

TODAY'S TOPICS

16/10/26

- RADIAL DISTRIBUTION FUNCTION $g(r)$
(RDF)
- CALCULATION OF $g(r)$ FROM
SIMULATIONS

RADIAL DISTRIBUTION FUNCTION

$\tilde{P}(\vec{r}_1, \vec{r}_2) = \{ \text{PROBABILITY OF FINDING A PARTICLE IN } \vec{r}_1 \text{ AND ANOTHER ONE IN } \vec{r}_2 \}$

EVENT A = { A PARTICLE IS IN $\vec{r}_1$ }

EVENT B = { " " " " $\vec{r}_2$ }

$$P(A \cap B) = \tilde{P}(\vec{r}_1, \vec{r}_2)$$

$$P(A \cap B) = P(A|B) \cdot P(B)$$

↑
CONDITIONAL PROBABILITY

$$P(A|B) = \frac{P(A \cap B)}{P(B)}$$

IF A AND B INDEPENDENT

$$P(A|B) = \frac{P(A) \cancel{P(B)}}{\cancel{P(B)}} = P(A)$$

GOING BACK TO $\tilde{P}$:

$$\tilde{P}(\vec{r}_1, \vec{r}_2) = \tilde{P}(\vec{r}_1 | \vec{r}_2) \tilde{P}(\vec{r}_2) \quad (*)$$

WE DEFINE:

$$g^{(2)}(\vec{r}_1, \vec{r}_2) \equiv \frac{\tilde{P}(\vec{r}_1, \vec{r}_2)}{\tilde{P}(\vec{r}_1) \tilde{P}(\vec{r}_2)}$$

THIS IS
2-PARTICLE (PAIR)
DISTRIBUTION
FUNCTION

IF THE SYSTEM IS HOMOGENEOUS $\tilde{P}(\vec{r}_1) = \tilde{P}(\vec{r}_2) = \tilde{P}$
SO THAT:

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{P}(\vec{r}_1, \vec{r}_2)}{\tilde{P}^2}$$

BUT USING (*) WE HAVE:

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{P}(\vec{r}_1 | \vec{r}_2) \tilde{P}}{\tilde{P}^2}$$

$$= \frac{\tilde{P}(\vec{r}_1, \vec{r}_2)}{\tilde{P}}$$

SINCE SYSTEM IS HOMOGENEOUS
WE CAN EXPECT
 $g^{(2)}(\vec{r}_1, \vec{r}_2) = g^{(2)}(\vec{r}_1 - \vec{r}_2)$
 SO THAT $g^{(2)}(\vec{r}_1 - \vec{r}_2) = g^{(2)}(r)$
 AND $\tilde{P}(\vec{r}_1, \vec{r}_2) = \tilde{P}(r)$

i.e. $\tilde{P} g^{(2)}(\vec{r}_1, \vec{r}_2) = \tilde{P}(\vec{r}_1, \vec{r}_2)$

IDEAL GASES

$$\tilde{P}(\vec{r}_1, \vec{r}_2) = \tilde{P}(\vec{r}_1) = \tilde{P}$$

HENCE

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\tilde{P}}{\tilde{P}} = 1$$

HARD SPHERES

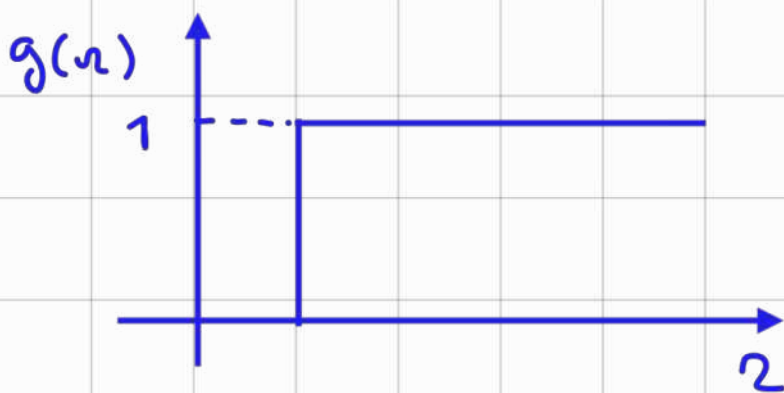
IF $\|\vec{r}_1 - \vec{r}_2\| < \sigma \Rightarrow g^{(2)}(\vec{r}_1, \vec{r}_2) = 0$

AND $g^{(2)}(\vec{r}_1, \vec{r}_2) = 0$

MOREOVER SYSTEM IS ISOTROPIC THEREFORE

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = g^{(2)}(\|\vec{r}_{12}\|) = g^{(2)}(r)$$

RADIAL DISTRIBUTION FUNCTION



AT VERY LOW
DENSITIES

BUT AT HIGH
DENSITIES?

WE WILL SEE ...

TWO POINTS DENSITY

$$\text{IF } N(\vec{r}_1, \dots, \vec{r}_N) = \frac{e^{-\beta U_N}}{Z}$$

$N(\vec{r}_1, \dots, \vec{r}_N) \cdot d\vec{r}_1 \dots d\vec{r}_N$ IS THE PROBABILITY OF FINDING PARTICLES AT POSITIONS $\vec{r}_1, \dots, \vec{r}_N$

HENCE THE PROBABILITY DENSITY TO FIND ONE PARTICLE IN $\vec{r}_1$ IS:

$$\tilde{P}(\vec{r}_1) = \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_2 \dots d\vec{r}_N$$

NOTE THAT WE ARE NOT INTEGRATING OVER $d\vec{r}_1$

AND THE (1-PARTICLE) DENSITY IS:

$$P(\vec{r}_1) = N \cdot \tilde{P}(\vec{r}_1) = N \cdot \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_2 \dots d\vec{r}_N$$

TOTAL NUMBER OF PARTICLES

NOTE THAT $\int \tilde{P}(\vec{r}_1) d\vec{r}_1 = 1$ AND

THAT $\int N \tilde{P}(\vec{r}_1) d\vec{r}_1 = \{ \text{NUMBER OF PARTICLES IN } d\vec{r}_1 \}$

MOREOVER IF THE SYSTEM IS HOMOGENEOUS

$$P(\vec{r}_1) = \frac{N}{V}$$

SIMILARLY THE PROBABILITY DENSITY OF FINDING A PARTICLE IN $\vec{r}_1$ AND $\vec{r}_2$ IS

$$\tilde{P}(\vec{r}_1, \vec{r}_2) = \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_3 \dots d\vec{r}_N$$

NOTE THAT WE ARE NOT INTEGRATING OVER $\vec{r}_1$ AND $\vec{r}_2$

SO THAT

$$\underbrace{N(N-1)}_{\substack{\text{TOTAL NUMBER} \\ \text{OF POSSIBLE PAIRS}}} \tilde{\rho}(\vec{r}_1, \vec{r}_2) = \left\{ \text{NUMBER OF PAIRS IN } d\vec{r}_1 \text{ AND } d\vec{r}_2 \right\}$$

AND WE DEFINE THE TWO PARTICLE DENSITY AS FOLLOWS

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_3^{(N-2)}$$

IDEAL GAS

$$\rho^{(2)}(\vec{r}_1, \vec{r}_2) = N(N-1) \int \frac{e^{-\beta U_N}}{Z} d\vec{r}_3 \dots d\vec{r}_N$$

$$U_N = 0$$

$$= N(N-1) \int \frac{d\vec{r}_3 \dots d\vec{r}_N}{Z} = N \overbrace{(N-1)}^{\approx N} \frac{V^{N-2}}{V^N} =$$

$$\text{SINCE } Z = \int e^{-\beta U_N} d\vec{r}_1 \dots d\vec{r}_N = V^N$$

$$\approx \frac{N^2}{V^2} = \rho^2 \text{ HENCE}$$

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\rho^{(2)}(\vec{r}_1, \vec{r}_2)}{\rho^2} = \frac{\rho^2}{\rho^2} = 1$$

ALTERNATIVE WAYS OF CALCULATING 1-POINT AND 2-POINT DENSITIES

$$\rho(\underline{\vec{r}}) = \frac{N}{Z} \int e^{-\beta U_N} d^{(N-1)}\underline{\vec{r}} \quad \xrightarrow{U_N = U_N(\underline{\vec{r}}, \vec{r}_2 \dots \vec{r}_N)}$$

$$= \frac{N}{Z} \int e^{-\beta U_N} \delta(\underline{\vec{r}} - \vec{r}_1) d^N \underline{\vec{r}} \quad \xrightarrow{\text{NOW } U_N = U_N(\vec{r}_1 \dots \vec{r}_N)}$$

$$= \frac{1}{Z} \left[\sum_i^N \int e^{-\beta U_N} \delta(\vec{r} - \vec{r}_i) d^N \underline{\vec{r}} \right] \quad \text{INTEGRAL DOES NOT DEPEND ON PARTICLE INDEX}$$

$$= \left\langle \sum_i^N \delta(\vec{r} - \vec{r}_i) \right\rangle$$

NOTE THAT

$$U_2(\vec{r}_1, \vec{r}_2) = U_2(\vec{r}_2, \vec{r}_1)$$

TAKE A SYSTEM OF 3 PARTICLES
CONSIDER $\vec{r}_2$ AND $\vec{r}_3$
INSTEAD OF $\vec{r}_1$, THEN SWAP
INDICES TO RECOVER
CASE ABOVE ($\vec{r}_1$)

WHERE $\langle \dots \rangle = \int \dots \frac{e^{-\beta U_N}}{Z} d^N \vec{r}$

SIMILARLY

$$p^{(2)}(\vec{r}', \vec{r}) = \langle \sum'_{i,j} \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \rangle$$

$i \neq j$

$U_N = U_N(\vec{r}', \vec{r}, \vec{r}_2, \dots, \vec{r}_N)$

INDEED

$$p^{(2)}(\vec{r}', \vec{r}) = N(N-1) \int \frac{e^{-\beta U_N}}{Z} d^{(N-2)} \vec{r} =$$

$U_N = U_N(\vec{r}_2, \dots, \vec{r}_N)$

$$= N(N-1) \int \delta(\vec{r}' - \vec{r}_1) \delta(\vec{r} - \vec{r}_2) \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 d\vec{r}_2.$$

TAKE AGAIN A SYSTEM OF 3 PARTICLES AND USE $(\vec{r}_2, \vec{r}_3)$ INSTEAD OF $(\vec{r}_1, \vec{r}_2)$

INTEGRAL DOES NOT DEPEND ON WHICH PAIR OF INDICES WE ARE CONSIDERING

$$= \sum'_{i,j} \int \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \frac{e^{-\beta U_N}}{Z} d^N \vec{r} =$$

$$= \langle \sum'_{i,j} \delta(\vec{r}' - \vec{r}_i) \delta(\vec{r} - \vec{r}_j) \rangle = p^{(2)}(\vec{r}', \vec{r})$$

$p^{(2)}(\vec{r}', \vec{r})$ IN THE HOMOGENEOUS CASE

LET'S CONSIDER

$$\langle \frac{1}{N^2} \sum'_{i,j} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \rangle =$$

FUNCTION OF $\vec{r}$ AND WE AVERAGE OVER $\vec{r}_1, \dots, \vec{r}_N$

$$= \langle \frac{1}{N^2} \sum'_{i,j} \delta(\vec{r} - \vec{r}_i + \vec{r}_j) \rangle =$$

$$= \langle \frac{1}{N^2} \int \sum'_{i,j} \delta(\vec{r} - \vec{r}_i + \vec{r}') \cdot \delta(\vec{r}' - \vec{r}_j) d\vec{r}' \rangle =$$

$p^{(2)}(\vec{r} + \vec{r}', \vec{r}')$

$$= \frac{1}{N^2} \int \langle \sum'_{i,j} \delta((\vec{r} + \vec{r}') - \vec{r}_i) \cdot \delta(\vec{r}' - \vec{r}_j) \rangle d\vec{r}' =$$

$$= \frac{1}{N\rho} \int p^{(2)}(\vec{r} + \vec{r}', \vec{r}') d\vec{r}' =$$

BUT THE SYSTEM IS HOMOGENEOUS
THEREFORE $p^{(2)}(\vec{r} + \vec{r}', \vec{r}') = p^{(2)}(\vec{r})$
I.E IT IS INDEPENDENT OF $\vec{r}'$

$$= \frac{1}{N\rho} \int p^{(2)}(\vec{r}) d\vec{r}' = \frac{V}{N\rho} p^{(2)}(\vec{r})$$

$$= \frac{1}{\rho^2} p^{(2)}(\vec{r}) = \frac{g^{(2)}(\vec{r})}{\rho^2} =$$

$$= g^{(2)}(\vec{r})$$

WE PROVED THAT

$$g^{(2)}(\vec{r}) = \frac{1}{N\rho} \left\langle \sum_{i \neq j} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right\rangle$$

$$= \frac{1}{N\rho} \left\langle \sum_{i \neq j} \delta(\vec{r} - \vec{r}_{ij}) \right\rangle \quad \vec{r}'_{ij} = \vec{r}_i - \vec{r}_j$$

AVERAGE VALUE OF $g(\vec{r})$ OVER A VOLUME ΔV AROUND $\vec{r}$

$$\bar{g}(\vec{r}) = \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} g(\vec{r}') d\vec{r}'$$

DEPENDENT ON CHOSEN $\Delta V_{\vec{r}}$ (IF $\Delta V_{\vec{r}}$ IS A CUBIC BOX, $\bar{g}$ DEPENDS ON ITS POSITION $\vec{r}$)

THIS IS TELLING THAT VOLUME ΔV IS AROUND $\vec{r}$

IN A MC SIMULATION:

$$\langle \mathcal{O}(\vec{r}^N) \rangle = \frac{1}{L} \sum_{k=1}^L \mathcal{O}(\vec{r}_k^N) =$$

OR EVERY A CERTAIN AMOUNT OF STEPS

$$= \frac{1}{L} \sum_{k=1}^L \mathcal{O}_k$$

SUM OVER MC STEPS

HENCE CONSIDER THE FOLLOWING OBSERVABLE

$$\bar{g}(\vec{r}; \vec{r}_1, \dots, \vec{r}_N) \equiv \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N\rho} \sum_{i \neq j} \delta(\vec{r}' - \vec{r}_{ij}) d\vec{r}'$$

$g(\vec{r})$ OF ONE CONFIGURATION (NO AVERAGE WRT $\frac{e^{-\beta U}}{Z}$)

ITS AVERAGE VALUE IS

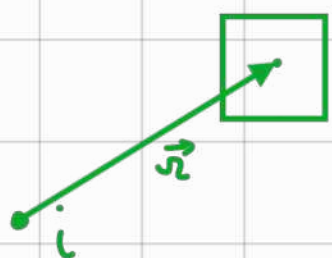
$$\begin{aligned} \langle \bar{g} \rangle &= \left\langle \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N_P} \sum_{i,T} \delta(\vec{r}' - \vec{r}_{i,T}) d\vec{r}' \right\rangle \\ &= \int \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N_P} \sum_{i,T} \delta(\vec{r}' - \vec{r}_{i,T}) d\vec{r}' \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 \dots d\vec{r}_N d\vec{r} \\ &= \frac{1}{L} \sum_{k=1}^L \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N_P} \sum_{i,T} \delta(\vec{r}' - \vec{r}_{i,T}^{(k)}) d\vec{r}' = \frac{1}{L} \sum_k \bar{g}_k \end{aligned}$$

$\bar{g}_k$ IS OUR OBSERVABLE (AS $\mathcal{O}_k$)
CALCULATED AT k -th MC STEP

$$\bar{g}_k(\vec{r}) = \frac{1}{\Delta V} \int_{\Delta V_{\vec{r}}} \frac{1}{N_P} \sum_{i,T} \delta(\vec{r}' - \vec{r}_{i,T}^{(k)}) d\vec{r}'$$

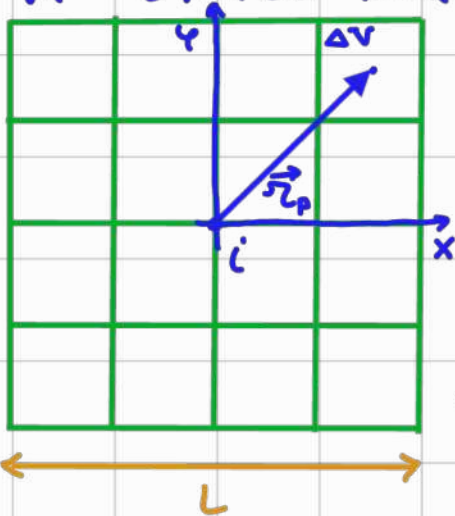
AVERAGE OVER ALL PARTICLES

$$= \frac{1}{\Delta V} \frac{1}{N} \sum_i \int_{\Delta V_{\vec{r}}} \sum_T \delta(\vec{r}' - \vec{r}_{i,T}^{(k)}) d\vec{r}'$$



PARTICLES IN $\Delta V_{\vec{r}}$
A DISTANCE $\vec{r}$
FROM PARTICLE i

BOX CENTERED AT i OF VOLUME V DIVIDED
INTO M SMALL BOXES OF VOLUME ΔV



$\vec{r}_p$ WITH $p=1 \dots M$

IS THE CENTER

OF p -th BOX OF VOLUME ΔV

$$\vec{r}_p = \Delta r (k \hat{x} + l \hat{y} + m \hat{z})$$

k, l, m INTEGERS

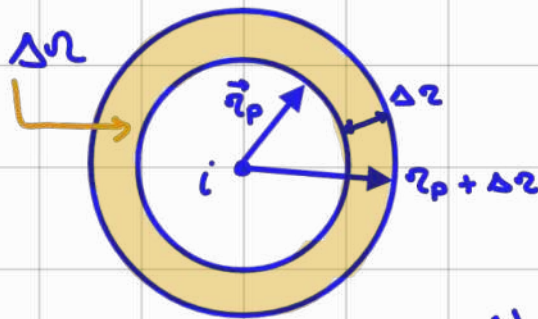
THUS OBTAINING

$$\bar{g}_k(\vec{r}_p) \approx g_k(\vec{r}_p) \text{ IF } \Delta V \text{ SMALL ENOUGH}$$

