^{(N)}, N) \\ \equiv U(N) \end{array}} \stackrel{\curvearrowright}{=} -k_B T \ln \left\{ \frac{\frac{V^{N+1}}{\lambda^{3(N+1)} (N+1)!} \int d\vec{s}^{(N+1)} e^{-\beta U(N+1)}}{\frac{V^N}{\lambda^{3N} N!} \int d\vec{s}^{(N)} e^{-\beta U(N)}} \right\}$$

$$= -k_B T \ln \left\{ \frac{V}{\lambda^{3(N+1)}} \frac{\int d\vec{s}^{(N+1)} e^{-\beta U(N+1)}}{\int d\vec{s}^{(N)} e^{-\beta U(N)}} \right\}$$

$$U(N+1) = U(N) + \Delta U_{N+1}$$

$$\Delta U_{N+1} = U(N+1) - U(N)$$

= energy change due to particle $N+1$

$$\mu = -k_B T \ln \left\{ \frac{V}{\lambda^3 (N+1)} \right\}$$

$$= -k_B T \ln \left\{ \frac{\int d\vec{s}^{(N+1)} e^{-\beta \Delta U_{N+1}} e^{-\beta U(N)}}{\int d\vec{s}^{(N)} e^{-\beta U(N)}} \right\}$$

$$= -k_B T \ln \left\{ \frac{V}{\lambda^3 (N+1)} \right\}$$

$$= -k_B T \ln \left\{ \int d\vec{s}_{N+1}^{(N+1)} \underbrace{\frac{\int d\vec{s}^{(N)} e^{-\beta \Delta U_{N+1}} e^{-\beta U(N)}}{\int d\vec{s}^{(N)} e^{-\beta U(N)}}}_{\langle e^{-\beta \Delta U_{N+1}} \rangle_N} \right\}$$

$$\Rightarrow \boxed{\begin{aligned} \mu &= \mu_{\text{ideal gas}} + \mu_{\text{ex}} \\ \mu_{\text{ideal gas}} &= -k_B T \ln \left\{ \frac{V}{\lambda^3 (N+1)} \right\} \\ \mu_{\text{ex}} &= -k_B T \ln \left\{ \int d\vec{s}_{N+1}^{(N+1)} \langle e^{-\beta \Delta U_{N+1}} \rangle_N \right\} \end{aligned}}$$

μ_{ex} : excess chemical potential (configurational part of μ)

MC scheme for calculation of μ_{ex} :

- $\langle \dots \rangle_N$: canonical average for N -particle system \rightarrow canonical Metropolis MC simulation
- $\int d\vec{s}^{(N+1)} \langle e^{-\beta \Delta U_{N+1}} \rangle_N$

computed via virtual insertions

use uniform random numbers to generate trial positions \vec{s}_{N+1} of particle $N+1$

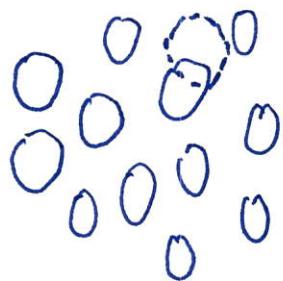
\rightarrow compute $e^{-\beta \Delta U_{N+1}}$
virtual

\rightarrow average over many trial insertions during canonical MC simulation leads to estimate

of $\int d\vec{s}_{N+1} \langle e^{-\beta \Delta U_{N+1}} \rangle_N$

remark:

method not working for dense system



overlap of $(N+1)$ th particle
with other particles very likely

trial positions $\vec{r}^{(N+1)}$ in regions of configuration space
where $e^{-\beta \Delta U}$ is extremely small

