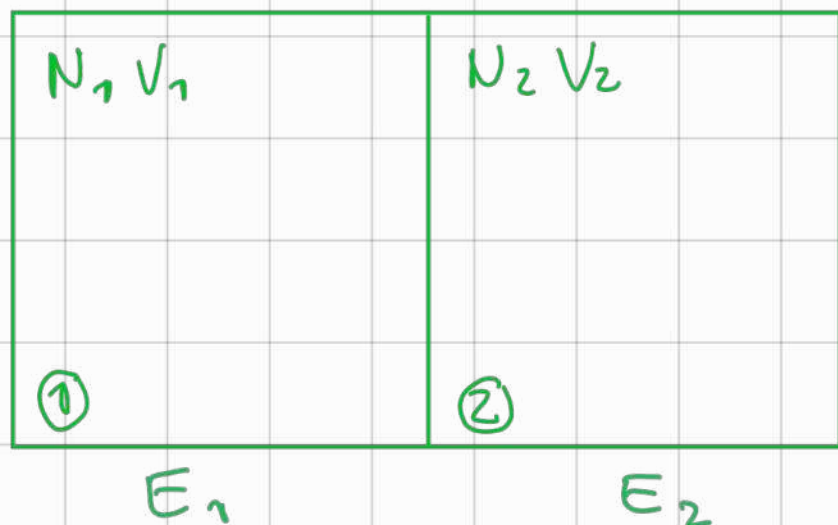


28/09/26

- RECALL OF STATISTICAL MECHANICS / NOTATION
- EQUILIBRATION
- MICROCANONICAL ENSEMBLE
- NTV ENSEMBLE

MICROCANONICAL ENSEMBLE



HYPOTHESES

- ISOLATED SYSTEM
- ① AND ② WEAKLY COUPLED
- MICROSCOPIC EQUIPROBABILITY

TOTAL ENERGY

$$E = E_1 + E_2 \Rightarrow E_2 = E - E_1$$

E IS CONSERVED

LET

$$\Omega_1(E_1) = \left\{ \# \text{ MICROSCOPIC STATES OF SYSTEM ① WITH ENERGY } E_1 \right\}$$

$$\Omega_2(E_2) = \left\{ \# \text{ MICROSCOPIC STATES OF SYSTEM ② WITH ENERGY } E_2 \right\}$$

TOTAL NUMBER OF MICROSCOPIC STATES

$$\Omega(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2)$$

Ω , Ω_1 AND Ω_2 ARE HUGE
HENCE USE OF LOGARITHM
CONVENIENT, I.E.

$$\ln [\Omega(E_1, E_2)] = \ln [\Omega_1(E_1)] + \ln [\Omega_2(E_2)]$$

BUT $E_2 = E - E_1$ SO THAT

$$\ln [\Omega(E_1, E - E_1)] = \ln [\Omega_1(E_1)] + \ln [\Omega_2(E - E_1)]$$

QUESTION:

WHAT IS THE MOST LIKELY
VALUE OF E_1 ?

WE MUST ENFORCE THE
CONDITION

$$\frac{\partial \ln [\Omega(E_1, E - E_1)]}{\partial E_1} = 0$$

I.E.



$$\frac{\partial \ln[\Omega_1(E_1)]}{\partial E_1} - \frac{\partial \ln[\Omega_2(E_2)]}{\partial E_2} \Big|_{E_2 = E - E_1} = 0$$

$$\frac{\partial \ln[\Omega_1(E_1)]}{\partial E_1} = \frac{\partial \ln[\Omega_2(E_2)]}{\partial E_2} \Big|_{E_2 = E - E_1}$$

IF WE DEFINE

$$\frac{\partial \ln \Omega_1(E_1)}{\partial E_1} \Big|_{N_1, V_1} = \beta_1$$

$$\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} \Big|_{N_2, V_2} = \beta_2$$

9 WE HAVE THE CONDITION:

$$\beta_1 = \beta_2$$

WHAT DOES IT MEAN?