ISOTROPIC CASE

SPHERICAL SHELL OF THICKNESS Δr

$$\Delta V_p = 4\pi r_p^2 \Delta r$$



PARTICLE INSIDE
P-th SHELL

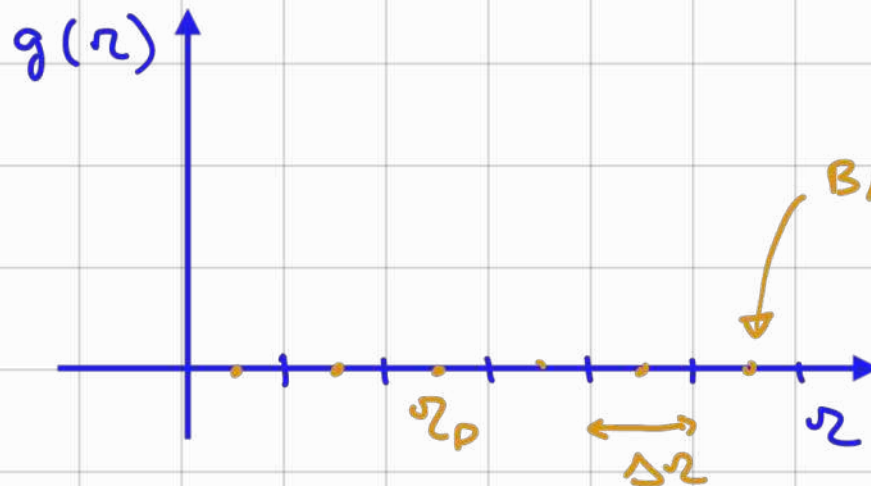
$$\bar{g}_k(r_p) = \frac{1}{4\pi r_p^2 \Delta r_p} \frac{1}{N} \sum_i^N \int_{\Delta V_p} \sum_j' \delta(\vec{r} - \vec{r}_{ij}) d\vec{r} =$$

NOTE THAT
THIS IS A
SCALAR

AVERAGE NUMBER
OF PARTICLES INSIDE ΔV_p

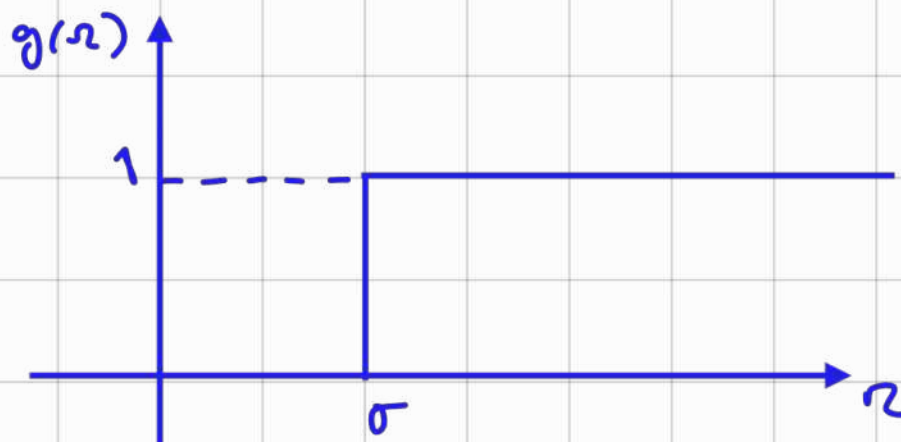
$\bar{g}_k(r_p) \approx g_k(r_p)$ IS THE RADIAL DISTRIBUTION
FUNCTION

IF Δr
IS SMALL
ENOUGH



BINNING

LOW CONCENTRATIONS

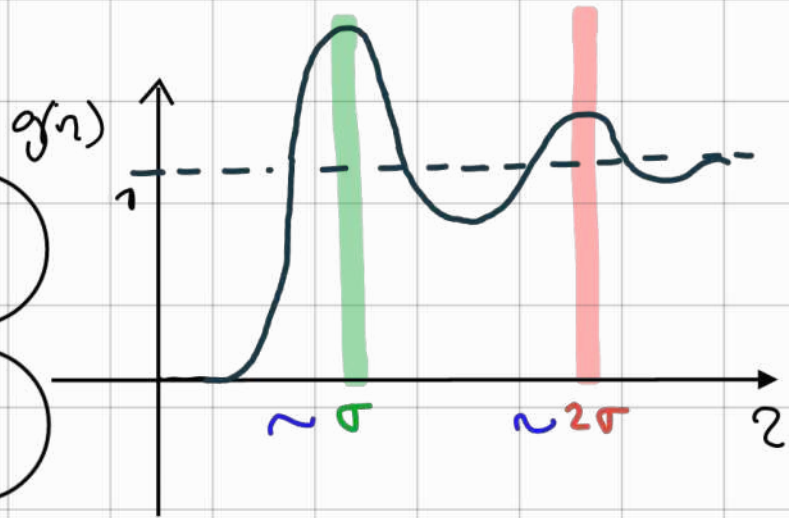
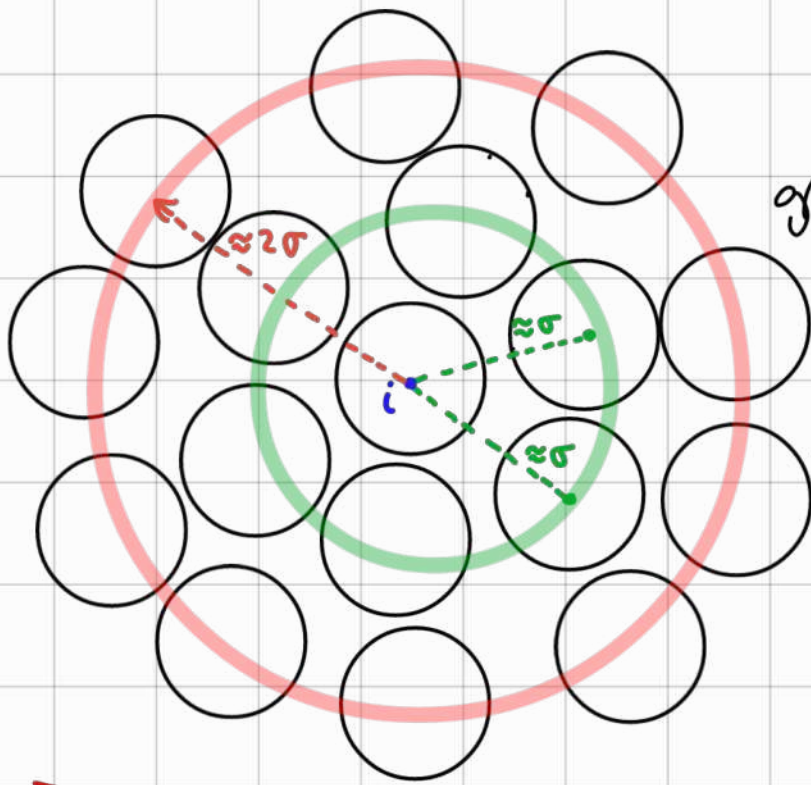


TODAY'S TOPICS

19/10/26

- CALCULATION OF ENERGY AND PRESSURE FROM $\eta(r)$
- TAIL CORRECTIONS
- STATIC STRUCTURE FACTOR AND MEAN SQUARED DISPLACEMENT

HIGH CONCENTRATION IN FLUID PHASE



(CALCULATION OF ENERGY FROM

$g(r)$

$$\begin{aligned}
 \langle U_N \rangle &= U_{\text{ex}} = \int \frac{1}{2} \sum'_{i,j} U_2(\vec{r}_{ij}) \frac{e^{-\beta U_N}}{Z} d^N \vec{r} = \\
 &= \frac{1}{2} N(N-1) \int U_2(\vec{r}_{12}) \frac{e^{-\beta U_N}}{Z} d\vec{r}_1 d\vec{r}_2 d\vec{r}_3^{(N-2)} \\
 &= \frac{1}{2} \int U_2(\vec{r}_{12}) \underbrace{\int N(N-1) \frac{e^{-\beta U_N}}{Z} d\vec{r}_3^{(N-2)}}_{\rho^{(2)}(\vec{r}_1, \vec{r}_2)} d\vec{r}_1 d\vec{r}_2 \\
 &= \frac{1}{2} \int U_2(\vec{r}_{12}) \rho^{(2)}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 \\
 \text{BUT } \rho^{(2)}(\vec{r}_1, \vec{r}_2) &= \rho^2 g(\vec{r}_{12}) \quad \leftarrow \text{HOMOGENEOUS CASE} \\
 &= \frac{\rho^2}{2} \int U_2(\vec{r}_{12}) g(\vec{r}_{12}) d\vec{r}_1 d\vec{r}_2
 \end{aligned}$$

IF WE CHANGE VARIABLES

$$(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{r}_2, \vec{r}) \text{ WHERE}$$

$$\vec{r} = \vec{r}_{12} = \vec{r}_1 - \vec{r}_2$$

$$= \frac{\rho^2}{2} \int U_2(\vec{r}) g(\vec{r}) d\vec{r} d\vec{r}_2 =$$

$$\langle U_N \rangle = V \frac{\rho^2}{2} \int U_2(\vec{r}) g(\vec{r}) d\vec{r} = U_{EX}$$

IF THE SYSTEM IS ISOTROPIC

$$= V \frac{\rho^2}{2} \int U_2(r) g(r) 4\pi r^2 dr$$

↑
RADIAL DISTRIBUTION
FUNCTION

TAIL CORRECTIONS

IN A SIMULATION $U_L(r) \rightarrow U_L^C(r)$

$$\text{WHERE } U_L^C = \begin{cases} U_L(r) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

HENCE

$$U_{EX} = \langle U_N \rangle = \frac{1}{2} V \rho^2 \int_0^\infty g(r) U_2(r) 4\pi r^2 dr$$

U_{EX}^C THIS IS WHAT WE HAVE FROM SIMULATION, I.E. $\frac{1}{2} \sum_{i,j}' U_2^C(r_{ij})$

$$= \frac{1}{2} V \rho^2 \int_0^{r_c} g(r) U_2(r) 4\pi r^2 dr +$$

$$+ \frac{1}{2} V \rho^2 \int_{r_c}^\infty g(r) U_2(r) 4\pi r^2 dr$$

TAIL CORRECTION

Q. CAN WE ESTIMATE SOMEHOW THE
TAIL CORRECTION?

$$U_{EX}^{TAIL} = \frac{1}{2} V \rho^2 \int_{r_c}^{\infty} g(r) U_2(r) 4\pi r^2 dr$$

↑
TAIL CORRECTION

IF r_c IS LARGE ENOUGH FOR $r > r_c$, $g(r) \approx 1$

HENCE

$$U_{EX}^{TAIL} = \frac{1}{2} V \rho^2 \int_{r_c}^{\infty} U_2(r) 4\pi r^2 dr$$

↓ THIS INTEGRAL CAN BE CALCULATED

EXAMPLE LENNARD-JONES SYSTEM

$$U_2(r) = U_{LJ}(r) = A \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

SO THAT

$$U_{EX}^{TAIL} = \frac{1}{2} V \rho^2 \int_{r_c}^{\infty} 4\pi r^2 A \epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] dr =$$

$$= V \frac{8\pi}{3} \epsilon \rho^2 \sigma^3 \left[\frac{1}{3} \left(\frac{\sigma}{r_c} \right)^9 - \left(\frac{\sigma}{r_c} \right)^3 \right]$$

WE CAN DO ALSO BETTER
ENERGY FROM SIMULATION

$$U_{EX} = \frac{1}{2} V \rho^2 \int_0^{r_c} g(r) U_2(r) 4\pi r^2 dr +$$

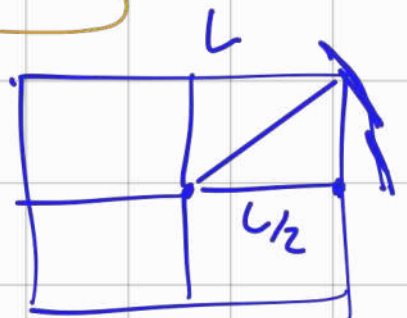
$$\frac{1}{2} V \rho^2 \int_{r_c}^{L/2} g(r) U_2(r) 4\pi r^2 dr +$$

$$\frac{1}{2} V \rho^2 \int_{L/2}^{+\infty} g(r) U_2(r) 4\pi r^2 dr =$$

↑ TAIL CORRECTION

↑ TAIL CORRECTION

$$= U_{EX}^C + U_{EX}^{TAIL}$$

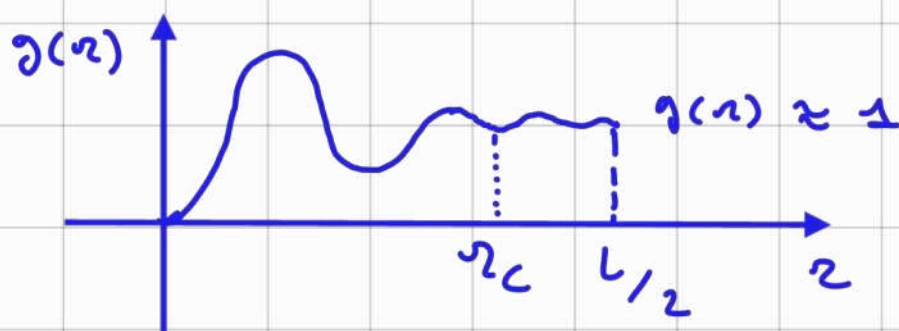


WHERE

$g(r)$ CALCULATED FROM SIMULATIONS

$$U_{\text{EX}}^{\text{TAIL}} = \frac{1}{2} V \rho^2 \int_{r_c}^{L/2} \overbrace{g(r)}^{\text{CALCULATED FROM SIMULATIONS}} u_L(r) 4\pi r^2 dr +$$

$$\underbrace{\frac{1}{2} V \rho^2 \int_{L/2}^{+\infty} u_L(r) 4\pi r^2 dr}_{\text{L/2}}$$



CALCULATION OF PRESSURE FROM

$g(r)$

$$P = \underline{K} + \underline{U}$$

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

$$Z = Z_{\text{ID}} \cdot Z_{\text{EX}} \quad Z_{\text{ID}} = V^N$$

$$Z_{\text{EX}} = \int e^{-\beta U_N(\vec{r}_1, \dots, \vec{r}_N)} d^N \vec{r}$$

SCALED COORDINATES:

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

$$F = -k_B T \ln Q \quad \text{BUT}$$

$$Q = \frac{\Lambda^{-3N}}{N!} Z$$

$$\text{WHERE } \Lambda = \sqrt{\frac{2\pi \hbar^2}{m k_B T}}$$

IT DOES NOT DEPEND ON V

$$P = k_B T \frac{\partial}{\partial V} (\ln Z_{\text{ID}} + \ln Z_{\text{EX}}) = k_B T \frac{\partial \ln V^N}{\partial V}$$

$$+ k_B T \frac{\partial \ln Z_{\text{EX}}}{\partial V} = \underbrace{k_B T \rho}_{P_{\text{ID}}} + \underbrace{k_B T \frac{\partial \ln Z_{\text{EX}}}{\partial V}}_{P_{\text{EX}}}$$

$$P = P_{\text{ID}} + P_{\text{EX}}$$

$$U_N = U_N(V^{1/3} \vec{\xi}_1, \dots, V^{1/3} \vec{\xi}_N)$$

$$P_{\text{EX}} = k_B T \frac{1}{Z_{\text{EX}}} \frac{\partial Z_{\text{EX}}}{\partial V} = \frac{k_B T}{Z_{\text{EX}}} \frac{\partial}{\partial V} \left(\int_0^1 e^{-\beta U_N} d^N \vec{\xi} \right) =$$

$$= - \cancel{k_B T} \beta \int \left(\frac{\partial U_N}{\partial V} \frac{e^{-\beta U_N}}{\mathcal{Z}_{ex}} \right) d\vec{r}^N = - \int \frac{\partial U_N}{\partial V} \frac{e^{-\beta U_N}}{\mathcal{Z}} d\vec{r}^N =$$

$$= - \left\langle \frac{\partial U_N}{\partial V} \right\rangle$$

$$P = P_{ID} - \left\langle \frac{\partial U_N}{\partial V} \right\rangle$$

(*) NOTE THAT WE CAN BRING $\frac{\partial}{\partial V}$ INSIDE THE INTEGRAL SINCE THE INTEGRATION DOMAIN DOES NOT DEPEND ON V IF WE USE SCALE COORDS.

$$U_N = \frac{1}{2} \sum'_{i,j} U_2(\vec{r}_{i,j}) \quad V = L^3 \Rightarrow \frac{\partial}{\partial V} = \frac{1}{3L^2} \frac{\partial}{\partial L}$$

$$P_{EX} = - \left\langle \frac{1}{3L^2} \frac{\partial U_N}{\partial L} \right\rangle = - \left\langle \frac{1}{3L^2} \frac{\partial}{\partial L} \left(\frac{1}{2} \sum'_{i,j} U_2(\vec{r}_{i,j}) \right) \right\rangle =$$

$$= - \left\langle \frac{1}{6L^2} \sum'_{i,j} \frac{\partial U_2}{\partial \vec{r}_{i,j}} \cdot \frac{\partial \vec{r}_{i,j}}{\partial L} \right\rangle = \left\langle \frac{1}{6L^3} \sum'_{i,j} \vec{f}_{i,j} \cdot \vec{r}_{i,j} \right\rangle =$$

NOTE THAT FOR A SYSTEM WITH PBC WE CAN RESTRICT THE CALCULATION TO "FIRST" BOX, SO THAT:

$$U_N = \frac{1}{2} \sum_{\vec{n}} \sum'_{i,j} U_2(\vec{r}_i - \vec{r}_j + L\vec{n})$$

WHERE $\vec{n} = (n_x, n_y, n_z)$

WITH n_i INTEGERS

HENCE

$$\frac{\partial U_N}{\partial L} = \frac{1}{2} \sum'_{i,j} \frac{\partial U_2(\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L} =$$

$$= \frac{1}{2} \sum'_{i,j} \frac{\partial U_2}{\partial \vec{r}_{i,j}} \cdot \frac{\partial (\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L}$$