II. 4.4.2. Thermodynamic integration

idea: parameterize potential energy by parameter δ

$$U_\delta = U(\delta, \vec{r}^{(N)}), \text{ e.g. } U_\delta = \delta U(\vec{r}^{(N)})$$

then integrate derivative of free energy with
respect to δ

$$F_\delta = F(\delta, N, V, T) \quad \text{Helmholtz free energy for } \delta\text{-parameterized potential energy}$$

$$F_\delta = -k_B T \ln Z_{\delta}(N, V, T)$$

↑
partition function

$$\Rightarrow \frac{\partial F_\delta}{\partial \delta} = -k_B T \frac{\partial}{\partial \delta} \ln Z_\delta(N, V, T)$$

$$= -k_B T \frac{1}{Z_\delta} \frac{\partial Z_\delta}{\partial \delta}$$

$$= \frac{\int d\vec{r}^{(N)} \frac{\partial U_\delta}{\partial \delta} e^{-\beta U_\delta}}{\int d\vec{r}^{(N)} e^{-\beta U_\delta}}$$

$$= \left\langle \frac{\partial U_\delta}{\partial \delta} \right\rangle_\delta$$

integrate from $\delta = 0$ to $\delta = 1 \Rightarrow$

$$\int_0^1 d\delta \frac{\partial F_\delta}{\partial \delta} = F(\delta = 1) - F(\delta = 0)$$

$$= \int_0^1 d\delta \left\langle \frac{\partial U_\delta}{\partial \delta} \right\rangle_\delta \quad (*)$$

thermodynamic integration gives free energy difference between system at $\delta = 1$ and system at $\delta = 0$

why is this useful?

- (i) F known for system I, but unknown for system II

δ - parameterization :

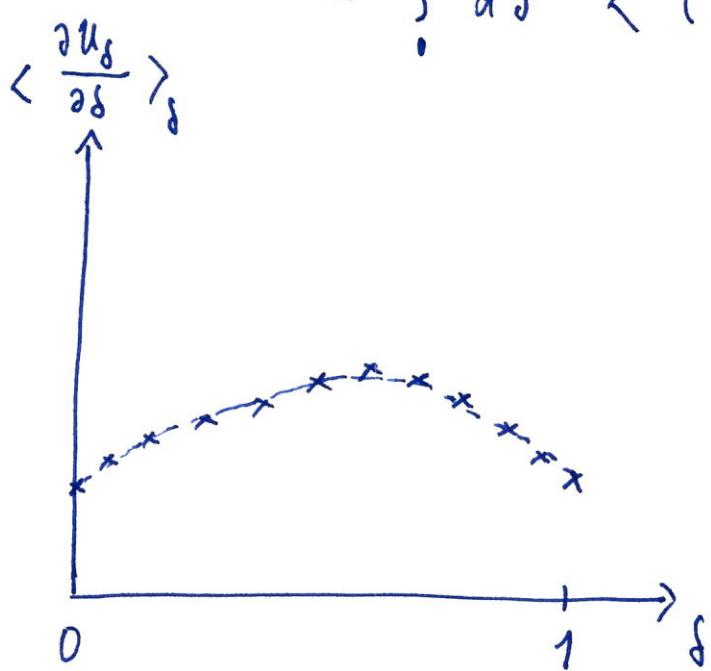
$$U_\delta = (1 - \delta) U_I + \delta U_{II}$$

$$= U_I + \delta (U_{II} - U_I)$$

free energy $F_I = F(\delta = 0)$, $F_{II} = F(\delta = 1)$

$$\Rightarrow F_{II} - F_I = \int_0^1 d\delta \left\langle \frac{\partial U_\delta}{\partial \delta} \right\rangle_\delta$$

$$= \int_0^1 d\delta \left\langle (U_{II} - U_I) \right\rangle_\delta$$



numerical integration over
this function gives

$$F_{II} - F_I$$

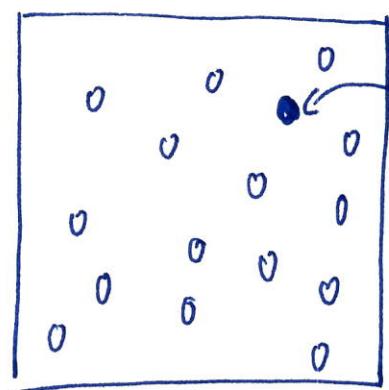
requires simulation at each
value of δ

requirements :

- $\left\langle \frac{\partial U_\delta}{\partial \delta} \right\rangle_\delta$ smooth function of δ .