$$[\beta] = \frac{1}{[E]}$$

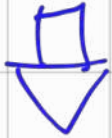
DEFINE

$$S \equiv k_B \ln[\Omega(N, V, E)] = S(N, V, E)$$

AND WE CALL IT ENTROPY

WE HAVE THAT

$$\frac{\partial (k_B \ln \Omega_1(E_1))}{k_B \partial E_1} = \frac{\partial (k_B \ln \Omega_2(E_2))}{k_B \partial E_2}$$



$$\frac{1}{k_B} \frac{\partial S_1}{\partial E_1} = \frac{1}{k_B} \frac{\partial S_2}{\partial E_2}$$

$$\text{BUT } \left[\frac{\partial S}{\partial E_1} \right] = \frac{1}{[T]}$$

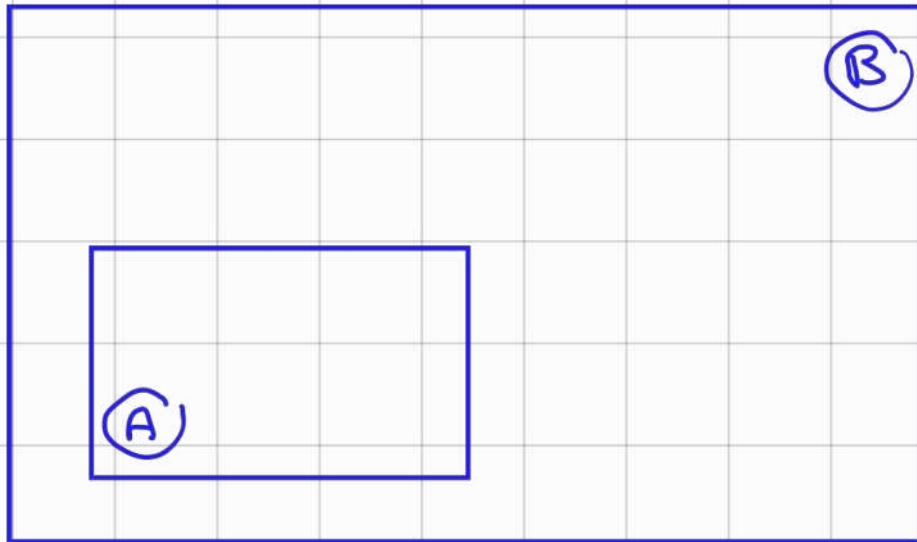
HENCE

$$\frac{1}{k_B T_1} = \frac{1}{k_B T_2}$$

i. e. $\boxed{T_1 = T_2}$ EQUILIBRIUM CONDITION.

AND $\beta_1 = \frac{1}{k_B T}$ $\beta_2 = \frac{1}{k_B T}$

CANONICAL ENSEMBLE



HYPOTHESES

- SYSTEM IS ISOLATED
- $E_A \ll E_B$ (I.E. (B) IS A THERMAL BATH)
- (A) AND (B) WEAKLY COUPLED

$|i\rangle$ QUANTUM STATE OF (A)

$P_i = \{ \text{PROBABILITY FOR (A) OF BEING IN STATE } |i\rangle \}$

GOAL IS TO CALCULATE P_i

$E_i = \{ \text{ENERGY OF (A) BEING IN STATE } |i\rangle \}$

$$E_i + E_B = E$$

$$\Omega(i, E_B) = \Omega(i, E - E_i)$$

$$= \Omega_A(i) \cdot \Omega_B(E - E_i)$$

AND WE CAN DEFINE THE FOLLOWING PROBABILITY

$$P_i \equiv \frac{\Omega(i, E_B)}{\sum_i \Omega(i, E_B)}$$

AGAIN WE MAKE USE OF LOGARITHM

$$\ln \Omega(i, E - E_i) =$$

$$\ln \Omega_A(i) + \ln \Omega_B(E - E_i)$$

BUT $E_i \ll E$ HENCE

$$\underbrace{\ln \Omega_B(E - E_i)}_{\approx} \ln \Omega_B(E) - E_i \frac{\partial \ln \Omega_B}{\partial E_B} \Big|_{E_B = E - E_i}$$