BUT

$$\frac{\partial (\vec{r}_i - (\vec{r}_j + L\vec{n}))}{\partial L} = \frac{\vec{r}_i - (\vec{r}_j + L\vec{n})}{L} = \frac{\vec{r}_{i,j}}{L}$$

WHERE j RUNS OVER ALSO PERIODIC PARTICLES

(FORCE ACTING BETWEEN I AND J)

$$= \frac{1}{6V} \left\langle \sum'_{i,j} \vec{f}_{ij} \cdot \vec{r}_{ij} \right\rangle \quad \text{SIMILAR EXPRESSION FOR MOLECULAR PRESSURE}$$

$$P = \rho k_B T + \frac{1}{6V} \left\langle \sum'_{i,j} \vec{f}_{ij} \cdot \vec{r}_{ij} \right\rangle \quad P_{EX}$$

WE CAN NOW WRITE P_{EX} IN TERMS OF $g(\vec{r})$

ALL TERMS OF $\sum'_{i,j}$ ARE EQUAL

$$P_{EX} = \frac{N(N-1)}{6V} \int \frac{e^{-\beta U_N}}{Z} \vec{f}_{12} \cdot \vec{r}_{12} d\vec{r}_1 d\vec{r}_2 \underbrace{d\vec{r}^{(N-2)}} =$$

$$= \frac{1}{6V} \int \rho^{(2)}(\vec{r}_1, \vec{r}_2) \vec{f}_{12} \cdot \vec{r}_{12} d\vec{r}_1 d\vec{r}_2$$

CHANGE OF VARIABLES

$(\vec{r}_1, \vec{r}_2) \rightarrow (\vec{r}, \vec{r}_2)$ WHERE $\vec{r} = \vec{r}_1 - \vec{r}_2$

$$= \frac{1}{6V} \int \rho^{(2)}(\vec{r} + \vec{r}_2, \vec{r}_2) \vec{f}(\vec{r}) \cdot \vec{r} d\vec{r} d\vec{r}_2 =$$

IF SYSTEM IS HOMOGENEOUS

$$\rho^{(2)}(\vec{r} + \vec{r}_2, \vec{r}_2) = \rho^{(2)}(\vec{r}) \quad \text{HENCE}$$

$$= \frac{1}{6} \int \rho^{(2)}(\vec{r}) \vec{f}(\vec{r}) \cdot \vec{r} d\vec{r}$$

$$\text{BUT } \rho^{(2)}(\vec{r}) = \rho^2 g(\vec{r})$$

$$= \frac{\rho^2}{6} \int \vec{f}(\vec{r}) \cdot \vec{r} g(\vec{r}) d\vec{r} \leftarrow$$

IF THE SYSTEM IS ISOTROPIC

$$P_{EX} = \frac{\rho^2}{6} \int f(r) g(r) 4\pi r^2 dr \leftarrow$$

TAIL CORRECTIONS P_{SIM} FROM SIMULATIONS

$$P_{EX} = \frac{\rho^2}{6} \int_0^{r_c} f(r) g(r) 4\pi r^3 dr + \underbrace{\frac{\rho^2}{6} \int_{r_c}^{+\infty} f(r) \overset{\approx 1}{g(r)} 4\pi r^3 dr}_{\text{FOR LT WE CAN CALCULATE THIS ANALYTICALLY}} = \text{P}_{TAIL}$$

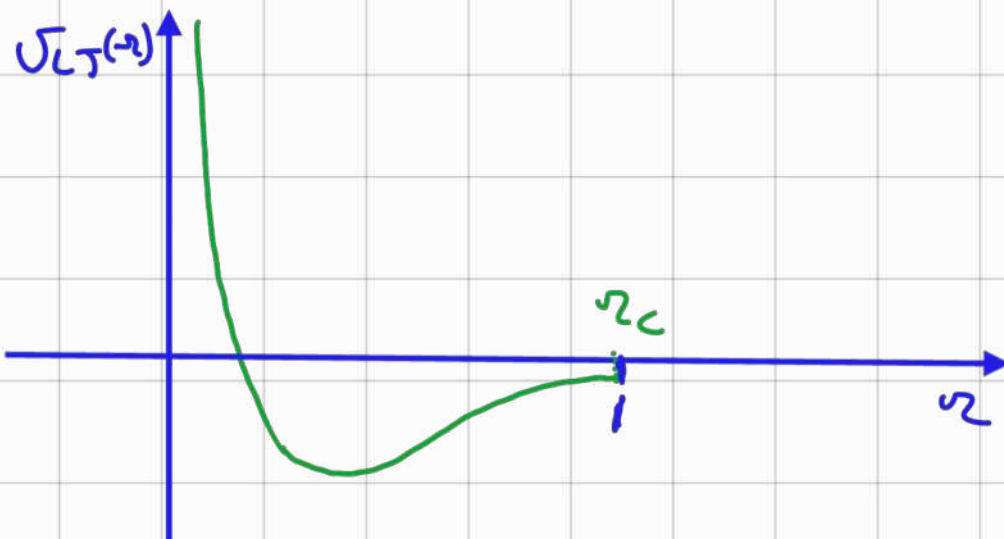
(*) NOTE THAT

WE CAN CALCULATE THIS FROM SIMULATIONS

$$P_{SIM} = \frac{\rho^2}{6} \int_0^{r_c} F(r) g(r) 4\pi r^3 dr = \frac{1}{6V} \left\langle \sum_{i,j}' \vec{F}_{ij}^c \cdot \vec{r}_{ij} \right\rangle$$

THE ABOVE TAIL CORRECTION APPLIES IF WE WANT TO COMPARE OUR RESULTS WITH A SYSTEM WITHOUT CUTOFF, I.E. WE HAVE : $P = P_{SIM} + P_{TAIL}$

Q. BUT WHAT IS THE PRESSURE OF A SYSTEM WITH TRUNCATED INTERACTIONS?
FOR EXAMPLE CONSIDER A TRUNCATED LJ SYSTEM



AROUND r_c ONE HAS

$$U_{LT}(r) \approx \theta(r_c - r) U_{LT}(r_c)$$

$$\text{WHERE } \theta(x) = \begin{cases} 1 & x \geq 0 \\ 0 & x < 0 \end{cases}$$

$$f(r) = - \frac{dU}{dr} = U_{LT}(r_c) \delta(r - r_c)$$

$$\text{SINCE } \frac{d}{dx} \theta(x) = \delta(x)$$

HENCE WE HAVE

$$P_{IMP} = \frac{1}{6} \rho^2 \int_{r_c - \epsilon}^{\infty} U_{LT}(r_c) \delta(r - r_c) 4\pi r^3 dr =$$
$$= \frac{1}{6} \rho^2 U_{LT}(r_c) 4\pi r_c^3$$

"IMPULSIVE" CORRECTION TO PRESSURE

TODAY'S TOPICS 23/10/26

- STATIC STRUCTURE FACTOR
- SETTING-UP A SIMULATION :
INITIAL CONFIGURATION
- TRICKS OF THE TRADE :
LINKED CELL LISTS AND
NEAREST NEIGHBOUR LISTS
- ISOBARIC ENSEMBLE

STATIC STRUCTURE FACTOR

1 POINT DENSITY

$$\rho(\vec{r}) = \left\langle \sum_i \delta(\vec{r} - \vec{r}_i) \right\rangle$$

$$\vec{k} = \frac{2\pi}{L} (n_1, n_2, n_3)$$

$$\rho(\vec{r})$$

THEN

FOURIER TRANSFORM

$$\langle \rho(\vec{k}) \rangle = \int \rho(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d\vec{r} = \left\langle \sum_i e^{-i\vec{k} \cdot \vec{r}_i} \right\rangle$$

WHERE

$$\rho(\vec{r}) = \sum_i^N e^{-i\vec{k} \cdot \vec{r}_i}$$

ENSEMBLE AVERAGE

WE DEFINE

$$S(\vec{k}) \equiv \frac{1}{N} \langle \rho(\vec{k}) \rho^*(\vec{k}) \rangle$$

ENSEMBLE AVERAGE

$S(\vec{k})$ CAN BE MEASURED
EXPERIMENTALLY
THROUGH SCATTERING
EXPERIMENTS

BUT

$$S(\vec{k}) = \frac{1}{N} \left\langle \sum_{i,j} e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{i,j}^{\neq} e^{-i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \right\rangle$$

$$= 1 + \frac{1}{N} \left\langle \int \sum_{i,j}^{\neq} e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) d\vec{r} d\vec{r}' \right\rangle =$$

$\rho^{(2)}(\vec{r}, \vec{r}')$

$$= 1 + \frac{1}{N} \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \left\langle \sum_{i,j}^{\neq} \delta(\vec{r} - \vec{r}_i) \delta(\vec{r}' - \vec{r}_j) \right\rangle =$$

$$= 1 + \frac{1}{N} \int d\vec{r} d\vec{r}' e^{-i\vec{k} \cdot (\vec{r} - \vec{r}')} \rho^{(2)}(\vec{r}, \vec{r}') =$$

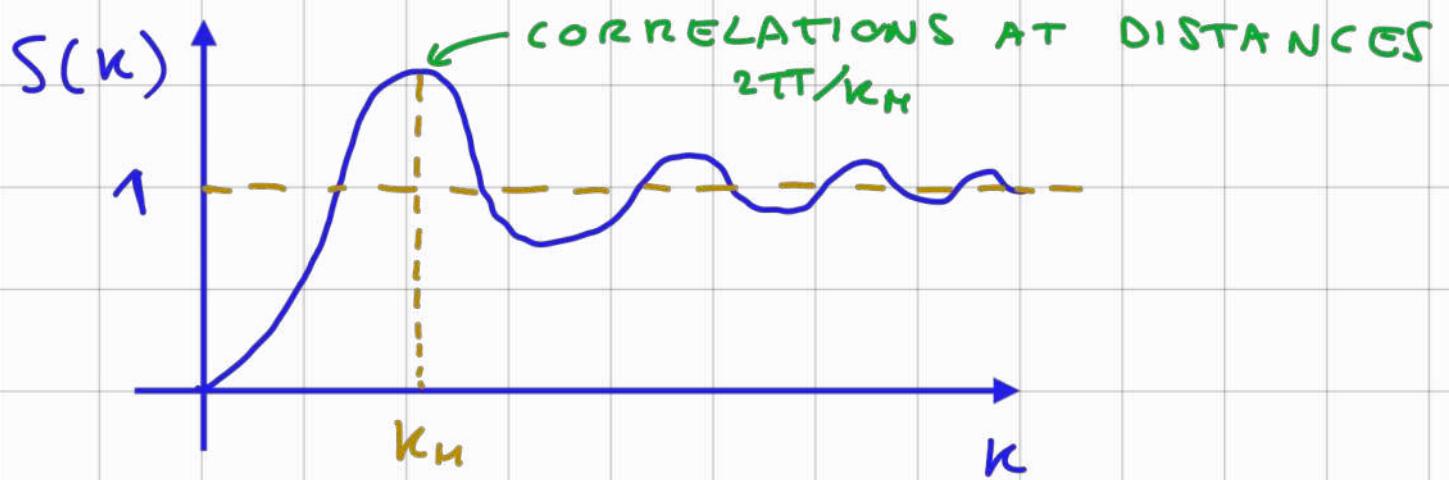
ASSUMING THE SYSTEM HOMOGENEOUS

$$= 1 + \frac{\rho^2}{N} V \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} g(\vec{r}) =$$

$$= 1 + \rho \int d\vec{r} e^{-i\vec{k} \cdot \vec{r}} g(\vec{r})$$

FOURIER TRANSFORM OF $g(\vec{r})$

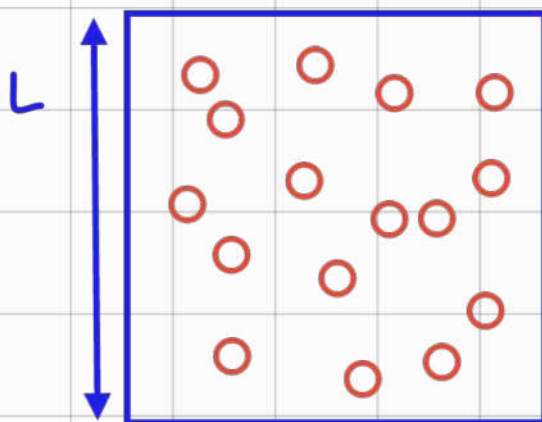
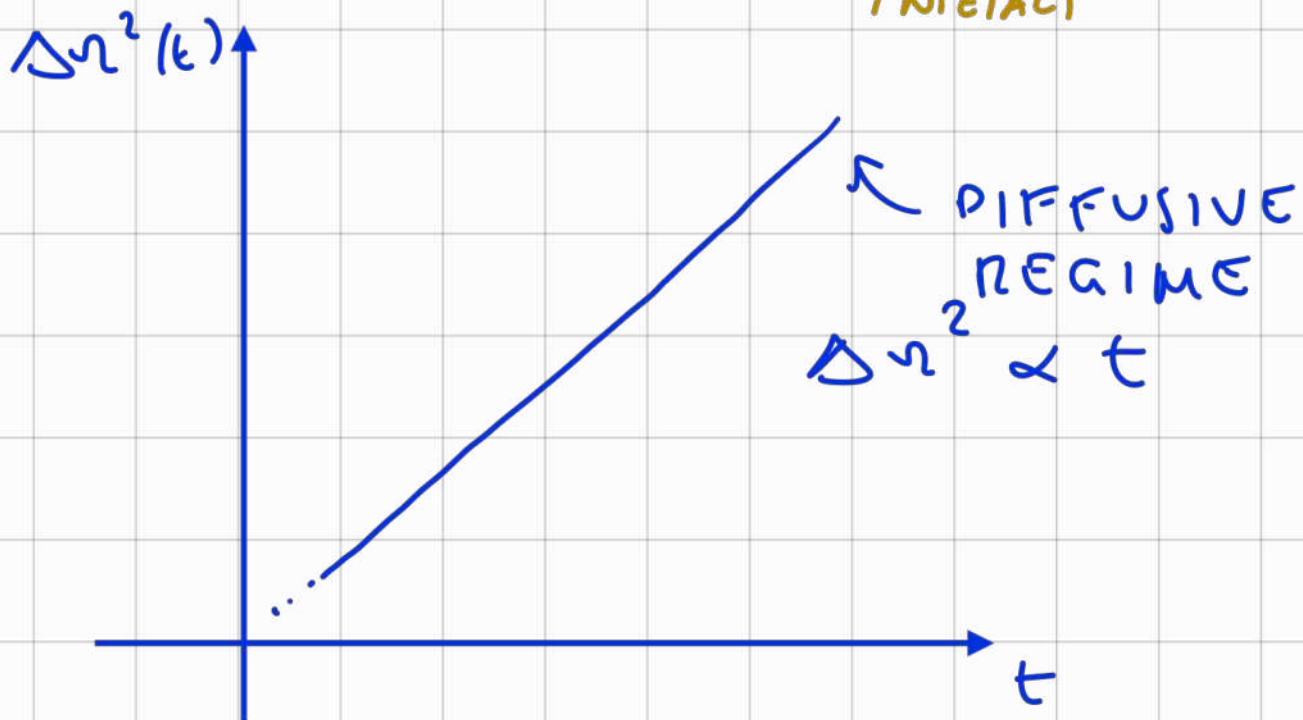
IN THE ISOTROPIC CASE



MEAN SQUARED DISPLACEMENT

$$\Delta r^2(t) \equiv \frac{1}{N} \sum_{i=1}^N \|\vec{r}_i(t) - \vec{r}_i(0)\|^2$$

$\uparrow$ FUNCTION OF t
 $\uparrow$ PASSO MC
 $\uparrow$ POSIZIONI INIZIALI



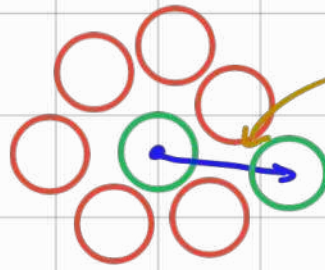
$$\sqrt{\Delta r^2} \gtrsim L$$

THE SYSTEM CAN BE CONSIDERED EQUILIBRATED SINCE ALL PARTICLES HAVE MOVED ENOUGH I.E. HAVE FULLY EXPLORED THE CONFIGURATION SPACE

WE COULD ALSO USE A LESS STRINGENT
CONDITION, I.E.