- thermodynamic path $I \rightarrow II$ reversible (e.g. no phase transition between $\delta = 0$ and $\delta = 1$).

(ii) calculation of chemical potential



vary interaction strength of $(N+1)$ th particle
with other particles

$$U_{N+1}(\delta) = U(N) + \Delta U(\delta)$$

$$\Delta U(\delta=0) = 0 \quad N \text{ particle system}$$

$$\Delta U(\delta=1) = \Delta U_{N+1} = U(N+1) - U(N)$$

thermodynamic integration

$$\Delta F = F(\delta=1) - F(\delta=0)$$

$$= F_{N+1} - F_N$$

$$= \mu$$

$$= \int_0^1 d\delta \left\langle \frac{\partial \Delta U(\delta)}{\partial \delta} \right\rangle_\delta$$

example: Lennard - Jones system

$$U(N) = \sum_{i=1}^N \sum_{j>i}^N u(r_{ij})$$

$\underbrace{r_{ij} = |\vec{r}_i - \vec{r}_j|}$

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

here: good choice for δ - parameterization

$$\Delta U(\delta) = \sum_{\substack{i=1 \\ i \neq k}}^N \left\{ 4\epsilon \left[\left(\frac{\delta r_k}{r_{ki}}\right)^{12} - \left(\frac{\delta r_k}{r_{ki}}\right)^6 \right] \right\}$$

$= u\left(\frac{r_{ki}}{\delta}\right)$

I. 4. 4. 3. More on Widom's method

(i) N p T ensemble

thermodynamic potential : gibbs free energy

$$G(N, p, T) \equiv G_N$$

chemical potential :

$$\mu = \frac{\partial G_N}{\partial N} \Big|_{p, T} \underset{N \rightarrow \infty}{\approx} \underset{\uparrow}{G_{N+1}} - G_N$$

$$G_N = -k_B T \ln \left\{ \int dV \frac{V^N e^{-\beta p V}}{\lambda^{3N} N!} \int d\vec{s}^{(N)} e^{-\beta U(\vec{s}^{(N)}, V)} \right\}$$

derivation analog to NVT ensemble:

$$\mu = -k_B T \ln \left(\frac{k_B T}{p \lambda^3} \right)$$

$$= -k_B T \ln \left\langle \frac{pV}{(N+1)k_B T} \int d\vec{s}_{N+1} e^{-\beta \Delta U} \right\rangle$$

$$= \mu_{\text{ideal gas}}(p) + \mu_{\text{ex}}(p)$$

→ gas reference state at the same pressure

→ now average over $V e^{-\beta \Delta U}$ (V fluctuating!)

(148)

(ii) "inverse" Widom method

idea: do virtual deletion of particle, instead of insertion

consider canonical ensemble

$$\mu = -k_B T \ln \left\{ \frac{Z(N+1)}{Z(N)} \right\}$$

$$= k_B T \ln \left\{ \frac{Z(N)}{Z(N+1)} \right\}$$

$$= k_B T \ln \left\{ \frac{\lambda^3(N+1)}{V} \frac{\int d\vec{s}^{(N)} e^{-\beta U(N)}}{\int d\vec{s}^{(N+1)} e^{-\beta U(N+1)}} \right\}$$

$$U(N) = U(N+1) - \Delta U_{N+1}$$

$$\mu = -k_B T \ln \left\{ \frac{V}{\lambda^3(N+1)} \right\}$$

$$+ k_B T \ln \left\{ \frac{\int d\vec{s}^{(N)} e^{-\beta U(N+1)}}{\int d\vec{s}^{(N+1)} e^{-\beta U(N+1)}} e^{\beta \Delta U_{N+1}} \right\}$$

$$= \mu_{\text{ideal gas}} + k_B T \ln \left\langle e^{\beta \Delta U_{N+1}} \right\rangle_{N+1}$$