MOREOVER

$$\Omega_A(i) = 1 \Rightarrow \ln \Omega_A(i) = 0$$

THUS HAVING

$$\ln \Omega(i, E - E_i) \approx$$

$$\ln \Omega_B(E) - \beta E_i$$

BY PLUGGING THIS INTO P_i
DEFINITION ONE HAS

$$P_i = \frac{\cancel{\Omega_B(E)} e^{-\beta E_i}}{\sum_i \cancel{\Omega_B(E)} \cdot e^{-\beta E_i}} =$$

$$= \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

IF WE DEFINE $Q = \sum_i e^{-\beta E_i}$
WE HAVE:

$$P_i = \frac{e^{-\beta E_i}}{Q}$$

Q IS CALLED THE

PARTITION FUNCTION

FROM Q ONE CAN CALCULATE
THE INTERNAL ENERGY U:

$$U \equiv \underline{\langle E \rangle} = \frac{1}{Q} \sum_i E_i e^{-\beta E_i} =$$

$$\text{BUT } \frac{\partial \ln Q}{\partial \beta} = \frac{\partial}{\partial \beta} \left(\sum_i e^{-\beta E_i} \right) =$$

$$= - \frac{1}{Q} \sum_i E_i e^{-\beta E_i} = -U$$

HENCE

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

Q. IS THERE A RELATION
BETWEEN FREE ENERGY
AND Q?

FROM THERMODYNAMIC:

$$F = U - TS \quad F = F(T, V)$$

$$\left. \frac{\partial (F/T)}{\partial (1/T)} \right|_V = \frac{1}{T} \frac{\partial F}{\partial (1/T)} + F =$$

$$= \frac{1}{T} \frac{\partial F}{\partial T} \bigg|_V \frac{\partial T}{\partial (1/T)} + F =$$

$$= \frac{1}{T} \frac{\partial F}{\partial T} \bigg|_V \frac{1}{\frac{\partial(1/T)}{\partial T}} + F =$$

$$= -T \frac{\partial F}{\partial T} \bigg|_V + F = \frac{\partial(F/T)}{\partial(1/T)} \bigg|_V$$

BUT $\frac{\partial F}{\partial T} \bigg|_V = -S$ HENCE

$$= TS + F = \cancel{TS} + U - \cancel{TS}$$

$$= U \quad \text{i.e.}$$

$$\frac{\partial(F/T)}{\partial(1/T)} = U = - \frac{\partial(\ln Q)}{\partial \beta} = \frac{\partial(\ln Q)}{\partial \left(\frac{1}{k_B T}\right)}$$

FROM WHICH FOLLOWS THAT

$$Q = \sum_i e^{-\beta E_i}$$

$$\frac{F}{T} = -k_B \ln Q$$

$$F = -k_B T \ln Q$$

WORKHORSE OF STATISTICAL
MECHANICS

CLASSICAL LIMIT OF STATISTICAL MECHANICS

[$\hbar \rightarrow 0$]

LET $\hat{A}$ BE AN OBSERVABLE

$$\langle \hat{A} \rangle = \frac{\sum_i \langle i | \hat{A} | i \rangle e^{-\beta E_i}}{Q} \quad p_i = \frac{e^{-\beta E_i}}{Q}$$

↑ STATISTICAL AVERAGE

↓ AUTOSTATES OF $\hat{\mathcal{H}}$

WHERE $\hat{\mathcal{H}} |i\rangle = E_i |i\rangle$

INSTEAD OF EIGENSTATES OF $\hat{\mathcal{H}}$ WE CAN USE A GENERIC COMPLETE SET, I.E.

$$\langle \hat{A} \rangle = \frac{\sum_{|\alpha\rangle} \langle \alpha | \hat{A} e^{-\beta \hat{\mathcal{H}}} | \alpha \rangle}{Q}$$

WHERE $|\alpha\rangle$ IS A COMPLETE (*) SET OF STATES, I.E.

$$\sum_{\alpha} |\alpha\rangle \langle \alpha| = \mathbb{I}$$

↑ IDENTITY

↑ ARBITRARY!
NOW DIAGONAL TERMS ARE 0 → POSTULATE (SEE HUANG 8.7)