TYPICAL
PARTICLE SIZE

$$\sqrt{\Delta r^2} \gtrsim \sigma$$

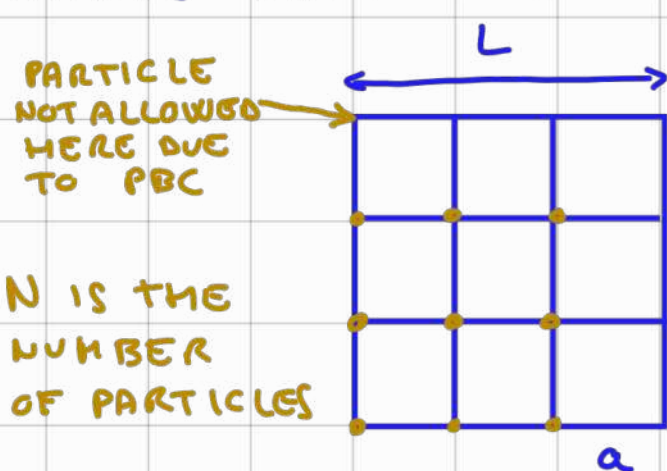


DISPLACEMENT
 $\sim \sigma$

MAIN CONTRIBUTION TO SPATIAL CORRELATIONS COMES
FROM FIRST PEAK OF $S(r)$ WHICH ROUGHLY
CORRESPONDS TO A DISTANCE EQUAL TO σ

INITIAL CONFIGURATION

CUBIC LATTICE



N IS THE NUMBER OF PARTICLES

$$\phi = \frac{N \sigma_0}{L^3} = \frac{n \left(\frac{L}{a}\right)^3 \sigma_0}{L^3}$$

WHERE σ_0 IS THE VOLUME OF A PARTICLE

AND n IS THE NUMBER OF PARTICLES PER UNIT CELL ($n=1$ IN THIS CASE)

$$= n \frac{\sigma_0}{a^3} = \frac{n \sigma_0}{a^3}$$

BUT $\sigma_0 = \frac{\pi}{6} \sigma^3$ IF PARTICLE IS SPHERICAL

HENCE CONSIDERING THAT $a^* = \sigma$

$$\phi^* = \{ \text{MAXIMUM } \phi \} = \frac{\sigma_0}{(a^*)^3} = \frac{\pi}{6} \frac{\sigma^3}{\sigma^3} = \frac{\pi}{6}$$

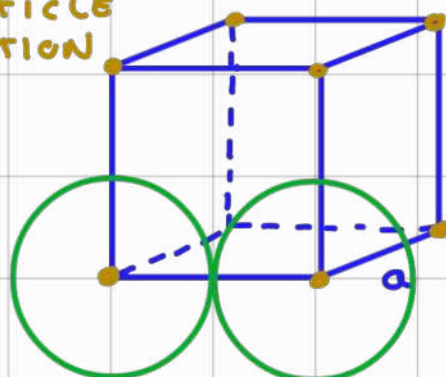
IF WE WANT A LOWER $\phi = \phi'$ IT IS JUST A MATTER TO EXPAND THE BOX AND SCALE PARTICLE POSITIONS BY A FACTOR ξ SUCH THAT

$$L' = \xi L \quad \vec{r}_i' = \xi \vec{r}_i$$

$$\text{WITH } \xi = \left(\frac{\phi^*}{\phi'} \right)^{1/3} \text{ I.E. } \phi' = \frac{\phi^*}{\xi^3}$$

EACH PARTICLE HAS DIAMETER σ

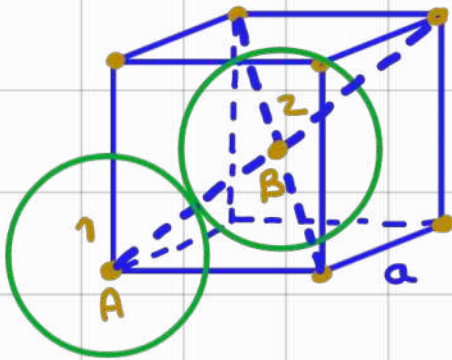
• PARTICLE POSITION



a^* IS THE MINIMUM VALUE OF a

$$a^* = \sigma$$

HIGHER ϕ : BODY CENTERED CUBIC (BCC)



$$\phi^* = \frac{n V_0}{(a^*)^3}$$

WHERE IN THIS CASE

$$n = 2 \quad \text{AND}$$

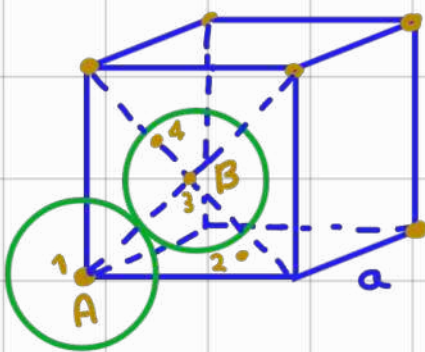
a^* IS SUCH THAT

$$\overline{AB} = \sigma = \frac{\sqrt{3} a^*}{2} \quad \text{i.e. } a^* = \frac{2}{\sqrt{3}} \sigma$$

SO THAT

$$\phi^* = \frac{2 \frac{\pi}{6} \sigma^3}{\left(\frac{2}{\sqrt{3}}\right)^3 \sigma^3} = \frac{\pi}{3} \left(\frac{\sqrt{3}}{2}\right)^3 \approx 0.68$$

EVEN HIGHER ϕ : FACE CENTERED CUBIC (FCC)



$$\phi^* = \frac{n V_0}{(a^*)^3}$$

WHERE IN THIS CASE

$$n = 4 \quad \text{AND}$$

a^* IS SUCH THAT

$$\overline{AB} = \sigma = \frac{\sqrt{2}}{2} a^* \quad \text{i.e. } a^* = \frac{2}{\sqrt{2}} \sigma$$

SO THAT

$$\phi^* = \frac{4 \frac{\pi}{6} \sigma^3}{\left(\frac{2}{\sqrt{2}}\right)^3 \sigma^3} = 2 \left(\frac{\sqrt{2}}{2}\right)^3 \frac{\pi}{3} \approx 0.74$$

LINKED CELL LISTS

IN A METROPOLIS MC A MC STEP
CONSISTS OF ATTEMPTING TO MOVE
N PARTICLE

FOR EACH PARTICLE

$$\text{acc}(0 \rightarrow n) = \min \{1, e^{-\beta \Delta U}\}$$

$$\Delta U = U_i' - U_i \quad \text{WHERE}$$

$$U_i = \sum_j U_2(\vec{r}_{ij}) \quad \text{WHICH REQUIRES}$$

(NOTE THAT EVEN IF
WE NEED TO
CALCULATE $|\vec{r}_{ij}|$)

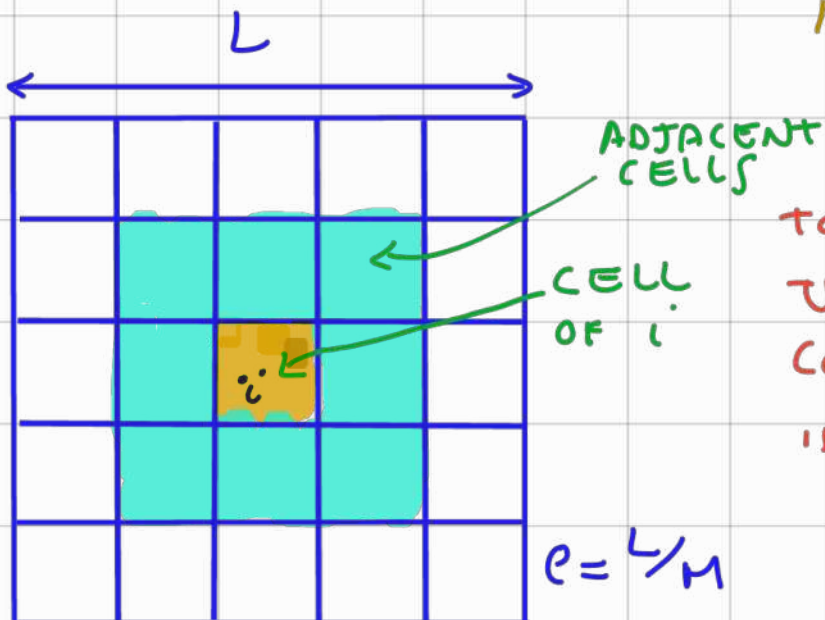
HENCE FOR A MC STEP COMPLEXITY

$$\text{IS } O(N \times N) = O(N^2)$$

WE WANT TO REDUCE THE NUMBER OF TIMES
WE HAVE TO CALCULATE U_2

LET'S CONSIDER M^3 CUBIC CELLS SUCH
THAT $L/M \geq r_c \leftarrow \text{CUTOFF RADIUS}$

I.E. M IS THE LARGEST
INTEGER SUCH THAT



$$c = \frac{L}{M} \geq r_c$$

TO CALCULATE U_i AND
 U_i' WE CAN JUST
CONSIDER PARTICLES
IN THE 27 CELLS
(I.E. THE CELL TO
WHICH PARTICLE i
BELONGS AND THE
26 ADJACENT CELLS)

WITH THIS STRATEGY FOR EACH MC MOVE WE HAVE TO CALCULATE $\tilde{N}$ TIMES τ_c WITH

$$\tilde{N} \approx N \tau_c^3 \rho = N \underbrace{\tau_c^3 \rho}_{\text{THIS IS A CONSTANT IF WE INCREASE BOX SIZE KEEPING FIXED } \rho} = O(N)$$

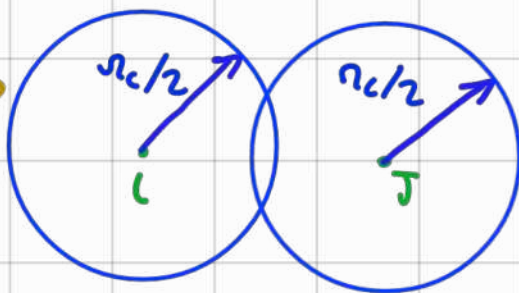
THIS IS A CONSTANT IF WE INCREASE BOX SIZE KEEPING FIXED ρ

AFTER PARTICLE i MOVE, IF CELL TO WHICH IT BELONGS CHANGES, CELL LISTS MUST BE UPDATED

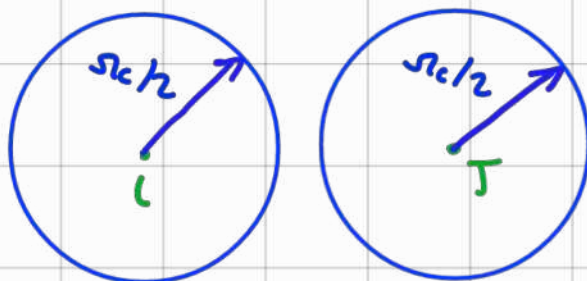
NEAREST NEIGHBOUR LISTS (NNL)

CONSIDER TWO PARTICLES i AND j AND OBSERVE THAT:

SPHERE OF DIAMETER τ_c (CUTOFF RADIUS)



THE TWO SPHERES OVERLAP HENCE i AND j INTERACT

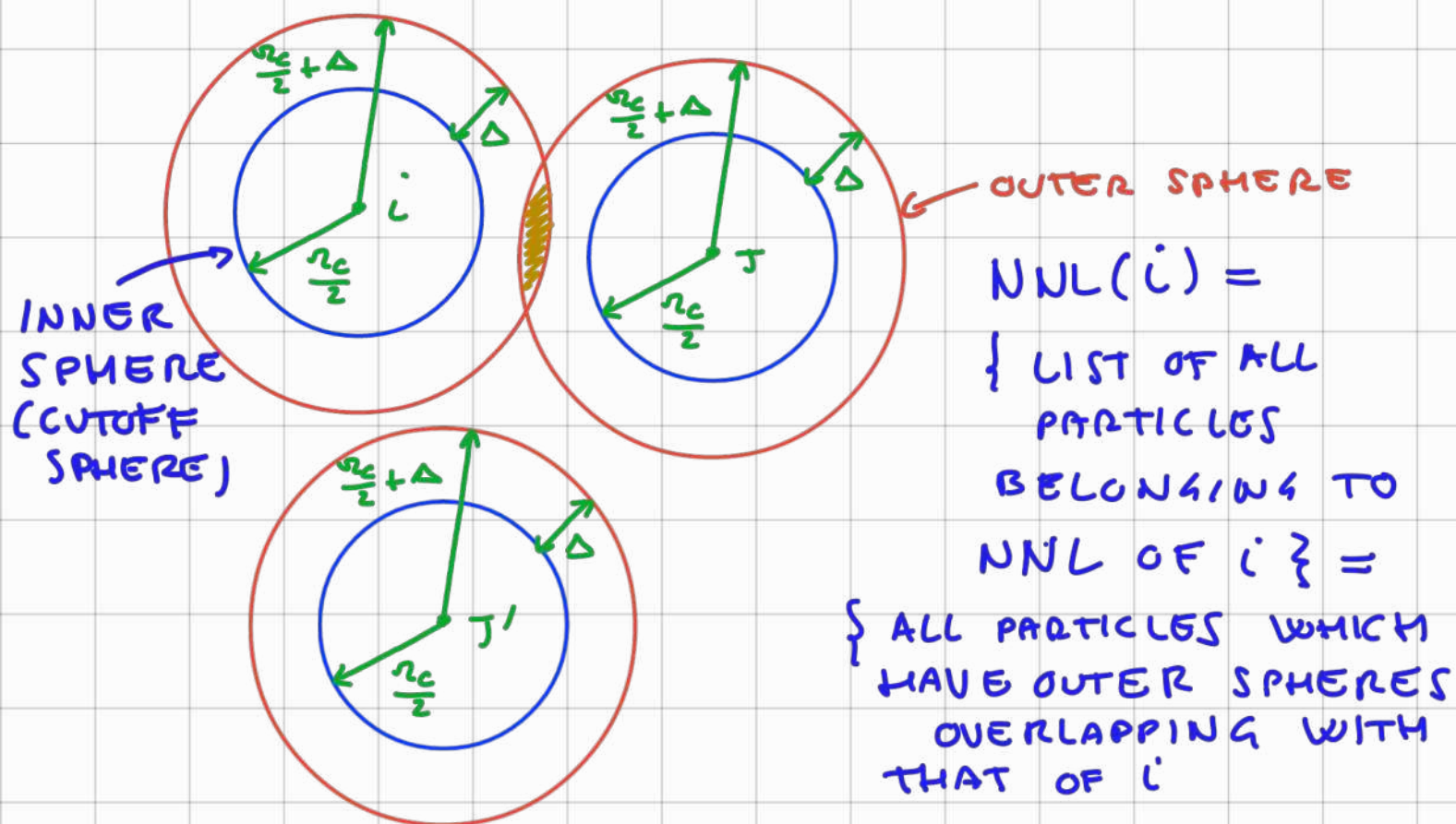


THE TWO SPHERES DO NOT OVERLAP HENCE i AND j DO NOT INTERACT

AT A CERTAIN TIME t_0 (MC STEP)

WE BUILD THE NNL OF ALL PARTICLES (STARTING FROM FIRST SIMULATION STEP)

CONSIDER THE BUILDING OF NNL OF A PARTICLE i
 j AND j' ARE TWO PARTICLES OTHER THAN i



HENCE IN THIS CASE: $j \in NNL(i)$ $j' \notin NNL(i)$

SINCE SPHERES OF RADIUS $\frac{r_c}{2} + \Delta$ OVERLAP

SINCE SPHERES OF RADIUS $\frac{r_c}{2} + \Delta$ DO NOT OVERLAP

FOR $t > t_0$ INNER SPHERE ARE PLACED WITH THEIR CENTER AT PARTICLE POSITION WHILE OUTER SPHERES KEEP FIXED AS LONG AS EACH INNER SPHERE REMAIN INSIDE ITS CORRESPONDING OUTER SPHERE WE CAN CALCULATE U_i AND U'_i BY CONSIDERING $\forall i$ THE PARTICLES $\in NNL(i)$

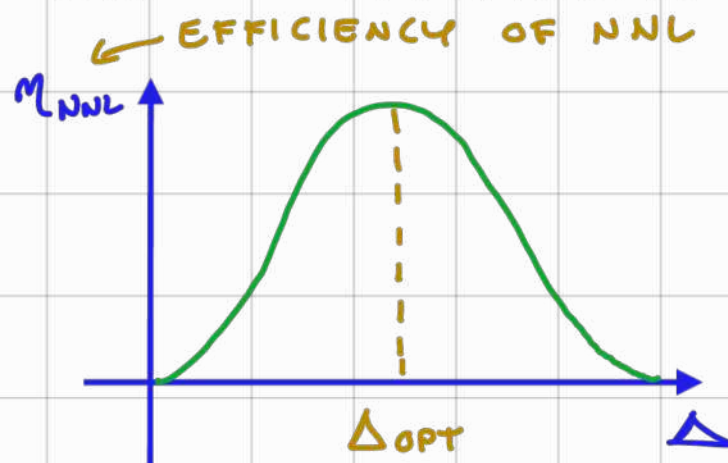
SINCE IF TWO INNER SPHERES
ARE INSIDE TWO NON OVERLAPPING
OUTER SPHERES THEY CAN NOT OVERLAP
(AND CORRESPONDING PARTICLES CAN
NOT INTERACT)

AN INNER SPHERE ESCAPE

$$\text{IF } \|\vec{r}_i(t) - \vec{r}_i(t_0)\| \geq \Delta$$

IF THIS HAPPENS ALL>NNL
MUST BE REBUILT

Δ IS A PARAMETER WHICH
MUST BE OPTIMIZED



AND IF η_{LL} IS THE EFFICIENCY
OF LL

$$\frac{\eta_{NWL}}{\eta_{LL}} = \frac{\{ \# \text{ PARTICLES IN THE } 27 \text{ LL CELLS} \}}{\{ \# \text{ PARTICLES IN THE NWL}(i) \}}$$

$$\frac{\rho r_c^3 27}{\frac{4\pi}{3} r_c^3 \rho} \approx \frac{27 \cdot 3}{4\pi} \approx 6$$

$\uparrow$
 IF $\Delta \ll r_c$

$\uparrow$ SINCE FOR EACH PARTICLE WE NEED TO TEST IF $r < r_c$

NPT ENSEMBLE

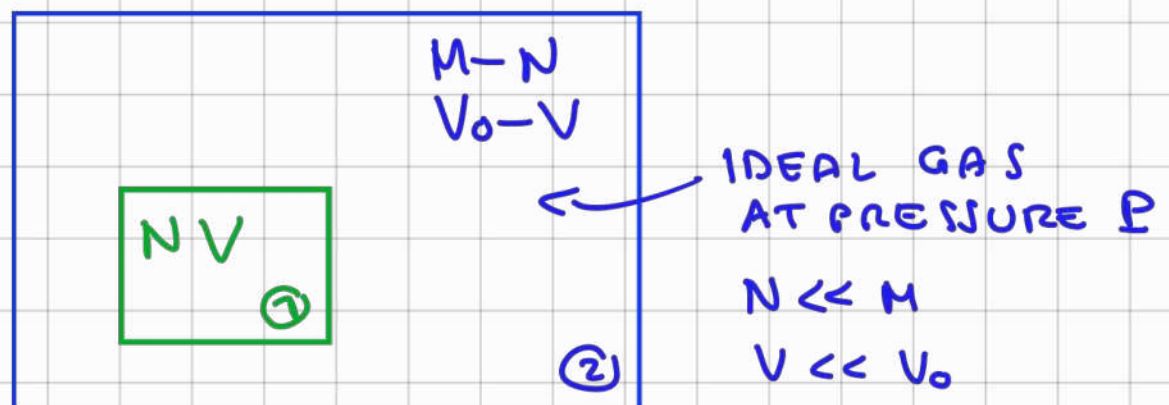
IF P IS A GENERIC DISTRIBUTION

$$P(o) \cdot \pi(o \rightarrow n) = P(n) \pi(n \rightarrow o)$$

WHERE $\pi(o \rightarrow n) = \overbrace{\alpha(o \rightarrow n)}^{\text{TRIAL MOVE}} \text{acc}(o \rightarrow n)$