$e^{\beta \Delta U_{N+1}}$ measured after removal of $(N+1)$ th particle (chosen randomly) in system of $N+1$ particles

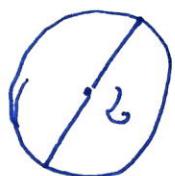
problem:

$e^{\beta \Delta U_{N+1}}$ large $\hat{=}$ small Boltzmann factor $e^{-\beta \Delta U_{N+1}}$

note that the Boltzmann factors determine how often a configuration is sampled in the Metropolis - MC

\Rightarrow most important contributions for $\langle e^{\beta \Delta U_{N+1}} \rangle_{N+1}$
not almost not sampled during MC run!

example: hard spheres



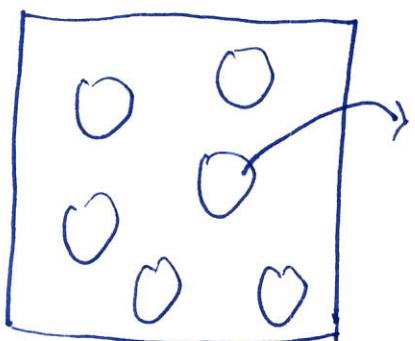
diameter 2

$$u(r) = \begin{cases} \infty & r < 2 \\ 0 & r \geq 2 \end{cases}$$

 forbidden
 allowed

control parameter: packing fraction ($d=3$)

$$\eta = \frac{(N+1) \frac{\pi}{6} 2^3}{V}$$



removal of particle from
($N+1$) - particle system

$$\Rightarrow \Delta U_{N+1} = 0$$

$$\Rightarrow \mu = 0$$

e.g. μ at $\gamma = 0.494$ (freezing point):

$$\beta \mu \approx 15$$

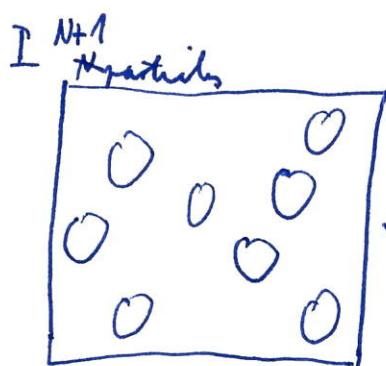
$$\beta = \frac{1}{k_B T}$$

possible solution

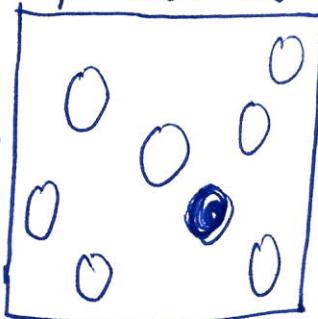
Boulougouris, Economou, Theodorou, Mol. Phys.

96, 905 (1999)

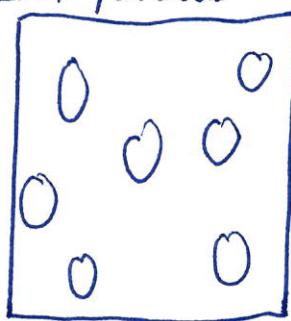
idea: introduce intermediate step where a particle in the system with $(N+1)$ particles is replaced by a hard sphere (HS)