LET'S ASSUME FURTHER THAT

$$\hat{A} = \hat{A}(\hat{q}) \quad \hat{\mathcal{H}} = \hat{K}(\hat{p}) + \hat{V}(\hat{q})$$

$$\text{WITH} \quad \hat{K} = \sum_{i=1}^N \frac{\hat{p}_i^2}{2m} \quad \hat{V} = \sum_{i=1}^N \frac{k}{2} \hat{q}_i^2$$

(*) NOT NECESSARILY ORTHONORMAL

$$\int d^3q |q\rangle \langle q| = \mathbb{1}$$

$$\int d^3p |p\rangle \langle p| = \mathbb{1}$$

SO THAT

$$\langle \hat{A} \rangle = \frac{\int d^3q \langle q | \hat{A} e^{-\beta \hat{H}} | q \rangle}{\int d^3q \langle q | e^{-\beta \hat{H}} | q \rangle}$$

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad \text{④}$$

YOU CAN EASILY PROVE THAT:

$$[\hat{A}, \hat{B}\hat{C}] = \hat{B}[\hat{A}, \hat{C}] + [\hat{A}, \hat{B}]\hat{C} \quad (1)$$

AND

$$[\hat{A}\hat{B}, \hat{C}] = \hat{A}[\hat{B}, \hat{C}] + [\hat{A}, \hat{C}]\hat{B} \quad (2)$$

FROM THESE, IF $F(\hat{p})$ AND $G(\hat{q})$ ARE SMOOTH FUNCTIONS OF $\hat{p}$ AND $\hat{q}$ RESPECTIVELY, ONE HAS

$$[\hat{q}, F(\hat{p})] = i\hbar \frac{\partial F(\hat{p})}{\partial \hat{p}} \quad (3)$$

AND

$$\underbrace{[\hat{p}, G(\hat{q})]} = -i\hbar \frac{\partial G(\hat{q})}{\partial \hat{q}} \quad (4)$$

[SEE SAKURAI]
SEC. 2.2 PAG. 15

WE HAVE:

$$-\beta \hat{\mathcal{H}} = -\beta \hat{K} - \beta \hat{V}$$

BCH FORMULA TELLS US

$$e^{\hat{A}} e^{\hat{B}} = e^{\hat{A} + \hat{B} + \frac{1}{2} [\hat{A}, \hat{B}] + \frac{1}{12} ([\hat{A}, [\hat{A}, \hat{B}]] + \dots$$

$$\dots + [\hat{B}, [\hat{B}, \hat{A}]] + \dots} e^{\hat{A} + \hat{B}} = -\beta \hat{\mathcal{H}}$$

IF WE SET $\hat{A} = -\beta \hat{K}$ AND

$$\hat{B} = -\beta \hat{V} \quad \text{BCH FORMULA YIELDS:}$$

$$e^{-\beta \hat{K}} e^{-\beta \hat{V}} \approx e^{-\beta (\hat{K} + \hat{V} + \frac{1}{2} [\hat{K}, \hat{V}] + \dots + \frac{1}{12} ([\hat{K}, [\hat{K}, \hat{V}]] + [\hat{V}, [\hat{V}, \hat{K}]]))}$$

$$\text{BUT } [\hat{K}, \hat{V}] = \frac{\kappa}{4m} [\hat{p}^2, \hat{q}^2] =$$

$$= -\frac{\kappa}{4m} 2i(\hat{q} \hat{p} + \hat{p} \hat{q}) \hbar = \mathcal{O}(\hbar)$$

AND SIMILARLY

$$[\hat{K}, [\hat{K}, \hat{V}]] = O(\hbar^2)$$

$$[\hat{V}, [\hat{V}, \hat{K}]] = O(\hbar^2)$$

WHERE WE MADE USE OF
RELATIONS (1) - (4)

HENCE IN THE LIMIT OF $\hbar \rightarrow 0$
WE CAN NEGLECT $O(\hbar)$ TERMS

NOTE THAT $\hbar \rightarrow 0$ IS EQUIVALENT
TO LET $\Lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \rightarrow 0$

SO THAT

$$e^{-\beta \hat{\mathcal{H}}} = e^{-\beta \hat{K} - \beta \hat{V}} \approx e^{-\beta \hat{K}} e^{-\beta \hat{V}}$$