WITH $\text{acc}(o \rightarrow n) = \begin{cases} P(n)/P(o) & \text{IF } P(n) \leq P(o) \\ 1 & \text{OTHERWISE} \end{cases}$

GOAL: FIND P FOR NPT ENSEMBLE



WEAKLY INTERACTING SYSTEMS

$$E_{\text{TOT}} = E_1 + E_2$$

IF THE VOLUMES OF ① AND ② ARE FIXED

$$Q = \int \frac{d^{M-N} q^{(2)}}{\Lambda^{3(M-N)} (M-N)!} \int \frac{d^N q^{(1)} e^{-\beta U_N}}{\Lambda^{3N} N!} \quad U_N = \frac{1}{2} \sum_{i,j} U_L(\vec{r}_i, \vec{r}_j)$$

WHERE $\Lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$ ← THERMAL WAVELENGTH

SCALED COORDINATES

$$V' = V_0 - V$$

$$\vec{q}_i = V^{1/3} \vec{\xi}_i \quad \text{FOR } i \in \textcircled{1}$$

$$\vec{q}_L = (V')^{1/3} \vec{\xi}_i \quad \text{FOR } i \in \textcircled{2}$$

$$Q = \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \underbrace{\int d\vec{\xi}^{M-N}}_{=1} \int d\vec{\xi}^N e^{-\beta U_N} =$$

$$= \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \int d\vec{\xi}^N e^{-\beta U_N}$$

IF THE VOLUME IS ALLOWED TO CHANGE

$$Q = \int dV \frac{(V')^{M-N} V^N}{\Lambda^{3M} (M-N)! N!} \int d\vec{\xi}^N e^{-\beta U_N}$$

↑
WE HAVE ALSO TO SUM OVER
ALL POSSIBLE VOLUMES

FOR NVT ENSEMBLE

$$Z = \int e^{-\beta U_N} d^N q \quad p \propto e^{-\beta U_N}$$

HENCE WE HAVE

$$p(\underbrace{V, \vec{\xi}_1, \dots, \vec{\xi}_N}_{\text{STATE OF SYSTEM}}) \propto e^{-\beta U_N} V^N (V_0 - V)^{M-N}$$

NOTE THAT TO IMPLEMENT A METROPOLIS MC
WE NEED p UP TO A CONSTANT
SINCE ACCEPTANCE PROBABILITY DEPENDS
ON $p(n)/p(0)$

CONSIDER THE TERM

$$\begin{aligned} (V_0 - V)^{M-N} &= V_0^{M-N} \left(1 - \frac{V}{V_0}\right)^{M-N} = \\ &= V_0^{M-N} \left(1 - \rho \frac{V}{M-N}\right)^{M-N} = \end{aligned}$$

TODAY'S TOPICS 26/10/2026

- IMPLEMENTATION OF MC-NPT
- GIBBS FREE ENERGY
- HISTOGRAM REWEIGHTING
WITH AN EXAMPLE OF APPLICATION
- ORIENTATIONAL MOVES OF
UNIAXIAL PARTICLES
- GENERIC RIGID BODIES

$$M \gg N \text{ i.e. } M-N \rightarrow +\infty \quad \lim_{M-N \rightarrow +\infty} \left(1 - \frac{PV}{M-N}\right)^{M-N} = e^{-PV}$$

$$\lim_{x \rightarrow +\infty} \left(1 + \frac{k}{x}\right)^x = e^{kx}$$

$$= V_0^{M-N} e^{-PV} = V_0^{M-N} e^{-\beta PV}$$

$\beta P = \rho$ HEAT BATH V_N HENCE:

$$P(V, \vec{\xi}_1, \dots, \vec{\xi}_N) \propto e^{N \ln V} e^{-\beta PV} e^{-\beta U_N}$$

STATE OF THE SYSTEM IS GIVEN BY

$\{V, \vec{\xi}_1, \dots, \vec{\xi}_N\}$ HENCE WE NEED TO UPDATE BOTH

V AND $\{\vec{\xi}_1, \dots, \vec{\xi}_N\}$, i.e. WE NEED TWO

TYPES OF TRIAL MOVES: **PARTICLE MOVE**

(UPDATING RANDOMLY A PARTICLE) AND

A VOLUME MOVE

1) **PARTICLE MOVE:**

CHOOSE RANDOMLY A PARTICLE AND
UPDATE ITS POSITION $\vec{\xi}_i$

NOW NOTE THAT IF WE UPDATE PARTICLE i
POSITION AS IN A NVT MC, i.e.

$$\vec{r}_i' = \vec{r}_i + \Delta \vec{r}$$

THIS IS EQUIVALENT TO DO:

$$V^{1/3} \vec{\xi}_i' = V^{1/3} \vec{\xi}_i + \Delta \vec{r} \quad \text{i.e.}$$

$$\vec{\xi}_i' = \vec{\xi}_i + V^{-1/3} \Delta \vec{r}$$

i.e. WE ARE UPDATING $\vec{\xi}_i$ AS REQUESTED

THEN ACCEPT THE TRIAL MOVE AS FOLLOWS:

$$\text{acc}(0 \rightarrow n) = \min \left\{ 1, \frac{e^{N \ln V} e^{-\beta P V} e^{-\beta U_N(V, \vec{\xi}_1, \dots, \vec{\xi}_N)}}{e^{N \ln V} e^{-\beta P V} e^{-\beta U_N(V, \vec{\xi}_1, \dots, \vec{\xi}_N)} \right\}$$

$$= \min \{ 1, e^{-\beta \Delta U_N} \}$$

NOTE THAT THIS MOVE IS EQUIVALENT TO THAT OF A NVT MC

2) **VOLUME MOVE** $0 \rightarrow n$

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

$$V \rightarrow V'$$

$$\vec{r}_i' = (V')^{1/3} \vec{\xi}_i$$

$$V' = V + \delta V \eta$$

$$\eta \in (-1, 1) \leftarrow \text{RANDOM}$$

$$\vec{r}_i' = \vec{r}_i \left(\frac{V'}{V} \right)^{1/3}$$

VOLUME MOVE

AND $\text{acc}(0 \rightarrow n) = \min \left\{ 1, \frac{P(V', \vec{\xi}_1, \dots, \vec{\xi}_N)}{P(V, \vec{\xi}_1, \dots, \vec{\xi}_N)} \right\} =$

$$\frac{P(n)}{P(0)} =$$

$$= \min \left\{ 1, \frac{e^{-\beta U_N(V')} - \beta P V' + N \ln V'}{e^{-\beta U_N(V)} - \beta P V + N \ln V} \right\}$$

$$\text{IF } G \equiv U_N + P V - k_B T N \ln V$$

$$\Delta G = P \Delta V + \Delta U_N - N k_B T \ln \left(\frac{V(n)}{V(0)} \right)$$

$$\Delta V = V' - V$$

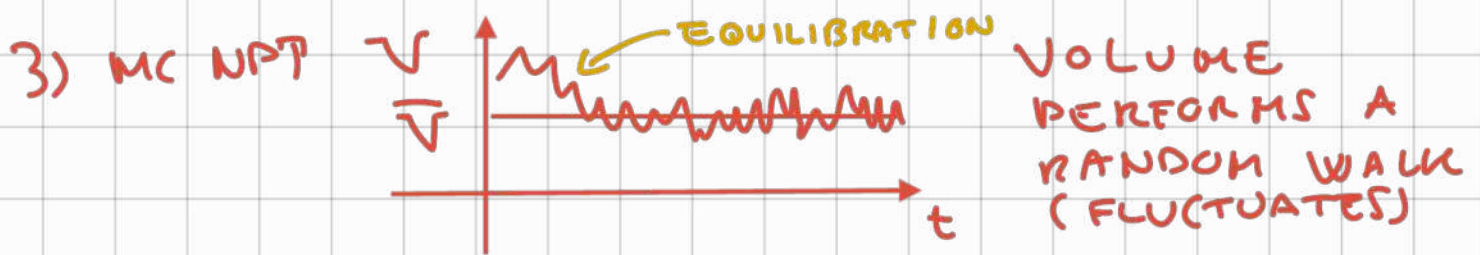
$$\Delta U_N = U_N(V') - U_N(V)$$

ACCEPTANCE PROBABILITY NPT:

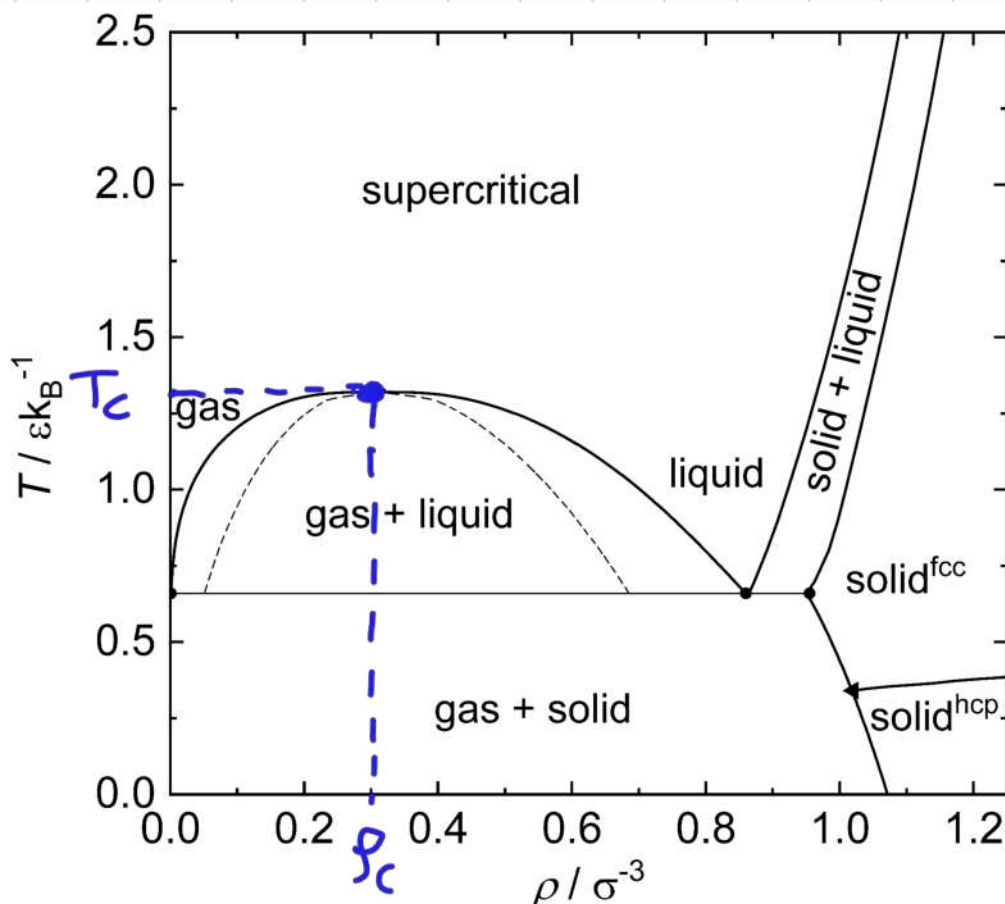
$$\text{acc}(0 \rightarrow n) = \min \{ 1, e^{-\beta \Delta G} \}$$

NOTE THAT:

- 1) δV MUST BE OPTIMIZED TO HAVE AN ACCEPTANCE RATE OF VOLUME MOVES AROUND 30% - 50% (AS δ)
- 2) THE TWO TYPES OF MOVE SELECTED RANDOMLY WHERE THE PROBABILITY OF SELECTING A VOLUME MOVE SHOULD BE EQUAL TO $1/N$ (BECAUSE EACH BOX MOVE INVOLVES N PARTICLES)

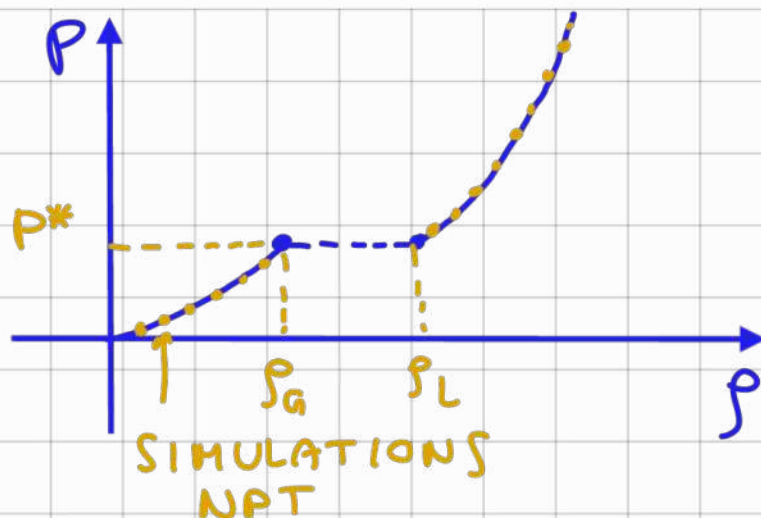


LENNARD-JONES PHASE DIAGRAM



For $T < T_c$

COEXISTENCE
PRESSURE



EQUATION
OF STATE

PROBABILITY OF A GIVEN CONFIGURATION:

$$P(V, \vec{\xi}_1, \dots, \vec{\xi}_N) = \frac{e^{-\beta U_N} e^{-\beta P V} V^N}{\int e^{-\beta U_N} e^{-\beta P V} V^N dV d\vec{\xi}}$$

PROBABILITY OF VOLUME V :

$$P(V) = \frac{\int e^{-\beta U_N} e^{-\beta P V} V^N d\vec{\xi}}{\int e^{-\beta U_N} e^{-\beta P V} V^N dV d\vec{\xi}} = \frac{e^{-\beta P V} Z(T, V)}{Z_{NPT}}$$

WHERE $Z(T, V) = \int e^{-\beta U_N} V^N d\vec{\xi}$ AND

$$Z_{NPT} = \int e^{-\beta U_N} e^{-\beta P V} V^N dV d\vec{\xi}$$

GIBBS FREE ENERGY

WE ALSO CONSIDER THE INTEGRAL OVER
MOMENTA AND THE CORRECT
BOLTZMANN COUNTING

$$Q_{NPT} \equiv \frac{Z_{NPT}}{\Lambda^{3N} N!}$$

$$-k_B T \ln(Q_{NPT}) = -k_B T \ln \left(\frac{\int e^{-\beta U_N} e^{-\beta P V} V^N dV d\vec{\xi}}{\Lambda^{3N} N!} \right)$$

CONTRIBUTE TO INTEGRAL WILL COME MOSTLY
FROM $\bar{V} = \langle V \rangle$ HENCE WE CAN WRITE:

$$= -k_B T \ln \left(\frac{\int e^{-\beta U_N} e^{-\beta P \bar{V}} \bar{V}^N d\vec{\xi}}{\Lambda^{3N} N!} \right) =$$

$$= -k_B T \ln \left(e^{-\beta P \bar{V}} \int e^{\beta U_N - \beta P \bar{V} N} \frac{d^N \xi}{\Lambda^{3N} N!} \right)$$

$$\text{But } \int e^{\beta U_N - \beta P \bar{V} N} \frac{d^N \xi}{\Lambda^{3N} N!} = Q_N(T, \bar{V})$$

↑
CANONICAL
PARTITION FUNCTION

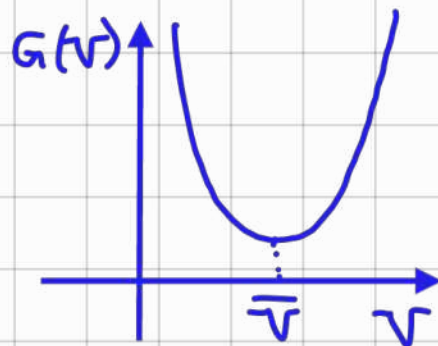
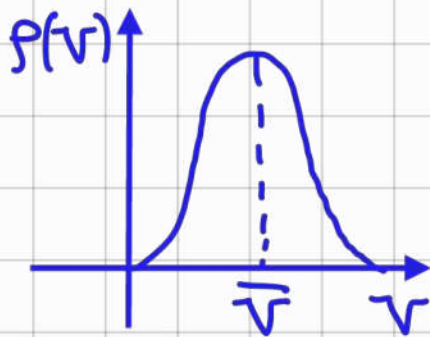
HENCE

$$= P \bar{V} - k_B T \ln Q_N(T, \bar{V}) = P \bar{V} + F(T, \bar{V}) =$$

$$= G(T, P) \leftarrow \text{GIBBS FREE ENERGY}$$

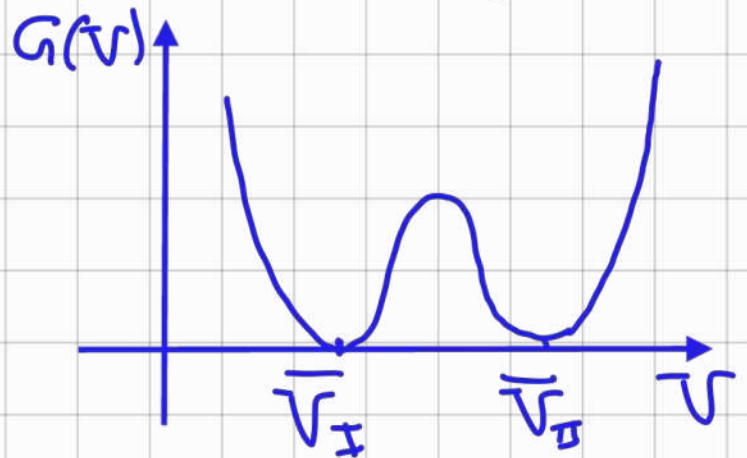
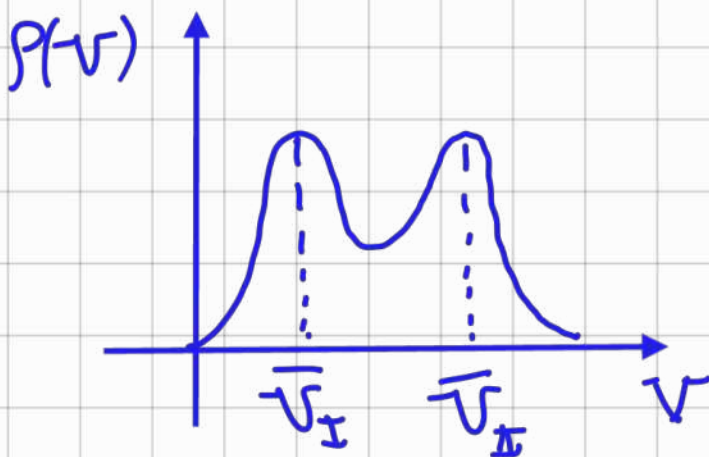
$$G(V) \equiv -k_B T \ln \rho(V) + K \leftarrow \begin{matrix} \text{CONSTANT} \\ \text{WHICH IS} \\ \text{INDEPENDENT} \\ \text{OF } V \end{matrix}$$