II. N particles + HS



III. N particles



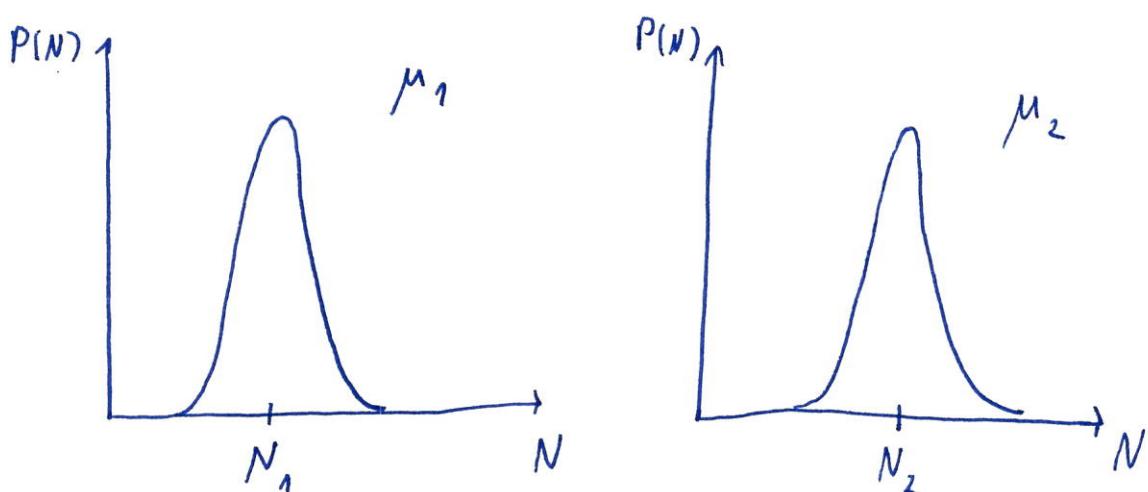
\Rightarrow chemical potential from free energy differences of the pairs I-II and III-II

I. 4. 4. 4. Grandcanonical Monte Carlo (GCMC)

$\mu V T$ ensemble \Rightarrow number of particles, N , fluctuates

probability distribution to obtain system with N particles $P(N)$ at given chemical potential μ

example: fluid in one-phase region



$$N_2 > N_1, \mu_2 > \mu_1$$

$P(N)$ Gausß function:

$$P(N) = \frac{1}{(2\pi k_B T \chi)^{1/2}} \exp \left\{ -\frac{(N - \langle N \rangle)^2}{2k_B T \chi} \right\}$$

$k_B T \chi$ measures the width of the Gausß function (variance)

χ is called susceptibility (in this case it is related to the isothermal compressibility $\propto K_T$)

$$\begin{aligned}
 k_B T \chi &= \langle N^2 \rangle - \langle N \rangle^2 \quad \text{≈ } \langle N^2 \rangle - \langle N \rangle^2 \\
 &= \text{particle number fluctuations} \\
 &= \frac{k_B T}{V} \langle N \rangle^2 K_T \\
 &= \frac{k_B T}{v} \langle N \rangle K_T \quad \text{with } v = \frac{V}{\langle N \rangle}
 \end{aligned}$$

relative fluctuations

$$\frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle} = \frac{1}{\langle N \rangle} \left(\frac{k_B T}{v} \langle N \rangle K_T \right)^{1/2} \propto \frac{1}{\sqrt{\langle N \rangle}}$$