LET'S WORKOUT THE PARTITION
FUNCTION

$$\begin{aligned} Q &= \int d^3q \langle q | e^{-\beta \hat{\mathcal{H}}} | q \rangle = \\ &= \int d^3q \langle q | e^{-\beta \hat{K}} e^{-\beta \hat{V}} | q \rangle \end{aligned}$$

IF WE INSERT $\int d^3p | p \rangle \langle p | = \mathbb{I}$
WE HAVE

$$= \int d^3q \int d^3p \langle q | e^{-\beta \hat{H}} | p \rangle \langle p | e^{-\beta \hat{V}} | q \rangle$$

FUNCTIONS OF q AND p !

$$= \int d^3q \int d^3p e^{-\beta(K(p) + V(q))} \langle q | p \rangle \langle p | q \rangle$$

BUT $\langle q | p \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{i \frac{p \cdot q}{\hbar}}$

$$\langle p | q \rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-i \frac{q \cdot p}{\hbar}}$$

HENCE WE OBTAIN

[SEE SAKURAI
SEC. 1.17
PAG. 54-56]

$$\langle q | p \rangle \langle p | q \rangle = \frac{1}{2\pi\hbar}$$

THUS HAVING

$$Q = \int \frac{d^3q \int d^3p}{(2\pi\hbar)^{3N}} e^{-\beta 2\ell(q,p)}$$

FUNCTION OF q AND p

$N!$

CORRECT BOLTZMANN
WAVE FUNCTIONS
MUST BE EITHER
SYM. OR ANTISYM.

SIMILARLY ONE CAN TREAT

$$\int d^{3N}q \langle q | \hat{A} e^{-\beta \hat{\mathcal{H}}} | q \rangle =$$

TO HAVE

$$= \int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} A(q,p) e^{-\beta \mathcal{H}(q,p)}$$

$\mathcal{H} = K + V$

TO FINALLY HAVE IN THE
LIMIT OF $\hbar \rightarrow 0$

$$\langle A \rangle = \frac{\int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} A e^{-\beta \mathcal{H}}}{\int \frac{d^{3N}q d^{3N}p}{(2\pi\hbar)^{3N} N!} e^{-\beta \mathcal{H}}} \quad \text{Q}$$

BUT SINCE $A = A(q)$, AS WE
ASSUMED, ONE HAS

$$\langle A \rangle = \frac{\int A(q) e^{-\beta V(q)} d^{3N}q}{Z}$$

WHERE

Z IS THE CONFIGURATIONAL

PARTITION FUNCTION

$$Z = \int d^{3N} q \, e^{-\beta V(q)}$$

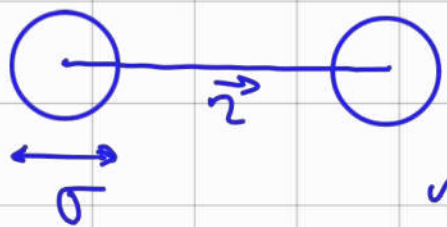
ALTERNATIVE WAY

$\beta \rightarrow 0$ (HIGH TEMPERATURES)

JUST NOTE THAT

$$\begin{aligned} e^{-\beta(\hat{K} + \hat{V})} &= 1 + \beta(\hat{K} + \hat{V}) + \\ &\mathcal{O}(\beta^2) \approx 1 + \beta(\hat{K} + \hat{V}) \\ &= e^{-\beta \hat{K}} e^{-\beta \hat{V}} + \mathcal{O}(\beta^2) \end{aligned}$$