ONE PHASE



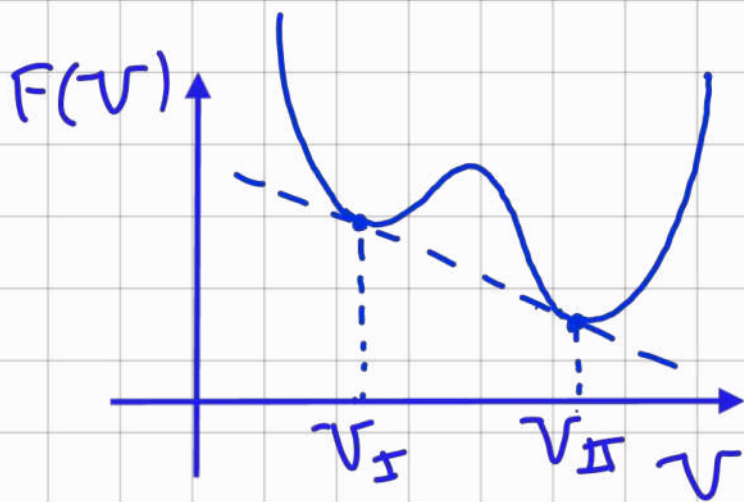
TWO PHASE COEXISTENCE (I AND II PHASES)

$$P = P^* = \{ \text{COEXISTENCE PRESSURE} \}$$



$$F(V) = G(V) - P V$$

↑
INTENDED AS $\bar{V} = \langle V \rangle$



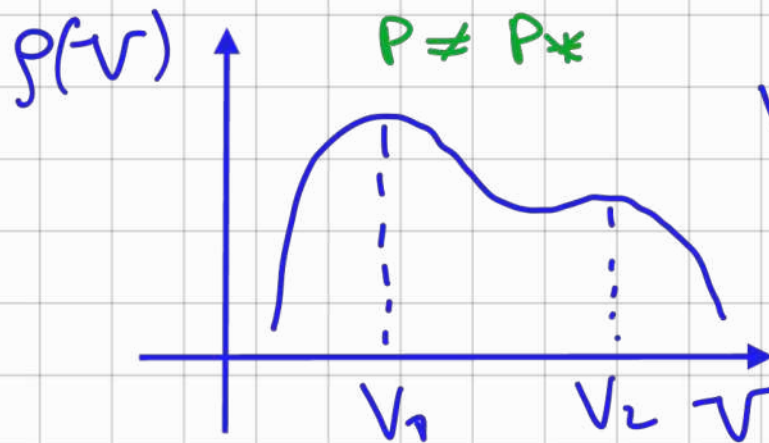
$$\frac{\partial F}{\partial V} \big|_{V=V_I} = -P^*$$

$$\frac{\partial F}{\partial V} \big|_{V=V_{II}} = -P^*$$

↑
COMMON
TANGENT

IN GENERAL $P \neq P^*$ HENCE

WE CAN NOT BE EXACTLY AT COEXISTENCE,
I.E.



$$V_1 \neq V_I$$

$$V_2 \neq V_{II}$$

IF $P \neq P^*$
POSITIONS OF
THE PEAKS ARE
NOT THOSE OF
COEXISTENCE

HISTOGRAM REWEIGHTING

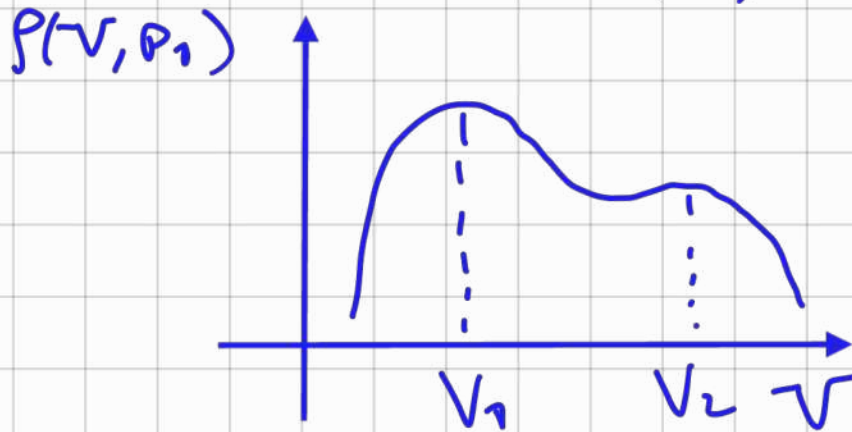
$$p(V, P_1) = \frac{e^{-\beta P_1 V} Z(T, V)}{Z_{NPT}(T, P_1)} \leftarrow \text{FROM A SIMULATION AT } P = P_1 \neq P^*$$

$$p(V, P_2) = \frac{e^{-\beta P_2 V} Z(T, V)}{Z_{NPT}(T, P_2)}$$

$$\frac{p(V, P_2)}{p(V, P_1)} = \frac{e^{-\beta P_2 V} \cancel{Z(T, V)}}{e^{-\beta P_1 V} \cancel{Z(T, V)}} \frac{Z_{NPT}(T, P_1)}{Z_{NPT}(T, P_2)} =$$

$$p(V, P_2) = p(V, P_1) \cdot e^{-\beta(P_2 - P_1)V} \quad k \quad (1)$$

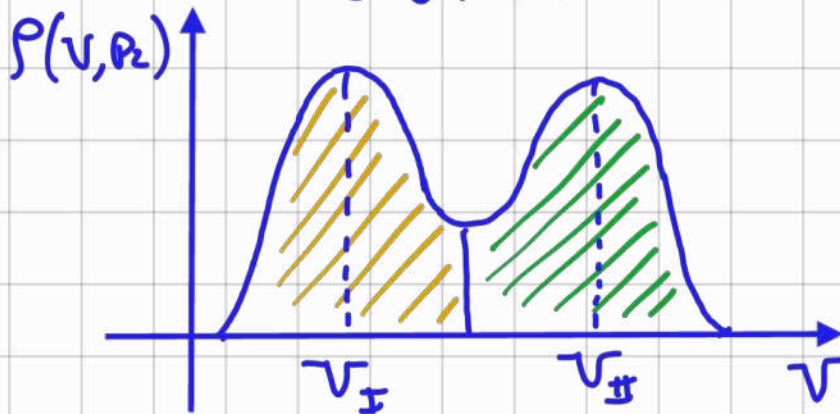
WHERE $k = \frac{Z_{NPT}(T, P_1)}{Z_{NPT}(T, P_2)}$ ← WHICH IS INDEPENDENT OF V (NORMALIZATION)



$$P_1 > P^*$$

BY USING EQ. (1)

WE CAN SEARCH FOR P_2 SUCH THAT THE TWO FOLLOWING AREAS (/// AND ///) ARE EQUAL (I.E. THE TWO PHASES ARE EQUALLY LIKELY)



HISTOGRAM REWEIGHTING

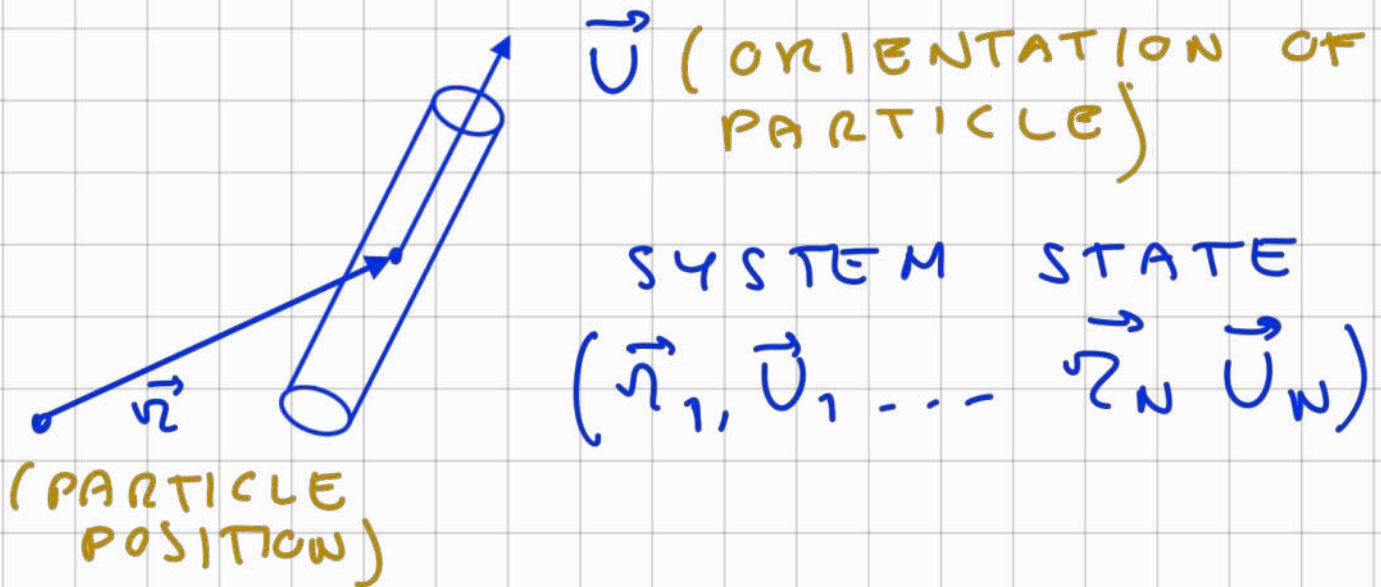
$$p_I = \frac{N}{V_I} \quad p_{II} = \frac{N}{V_{II}}$$

IF WE ARE NOT AT COEXISTENCE WE CAN EMPLOY HISTOGRAM REWEIGHTING, ANYWAY WE HAVE TO BE CLOSE ENOUGH ($P_1 \approx P^*$) SO THAT $p(V_{II}, P_1)$ IS NOT NEGLECTIBLE (WITHIN SIMULATION TIMES)

SHOW histogram-reweighting. nb (MATHEMATICA)

ORIENTATIONAL MOVES

UNIAXIAL PARTICLE
(E.G. CYLINDERS)



CHOOSE RANDOMLY WHETHER
DOING A TRANSLATIONAL OR A
ROTATIONAL MOVE

TRANSLATIONAL MOVE IS LIKE
WE ALREADY DISCUSSED

ROTATIONAL

TRIAL MOVE ($\alpha(0 \rightarrow n)$)

$$\vec{U}_0 \rightarrow \vec{U}_n = \frac{\vec{U}_0 + \gamma \Delta \vec{U}}{\|\vec{U}_0 + \gamma \Delta \vec{U}\|}$$

WHERE $\Delta \vec{U}$ IS A RANDOM UNIT
VECTOR (MARSAGLIA ALGORITHM)

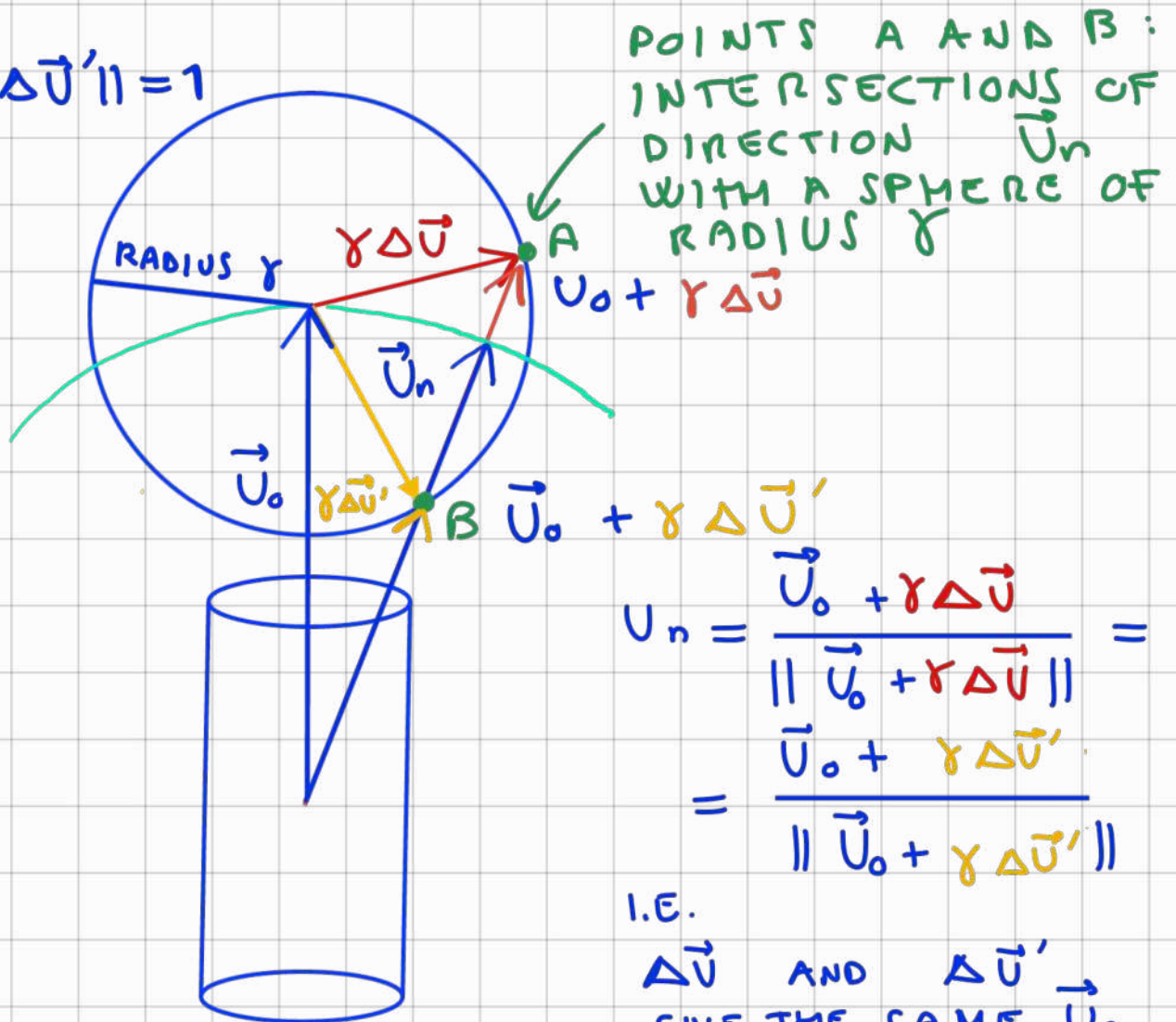
γ MUST BE OPTIMIZED AS $\int$
ACCEPTANCE DOES NOT CHANGE

THIS MOVE IS SYMMETRIC, I.E.

$$q(0 \rightarrow n) = q(n \rightarrow 0)$$

$$q(0 \rightarrow n)$$

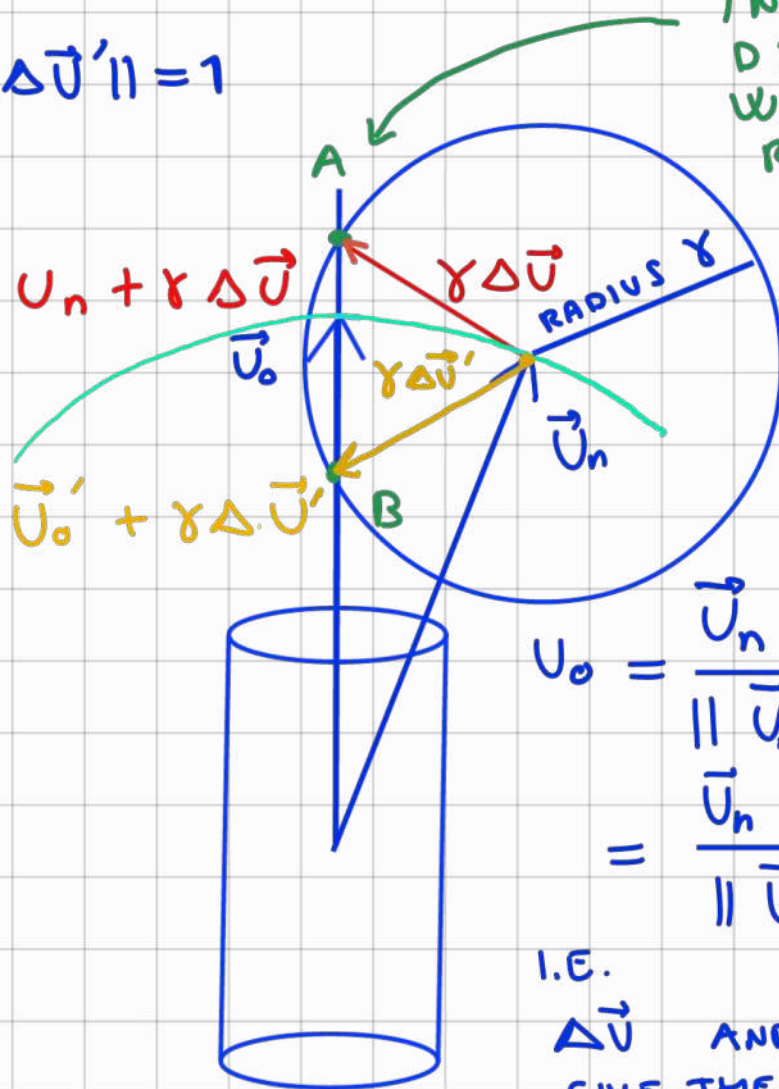
$$\|\Delta \vec{U}\| = \|\Delta \vec{U}'\| = 1$$