thermodynamic limit $N \rightarrow \infty, V \rightarrow \infty$ ~~fixed~~

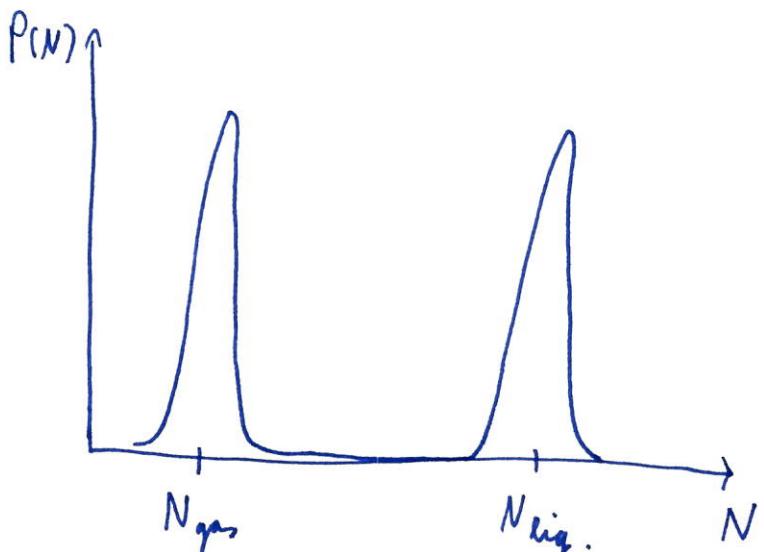
$\Rightarrow P(N)$ δ -function

remark: $\langle N^2 \rangle - \langle N \rangle^2 > 0$

and thus $K_T > 0$ (required for thermodynamic stability)

chemical potential μ as function of $\varrho = \frac{\langle N \rangle}{V}$
 can be obtained from GCMC simulations at
 different values of μ .

example: $P(N)$ at first-order phase transition
bimodal
→ consider liquid-gas transition

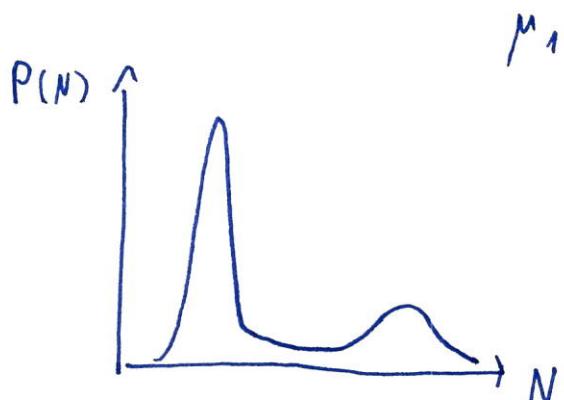


coexistence if area under both peaks equal
how does one obtain chemical potential at coexistence?
→ use histogram reweighting

A. M. Ferrenberg, R. H. Swendsen, Phys. Rev. Lett.

61, 2635 (1988)

starting point: $P(N)$ at a chemical potential



→ estimate via this distribution
 $P(N)$ at different chemical potential μ_2

$$P(N, \mu) = \frac{f(N, V, T)}{S(\mu, V, T)} e^{\beta \mu N}$$

$S(\mu, V, T)$: grandcanonical partition function

$f(N, V, T)$: function not dependent on μ

$$\Rightarrow \frac{P(N, \mu_2)}{P(N, \mu_1)} = N e^{\beta(\mu_2 - \mu_1) N}$$

$$\Rightarrow \ln P(N, \mu_2) = \ln P(N, \mu_1) + \beta(\mu_2 - \mu_1) N + \ln N$$