HARD SPHERE MODEL



$$U_{HS}(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

$r = |\vec{r}|$

$$\phi = \{ \text{VOLUME FRACTION} \} = \hat{U}_{HS} \frac{N}{V}$$

WHERE

$$\hat{U}_{HS} = \frac{\pi}{6} \sigma^3$$

NUMBER OF PARTICLES

VOLUME

$\hat{U}_{HS} N$ IS THE VOLUME OCCUPIED BY N SPHERES

Q. WHY HARD SPHERES CAN FORM A CRYSTAL?

HARD SPHERES ARE AN "ENTROPIC" SYSTEM SINCE

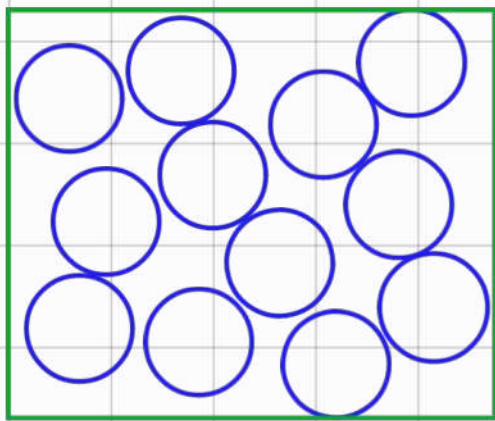
$$F = U - TS \quad \text{BUT} \quad U = \frac{3}{2} k_B T N + \cancel{U_{EX}}$$

EXCESS ENERGY

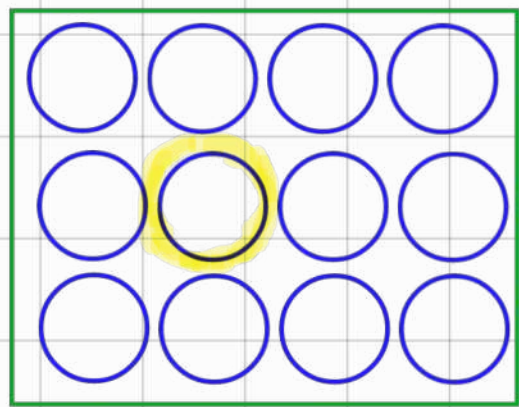
HENCE

$$F = \frac{3}{2} k_B T N - TS = T \left(\frac{3}{2} k_B N - S \right)$$

THIS IMPLIES THAT MINIMIZING
 F IS EQUIVALENT TO
 MAXIMIZE S (ENTROPY) I.E.
 THE NUMBER OF ACCESSIBLE STATES
 BUT



↑
 ALMOST ALL
 PARTICLES
 BLOCKED



GAIN OF
 ACCESSIBLE
 STATE, I.E.
 LARGER ENTROPY

HIT AND MISS MONTE CARLO:
 EXCLUDED VOLUME

IN 1D

$$\int_a^b f(x) dx = (b-a) \left(\underbrace{\frac{1}{b-a} \int_a^b f(x) dx}_{\langle f \rangle} \right) =$$

$$= (b-a) \langle f \rangle$$

IN 3 DIMENSIONS

$$\int_V f(\vec{x}) d^3x = V \left(\frac{1}{V} \int f(\vec{x}) d^3x \right) = V \langle f \rangle$$

VIRIAL EXPANSION

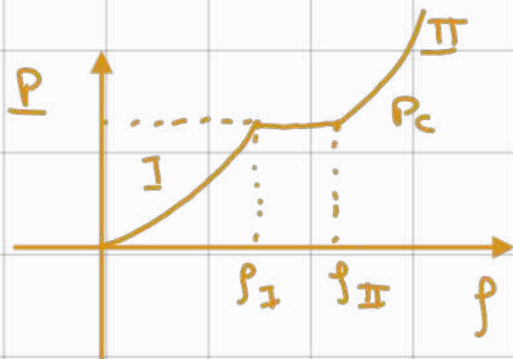
$$\beta P = \rho - \frac{1}{2} \rho^2 \int (e^{-\beta U_{HS}(r)} - 1) d^3r + O(\rho^3)$$

← HAYER
F-FUNCTION

$$\text{LET } F = e^{-\beta U_{HS}(r)} - 1$$

$$\beta P = \rho - \frac{1}{2} \rho^2 \int F(r) d^3r$$

IN PRESENCE OF A FIRST ORDER TRANSITION



TWO PHASES

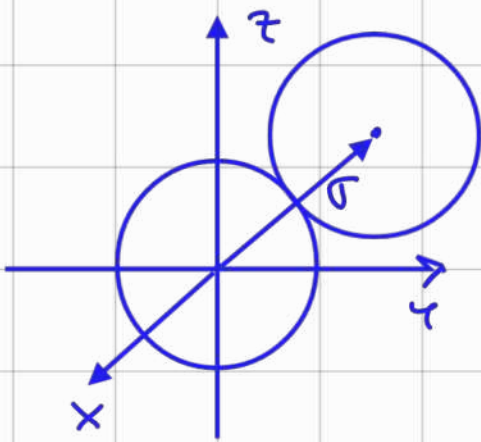
I AND II

(E.G. I = GAS
AND II = LIQUID)