IF YOU DO SAME CONSTRUCTION
FROM $\vec{U}_n$ YOU WILL HAVE THAT
PROBABILITY IS THE SAME
(CHANCE OF GENERATING TWO
ORIENTATIONS ON UNIT SPHERE)
INDEED:

$$\alpha(n \rightarrow 0)$$

$$\|\Delta \vec{U}\| = \|\Delta \vec{U}'\| = 1$$



POINTS A AND B.
INTERSECTIONS OF
DIRECTION $\vec{U}_0$
WITH A SPHERE OF
RADIUS γ

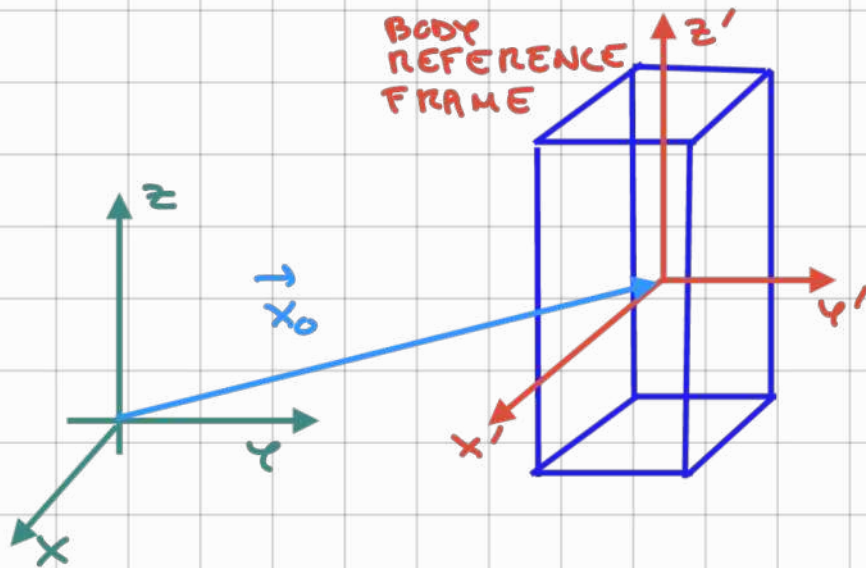
$$\begin{aligned} \vec{U}_0 &= \frac{\vec{U}_n + \gamma \Delta \vec{U}}{\|\vec{U}_n + \gamma \Delta \vec{U}\|} = \\ &= \frac{\vec{U}_n + \gamma \Delta \vec{U}'}{\|\vec{U}_n + \gamma \Delta \vec{U}'\|} \end{aligned}$$

I.E.
 $\Delta \vec{U}$ AND $\Delta \vec{U}'$
GIVE THE SAME $\vec{U}_0$

HENCE $\alpha(0 \rightarrow n) = \alpha(n \rightarrow 0)$, I.E.

PROBABILITY IS THE SAME BEING
THE CHANCE OF GENERATING TWO
ORIENTATIONS ON UNIT SPHERE

NOT UNIAXIAL PARTICLES



BODY
REFERENCE
FRAME

SYSTEM STATE
 $(\vec{\pi}_1, \Omega_1, \dots, \vec{\pi}_N, \Omega_N)$

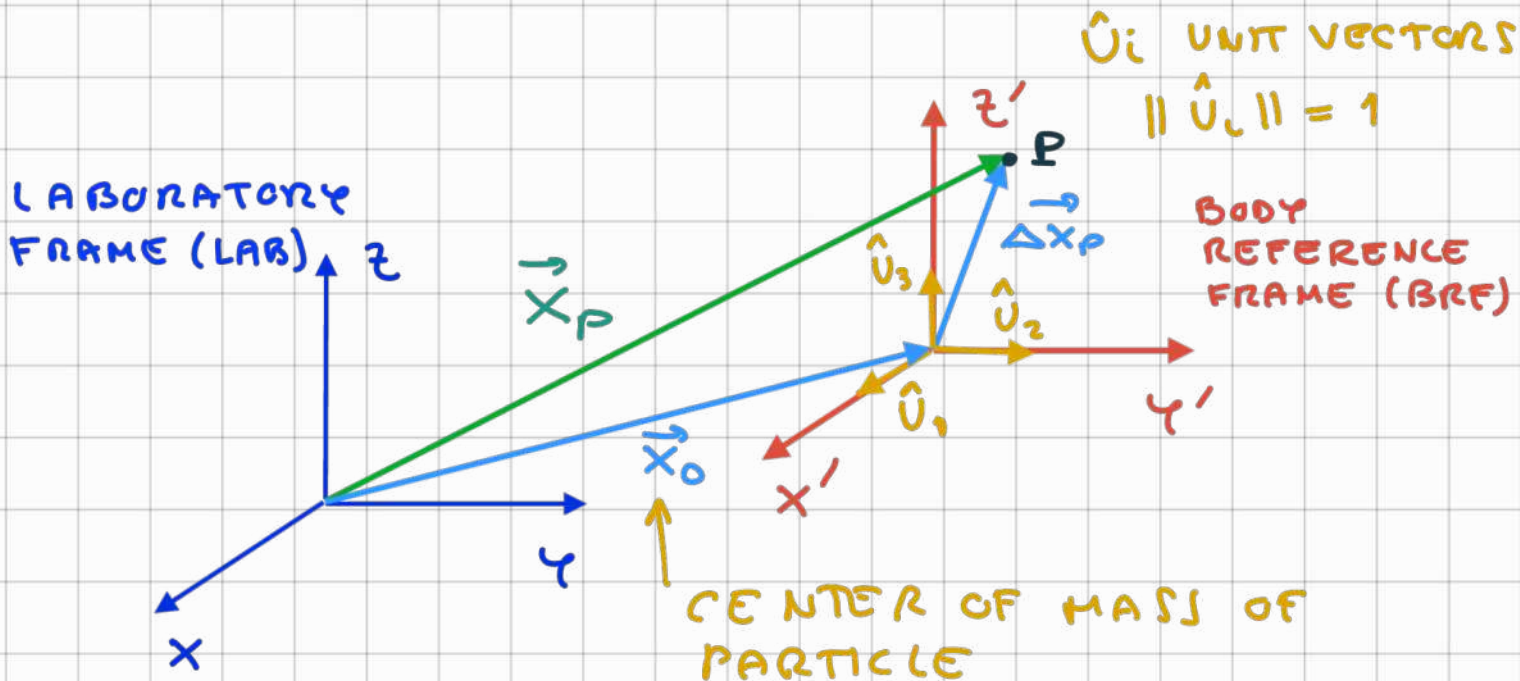
E.G. $\Omega_i = (\theta_i, \psi_i, \phi_i)$
EULER ANGLES

ALTERNATIVE TO EULER ANGLES
ROTATION MATRIX R SUCH THAT

$$\vec{x}' = R(\vec{x} - \vec{x}_0)$$

↑ BODY REFERENCE FRAME ↑ LABORATORY FRAME

CLOSER LOOK TO ROTATION MATRIX



$\hat{u}_i$ UNIT VECTORS
 $\|\hat{u}_i\| = 1$

BODY
REFERENCE
FRAME (BRF)

CENTER OF MASS OF
PARTICLE

$$\vec{x}_p = (x, y, z) \quad \text{LAB}$$

$$\vec{x}'_p = (x', y', z') \quad \text{BRF}$$

$$\vec{x}_p = \vec{x}_0 + (\vec{x}_p - \vec{x}_0) = \vec{x}_0 + \Delta \vec{x}_p$$

VECTORS WHOSE COORDINATES
ARE EXPRESSED IN LAB FRAME

$$\vec{\Delta X}_P = \vec{x}' \hat{U}_1 + \vec{y}' \hat{U}_2 + \vec{z}' \hat{U}_3$$

BREF COORDINATES OF P

I.E.

$$\vec{\Delta X}_P = \begin{pmatrix} \hat{U}_1 & \hat{U}_2 & \hat{U}_3 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} =$$

INTENDED AS COLUMN VECTORS

$$= \begin{pmatrix} \hat{U}_1 & \hat{U}_2 & \hat{U}_3 \end{pmatrix} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix}$$

COLUMN VECTORS

IF WE DEFINE

$$R \equiv \begin{pmatrix} U_{1x} & U_{1y} & U_{1z} \\ U_{2x} & U_{2y} & U_{2z} \\ U_{3x} & U_{3y} & U_{3z} \end{pmatrix}$$

← EACH ROW IS A UNIT VECTOR

THEN

$${}^t R = \begin{pmatrix} U_{1x} & U_{2x} & U_{3x} \\ U_{1y} & U_{2y} & U_{3y} \\ U_{1z} & U_{2z} & U_{3z} \end{pmatrix}$$

TRANSPOSE OF R

SO THAT

$$\vec{\Delta X}_P = {}^t R \vec{x}'$$

NOTE THAT:

$${}^t R R = \mathbb{I}$$

$$\text{HENCE } {}^t R = R^{-1}$$

I.E.

$$\vec{X}_P = \vec{X}_0 + {}^t R \vec{x}'$$

BREF

$$\vec{x}' = R (\vec{X}_P - \vec{X}_0)$$

GIVEN A POINT IN THE BODY REFERENCE FRAME ITS COORDINATES IN THE LAB

REFERENCE FRAME CAN BE OBTAINED THROUGH THE ROTATION MATRIX

IF WE ROTATE A PARTICLE BY AN ANGLE $\Delta\theta$ AROUND AN AXIS $\hat{U}_R = (U_x \ U_y \ U_z)$

WE HAVE

$$R' = R (I + M(\Delta\theta)) \quad (1)$$

WHERE

IDENTITY MATRIX
A MATRIX DEFINED IN THE FOLLOWING

$$M(\Delta\theta) = -\sin(\Delta\theta) \Omega + (1 - \cos(\Delta\theta)) \Omega^2$$

WITH

$$\Omega = \begin{pmatrix} 0 & -U_z & U_y \\ U_z & 0 & -U_x \\ -U_y & U_x & 0 \end{pmatrix}$$

COORDINATES OF ROTATION AXIS IN THE LAB FRAME

HENCE A ROTATIONAL TRIAL MOVE $\alpha(0 \rightarrow n)$ OF PARTICLE i

$$(\vec{r}_i, R_i) \rightarrow (\vec{r}_i, \vec{R}_i')$$

OLD(i)

NEW(n)

R_i IS UPDATED ACCORDING TO EQ. (1)

WHERE $\hat{U}_R$ IS CHOSEN RANDOMLY ON THE UNIT SPHERE AND $\Delta\theta$ IS RANDOM

I.E. $\Delta\theta = \Delta\theta_{\max} \xi_\theta$ WITH $\xi_\theta \in [-1, 1]$

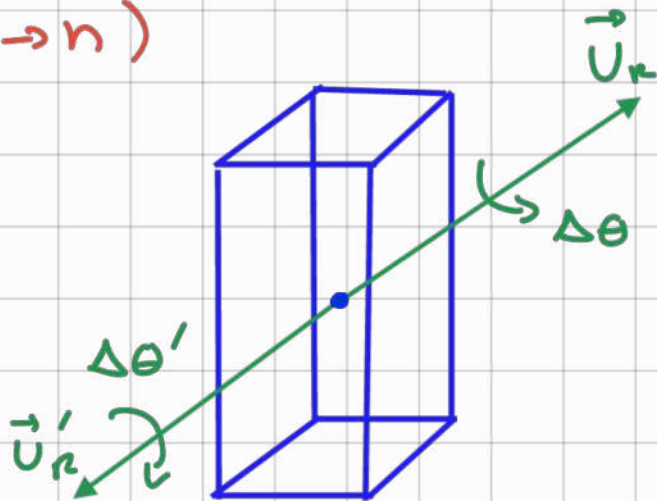
WHERE $\Delta\theta_{\max}$ MUST BE OPTIMIZED IN ORDER TO HAVE AN ACCEPTANCE RATIO FOR ROTATIONAL MOVE AROUND 30-50%

$$\alpha(0 \rightarrow n) = \alpha(n \rightarrow 0)$$

NOTE THAT THIS MOVE IS SYMMETRIC SINCE TO GO BACK WE HAVE TO CHOOSE SAME ORIENTATION $\hat{U}_R$ AND A ROTATION ANGLE $-\Delta\theta$

THIS ORIENTATIONAL MOVE IS SYMMETRIC
 $d(o \rightarrow n) = d(n \rightarrow o)$

$d(o \rightarrow n)$



I: $\vec{U}_R \quad \Delta\theta$ AND

II: $\vec{U}'_R = -\vec{U}_R \quad \Delta\theta' = -\Delta\theta$

GIVE SOME NEW ORIENTATION

REMEMBER THAT $R^n = R^o(I + M(\Delta\theta))$ WITH
 $M(\Delta\theta) = -\sin(\Delta\theta)\Omega + (1 - \cos(\Delta\theta))\Omega^2$

IF $\vec{U} \rightarrow -\vec{U}$ AND $\Delta\theta \rightarrow -\Delta\theta$

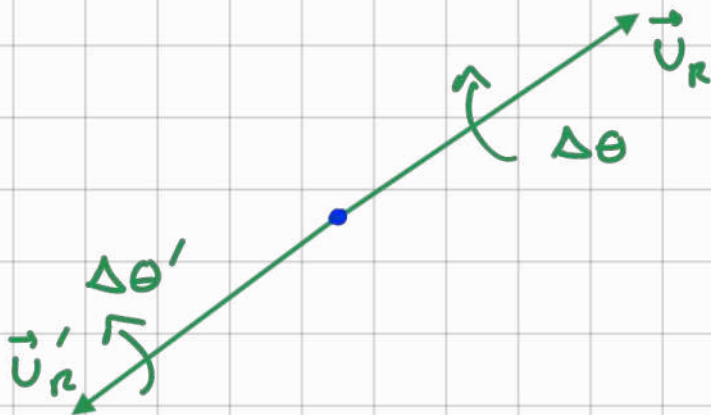
$\sin(\Delta\theta) \rightarrow -\sin(\Delta\theta)$

$\cos(\Delta\theta) \rightarrow \cos(-\Delta\theta) = \cos(\Delta\theta)$

$\Omega \rightarrow -\Omega$

HENCE M IS IDENTICAL FOR ROTATIONS I AND II

$d(n \rightarrow o)$



ROTATIONS

$\vec{U}_R \quad -\Delta\theta$ AND

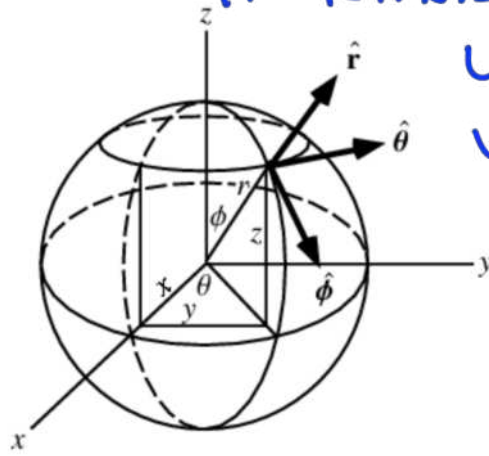
$\vec{U}'_R = -\vec{U}_R \quad \Delta\theta' = \Delta\theta$

GIVE SAME OLD ORIENTATION

HENCE $d(o \rightarrow n) = d(n \rightarrow o)$

FOR GENERATING

A RANDOM UNIT VECTOR
LEAD TO
WRONG RESULTS



$$d\Omega = \sin \theta d\theta d\phi$$

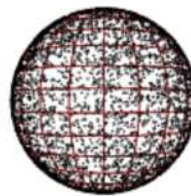
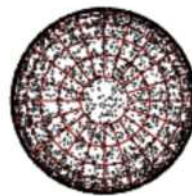
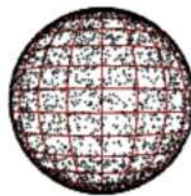
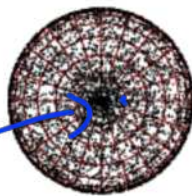
Sphere Point Picking

top view

side view

top view

side view



incorrectly distributed points

correctly distributed points

To pick a random point on the surface of a **unit sphere**, it is incorrect to select **spherical coordinates** θ and ϕ from uniform distributions $\theta \in [0, 2\pi)$ and $\phi \in [0, \pi]$, since the area element $d\Omega = \sin \phi d\theta d\phi$ is a function of ϕ , and hence points picked in this way will be "bunched" near the poles (left figure above).