\Rightarrow tune μ_2 such that area under both peaks in $P(N)$ becomes equal

II. 4. 5. Semigrandcanonical ensemble

consider now mixture of A and B particles,

e.g. Lennard-Jones system

→ interaction between pairs of particles, separated by distance r

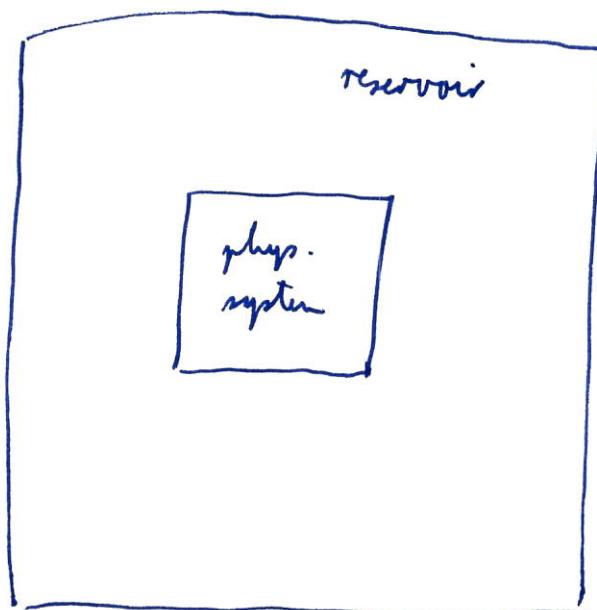
$$U_{AB} = 4 \epsilon_{AB} \left[\left(\frac{\sigma_{AB}}{r} \right)^{12} - \left(\frac{\sigma_{AB}}{r} \right)^6 \right]$$

$$\times_B = AA, AB, BB$$

goal: describe phase behavior of binary fluid

→ possibility of demixing transitions

starting point: physical system coupled to ideal gas particle reservoir of A and B particles



- reservoir + phys. system in canonical ensemble
- physical system volume V, temperature T constant as well as chemical potentials of A and B particles, μ_A and μ_B , respectively

$\Rightarrow N_A$ and N_B (number of A and B particles)
fluctuating variable

- total number of particles $N = N_A + N_B$ in physical system constant

$$\begin{aligned}\Rightarrow \mu_A N_A + \mu_B N_B &= \underbrace{(\mu_A - \mu_B) N_A}_{= \Delta \mu} + \mu_B (N_A + N_B) \\ &= \Delta \mu N_A + \underbrace{\mu_B N}_{= \text{const.}}\end{aligned}$$

$\Delta \mu$ thermodynamically conjugate variable to N_A
(or $-\Delta \mu$ conjugate to N_B)

semigrandcanonical ensemble:

$$N = N_A + N_B, \Delta \mu = \mu_A - \mu_B, V, T \text{ constant}$$

\rightarrow corresponding Monte Carlo moves:

identity switches of particles $A \rightarrow B$ or $B \rightarrow A$

II. 4. 5. 1. Monte Carlo algorithm

partition function : product of grandcanonical partition functions for A and B particles with $N = N_A + N_B$

$$Y(N, \mu_A, \mu_B, N, V, T)$$

$$= \sum_{\substack{N_A, N_B \\ N = N_A + N_B}} \frac{V^{N_A}}{N_A! \lambda_A^{3N_A}} \frac{V^{N_B}}{N_B! \lambda_B^{3N_B}} e^{\beta N_A \mu_A} e^{\beta N_B \mu_B} \times \int_0^1 d\vec{s}^{(N)} e^{-\beta U(\vec{s}^{(N)}, V)}$$

$$N_B = N - N_A$$

$$\downarrow = \sum_{N_A=0}^N \frac{V^{N_A}}{N_A! \lambda_A^{3N_A}} \frac{V^{N-N_A}}{(N-N_A)! \lambda_B^{3(N-N_A)}} e^{\beta N_A \Delta \mu} e^{\beta N \mu_B} \times \int_0^1 d\vec{s}^{(N)} e^{-\beta U(\vec{s}^{(N)}, V)}$$

$$= \underbrace{\frac{V^N}{\lambda_B^{3N}} e^{\beta N \mu_B}}_{= \text{const}} \sum_{N_A=0}^N \left(\frac{\lambda_B}{\lambda_A} \right)^{3N_A} \frac{1}{(N-N_A)! N_A!} e^{\beta N_A \Delta \mu} \times \int_0^1 d\vec{s}^{(N)} e^{-\beta U(\vec{s}^{(N)}, V)}$$