$$F = \begin{cases} -1 & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

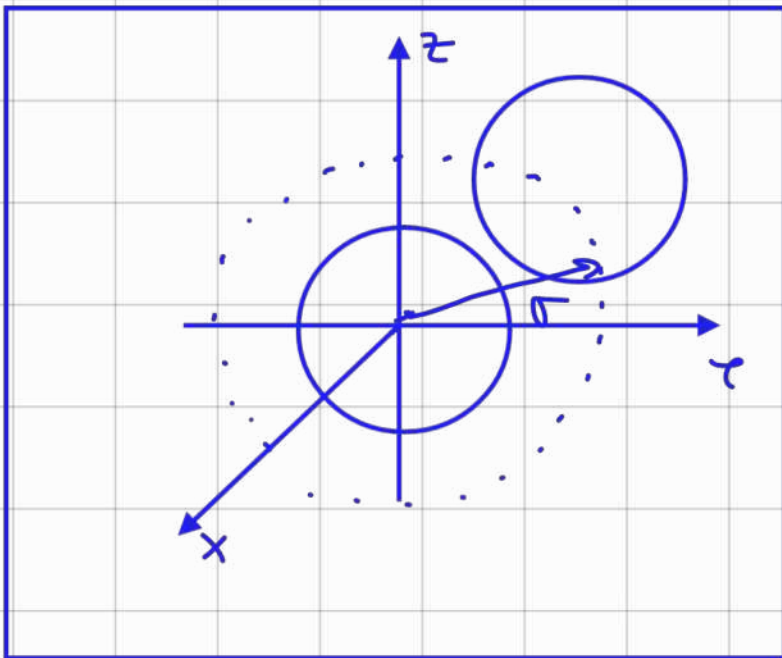
HENCE

$$-\int F(r) d^3r = \left\{ \text{VOLUME OF A SPHERE OF RADIUS } \sigma \right\} = \underbrace{\frac{4\pi}{3} \sigma^3}_{U_{\text{EXCL}}}$$



$$\beta P = \rho + \frac{\rho^2}{2} U_{\text{excl}} + O(\rho^2)$$

WE CAN CALCULATE U_{excl} THROUGH
A "HIT AND MISS" MONTE CARLO



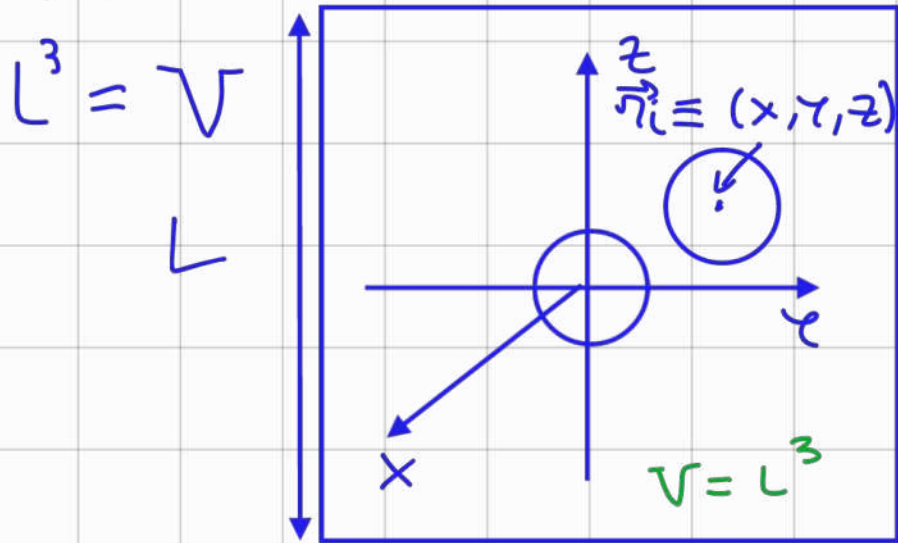
BOX OF VOLUME V

$$U_{\text{excl}} = V \left(\frac{1}{V} \int_V (1 - e^{-\beta U_{\text{HS}}(z)}) d^3z \right)$$

$$= V \langle \tilde{f} \rangle \quad \text{WHERE } \tilde{f} = -f$$

$\langle \tilde{f} \rangle$ CAN BE CALCULATED BY A
"HIT AND MISS" MONTE CARLO BY

INSERTING RANDOMLY A HS GIVEN
ONE FIXED AT ORIGIN .I.E.