HIGHER PROBABILITY AT POLES

SEE MARSAGLIA ALGORITHM
FOR A CORRECT WAY OF
RANDOM UNIT VECTORS

ANOTHER POSSIBILITY:

QUATERNIONS

REPRESENTS PARTICLE ORIENTATION

$$\vec{q} = (q_0, q_1, q_2, q_3) \quad \|\vec{q}\| = 1$$

INDEED EACH CAN BE MAPPED TO A ROTATION MATRIX AND VICE-VERSA

$$R \rightarrow \vec{q}$$

second

$$q_{IB} = \begin{bmatrix} \cos(\psi/2) \\ 0 \\ 0 \\ \sin(\psi/2) \end{bmatrix} \begin{bmatrix} \cos(\theta/2) \\ 0 \\ \sin(\theta/2) \\ 0 \end{bmatrix} \begin{bmatrix} \cos(\phi/2) \\ \sin(\phi/2) \\ 0 \\ 0 \end{bmatrix}$$

EULER ANGLES

$$= \begin{bmatrix} \cos(\phi/2) \cos(\theta/2) \cos(\psi/2) + \sin(\phi/2) \sin(\theta/2) \sin(\psi/2) \\ \sin(\phi/2) \cos(\theta/2) \cos(\psi/2) - \cos(\phi/2) \sin(\theta/2) \sin(\psi/2) \\ \cos(\phi/2) \sin(\theta/2) \cos(\psi/2) + \sin(\phi/2) \cos(\theta/2) \sin(\psi/2) \\ \cos(\phi/2) \cos(\theta/2) \sin(\psi/2) - \sin(\phi/2) \sin(\theta/2) \cos(\psi/2) \end{bmatrix}$$

EULER ANGLES CAN BE OBTAINED FROM THE ROTATION MATRIX

$$\vec{q} \rightarrow R$$

$$R = \begin{bmatrix} 1 - 2(q_2^2 + q_3^2) & 2(q_1 q_2 - q_0 q_3) & 2(q_0 q_2 + q_1 q_3) \\ 2(q_1 q_2 + q_0 q_3) & 1 - 2(q_1^2 + q_3^2) & 2(q_2 q_3 - q_0 q_1) \\ 2(q_1 q_3 - q_0 q_2) & 2(q_0 q_1 + q_2 q_3) & 1 - 2(q_1^2 + q_2^2) \end{bmatrix}$$

STATE OF THE SYSTEM

$$(\vec{n}_1, \vec{q}_1, \dots, \vec{n}_N, \vec{q}_N) \quad \|\vec{q}_i\| = 1$$

THE ROTATIONAL TRIAL MOVE $\alpha(0 \rightarrow n)$
CONSISTS IN DOING:

$$\vec{q}_n = \frac{\vec{q}_0 + \gamma \Delta \vec{q}}{\|\vec{q}_0 + \gamma \Delta \vec{q}\|}$$

γ MUST BE
OPTIMIZED
LIKE δ FOR
TRANSLATIONS

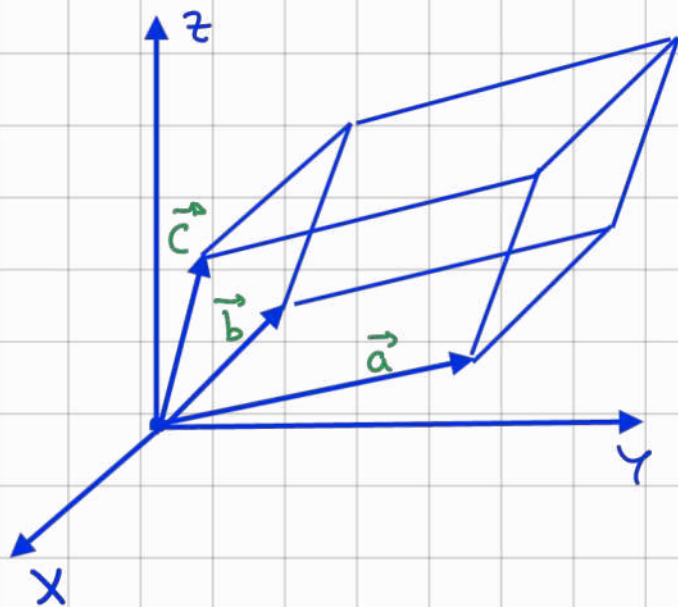
WHERE $\Delta \vec{q}$ IS A UNIT RANDOM VECTOR
ON THE 4D UNIT SPHERE
(AGAIN BY USING MARSAGLIA
ALGORITHM)

$$\gamma = \gamma_{\max} \xi_{\gamma} \quad \xi_{\gamma} \in [-1, 1]$$

AND $\gamma_{\max}$ MUST BE OPTIMIZED
TO HAVE 30-50% ACCEPTANCE
RATE OF ORIENTATIONAL MOVES

PARRINELLO-RAHMAN

ALLOW FOR CHANGES OF BOX SHAPE



$$\vec{a} = (a_x, a_y, a_z)$$

$$\vec{b} = (b_x, b_y, b_z)$$

$$\vec{c} = (c_x, c_y, c_z)$$

↑
EDGES OF SIMULATION
BOX
(NOT ORTHOGONAL)

$$Q = \frac{(V_0 - V)^{M-N}}{\underbrace{\Lambda^{3(M-N)} (M-N)!}_{\text{HEAT BATH}}}$$

$$\left. \frac{e^{-\beta U_N}}{\Lambda^{3N} N!} \right\} \int d^N \vec{r}$$

OUR SYSTEM
WITH NON ORTHOGONAL
EDGES

REDUCED COORDINATES

$$\vec{r}_i = \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} \vec{s}_i$$

||
M

NOTE THAT IF M =

WE HAVE STANDARD

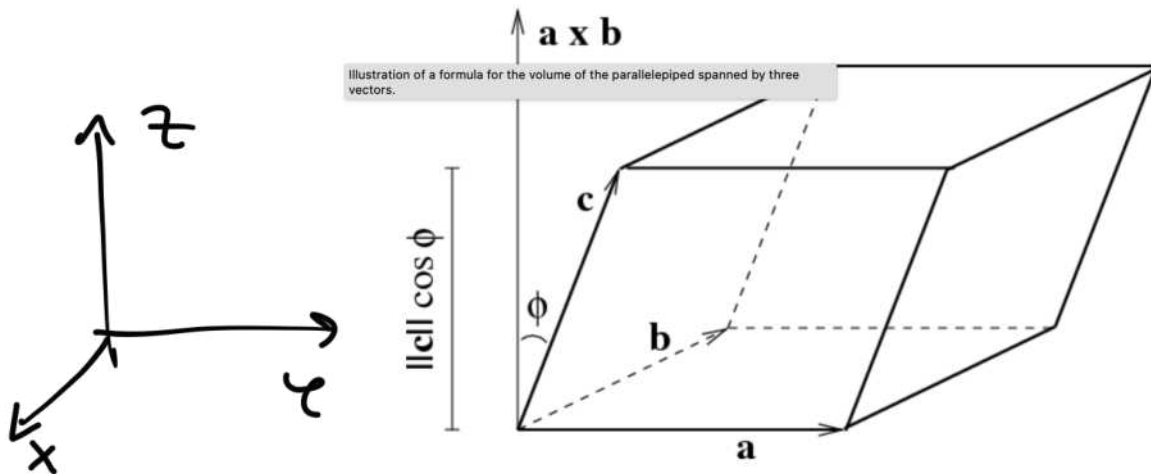
NPT ENSEMBLE

$$\begin{pmatrix} L & 0 & 0 \\ 0 & L & 0 \\ 0 & 0 & L \end{pmatrix}$$

$$Q = \frac{(\sqrt{V-V_0})^{M-N}}{\sqrt[3]{(M-N)!}} \int \frac{e^{-\beta U_N}}{\sqrt[3]{N!}} |\det M|^N d^N \xi$$

BUT

BOX VOLUME



This formula for the volume can be understood from the above figure. The volume of the parallelepiped is the area of the base times the height. From the **geometric definition of the cross product**, we know that its magnitude, $\|\mathbf{a} \times \mathbf{b}\|$, is the area of the parallelogram base, and that the direction of the vector $\mathbf{a} \times \mathbf{b}$ is perpendicular to the base. The height of the parallelepiped is the component of $\mathbf{c}$ in the direction normal to the base, i.e., in the direction of $\mathbf{a} \times \mathbf{b}$. Hence the height is $\|\mathbf{c}\| |\cos \phi|$, where ϕ is the angle between $\mathbf{c}$ and $\mathbf{a} \times \mathbf{b}$. (Why do we need the absolute value? If we swapped the locations of $\mathbf{a}$ and $\mathbf{b}$, in the above figure, then $\mathbf{a} \times \mathbf{b}$ would point downward. The angle ϕ would be larger than $\pi/2$, and $\cos \phi$ would be negative.)

$$V = | \vec{c} \cdot (\vec{a} \times \vec{b}) | = \det \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix}$$

$\parallel$
 M

$$= \det M$$

SO THAT

$$p(V, \xi_1, \dots, \xi_N) \propto e^{-\beta U_N} e^{-\beta P V} V^N$$

AND

$$acc(o \rightarrow r) = \min \left\{ 1, \frac{p(V', \xi_1', \dots, \xi_N')}{p(V, \xi_1, \dots, \xi_N)} \right\} =$$

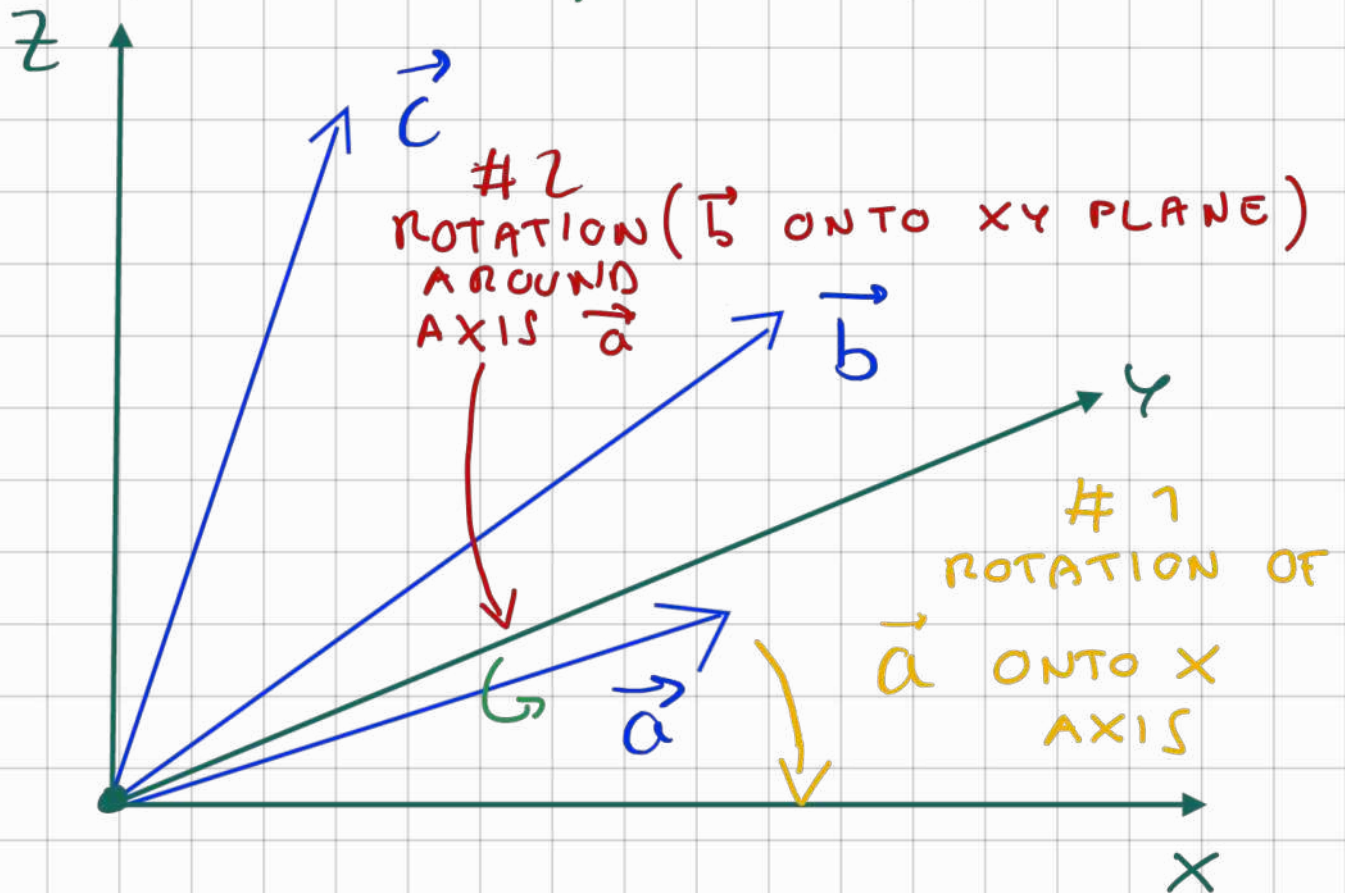
$$\min \{ 1, e^{-\beta \Delta G} \}$$

$$G = U + PV - k_B T N \ln V$$

IN GENERAL

$$M = \begin{pmatrix} a_x & b_x & c_x \\ 0 & b_y & c_y \\ 0 & 0 & c_z \end{pmatrix}$$

BY DOING #1
AND #2 WE
CAN REDUCE TO
THIS MATRIX



XYZ IS THE LAB FRAME

SPECIAL CASES

1)

$$M = \begin{pmatrix} \delta L_x & 0 & 0 \\ 0 & \delta L_x & 0 \\ 0 & 0 & \delta L_z \end{pmatrix}$$

ANISOTROPIC BCX
(I.E. NOT CUBIC)
BUT ISOTROPIC
VOLUME MOVES

IN THIS CASE δ CHANGES RANDOMLY
IN A VOLUME MOVE, I.E.

$$\gamma' = \gamma + \Delta\gamma$$

$$\Delta\gamma = \Delta\gamma_0 \eta$$

$\eta \in [-1, 1]$ IS A
STOCHASTIC VARIABLE

2) $M = \begin{pmatrix} L_x & 0 & 0 \\ 0 & L_y & 0 \\ 0 & 0 & L_z \end{pmatrix}$ ANISOTROPIC BOX
WHERE THE 3
EDGE SIZE CAN
CHANGE INDEPENDENTLY

IN A VOLUME MOVE A DIRECTION α IS
SELECTED RANDOMLY AND

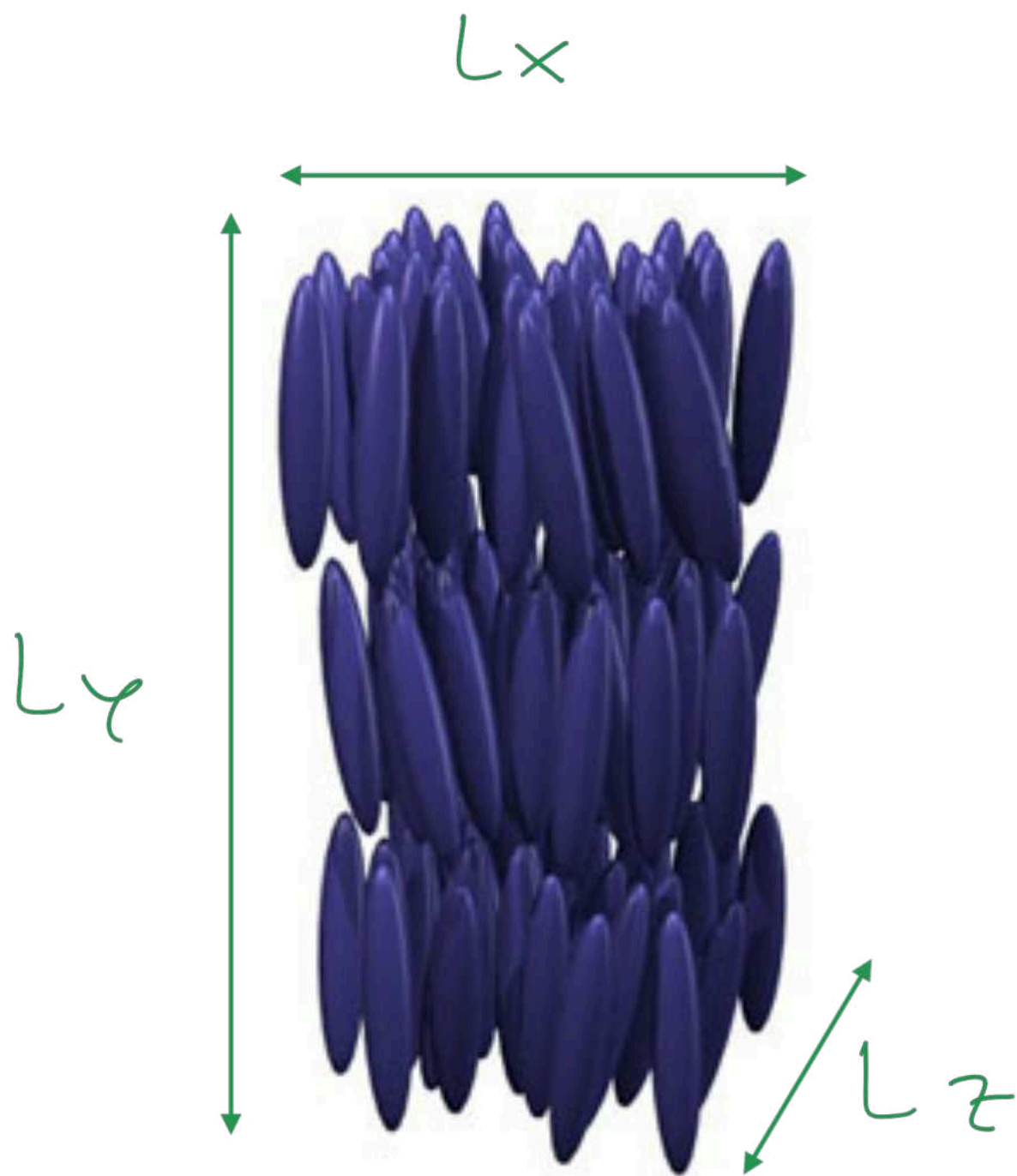
$$L'_\alpha = L_\alpha + \Delta L$$

WHERE $\alpha \in \{x, y, z\}$

AND $\Delta L = \Delta L_0 \eta \quad \eta \in [-1, 1]$

THIS TYPE OF MOVE [↑]RANDOM
CAN BE USEFUL FOR CRYSTALS
AND LIQUID CRYSTALS
(SEE BELOW)

EXAMPLE: SMECTIC PHASE



$$L_y \neq L_x, L_z$$