$$= \tilde{Y}(N, \Delta \mu \equiv \mu_A - \mu_B, V, T)$$

└ semigrandcanonical partition function

$$\begin{aligned}
 \left(\frac{\lambda_B}{\lambda_A}\right)^{3N_A} e^{\beta N_A \Delta \mu} &= \left(\frac{\beta \lambda_B}{\beta \lambda_A}\right)^{3N_A} e^{\beta N_A (\mu_A - \mu_B)} \\
 &= \exp \left\{ \beta N_A \left[\underbrace{(\mu_A - \ln \lambda_A^3)}_{=: \mu_A^{(0)}} - \underbrace{(\mu_B - \ln \lambda_B^3)}_{=: \mu_B^{(0)}} \right] \right\} \\
 &= \exp \left\{ \beta N_A (\mu_A^{(0)} - \mu_B^{(0)}) \right\} \\
 &= \exp \left\{ \beta N_A \Delta \mu^{(0)} \right\}
 \end{aligned}$$

probability density to find system with N_A particles in a given configuration $\vec{s}^{(N)}$ at volume V , chemical potential difference $\Delta \mu^{(0)}$ and temperature T :

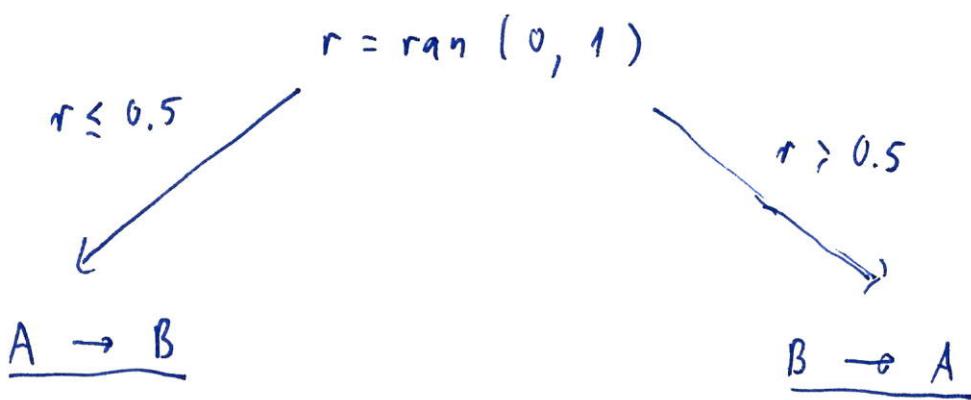
$$\begin{aligned}
 P \propto \exp \left\{ \ln \left(\frac{1}{(N-N_A)! N_A!} \right) + \beta N_A \Delta \mu^{(0)} + N \ln V \right. \\
 \left. - \beta U(\vec{s}^{(N)}, V) \right\}
 \end{aligned}$$

trial MC moves: identity switches $A \rightarrow B$, $B \rightarrow A$
relative probabilities required \Rightarrow prefactors

$$A \rightarrow B : \frac{(N-N_A)! N_A!}{(N-N_A+1)! (N_A-1)!} = \frac{N_A}{N-N_A+1} = \frac{N_A}{N_B+1}$$

$$B \rightarrow A : \frac{(N - N_A)! \ N_A!}{(N - N_A - 1)! \ (N_A + 1)!} = \frac{N - N_A}{N_A + 1} = \frac{N_B}{N_A + 1}$$

MC algorithm:



(i) choose randomly an A particle

(ii) accept with prob.

$$\text{acc}(A \rightarrow B) = \frac{P_{\text{new}}}{P_{\text{old}}}$$

$$= \min\left(1, \frac{N_A}{N_B + 1} e^{-\beta \Delta U + \beta \Delta \mu^{(0)}}\right)$$

(i) choose randomly a B particle

(ii) accept with prob.

$$\text{acc}(B \rightarrow A) = \frac{P_{\text{new}}}{P_{\text{old}}}$$

$$= \min\left(1, \frac{N_B}{N_A + 1} e^{-\beta \Delta U + \beta \Delta \mu^{(0)}}\right)$$

$$\Delta U = U_{\text{new}} - U_{\text{old}}$$