$$x = \xi_x L/2$$

$$y = \xi_y L/2$$

$$z = \xi_z L/2$$

ξ_d RANDOM NUMBER

$$-1 \leq \xi_d \leq 1$$

$$d \in \{x, y, z\}$$

$$\langle \tilde{f} \rangle = \frac{1}{N} \sum_i^N \tilde{f}(\vec{r}_i) = \frac{N_{ov}}{N}$$

$N = \{ \text{NUMBER OF INSERTIONS} \}$

$N_{ov} = \{ \text{NUMBER OF OVERLAPS} \}$

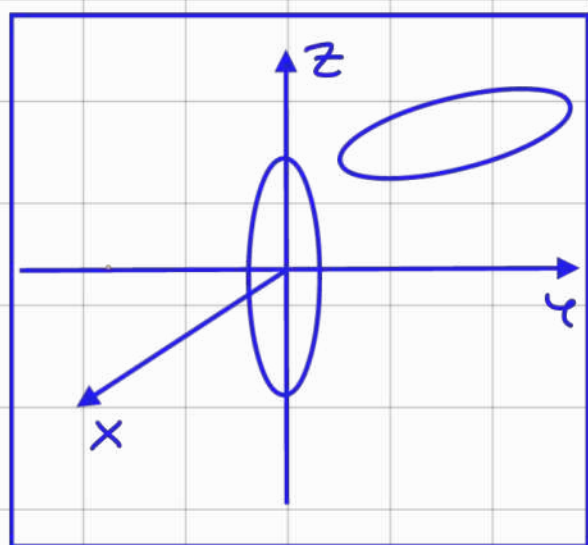
AND NOTE THAT

$$\tilde{f} = \begin{cases} 1 & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

ERROR $\propto \frac{1}{\sqrt{N}}$

$$V_{excl} = V \cdot \langle \tilde{f} \rangle = \frac{N_{ov}}{N}$$

MORE GENERALLY CONSIDER FOR EXAMPLE
HARD ELLIPSOIDS (HE)



← BOX OF VOLUME V

$$U_{HE} = U_{HE}(\vec{r}, \Omega)$$

$$\begin{aligned} U_{EXCL} &= \int (1 - e^{-\beta U_{HE}(\vec{r}, \Omega)}) d^3r \frac{d\Omega}{4\pi} = \\ &= V \cdot \int (1 - e^{-\beta U_{HE}(\vec{r}, \Omega)}) \frac{d^3r}{V} \frac{d\Omega}{4\pi} = \\ &= V \cdot \langle \tilde{f} \rangle \end{aligned}$$

$$\tilde{f} = \int (1 - e^{-\beta U_{HE}(\vec{r}, \Omega)}) \frac{d^3r}{V} \frac{d\Omega}{4\pi}$$

INSERTION OF HARD ELLIPSOIDS WITH
RANDOM POSITIONS AND ORIENTATIONS

$$\langle \tilde{f} \rangle = \frac{N_{ov}}{N} \quad \begin{array}{l} \leftarrow \text{NUMBER OF OVERLAPS} \\ \leftarrow \text{NUMBER OF INSERTIONS} \end{array}$$

$$U_{EXCL} = V \langle \tilde{f} \rangle$$

SO THAT WE WILL HAVE A ROUGH ESTIMATE
OF THEIR EQUATION OF STATE

$$\left(\beta P = \rho + \frac{\rho^2}{2} U_{EXCL} \right)$$

COMPLEX SYSTEMS

(ENSEMBLE OF N PARTICLES)

$$A = A(q^N, p^N) \quad q^N = \{\vec{q}_1, \dots, \vec{q}_N\}$$
$$p^N = \{\vec{p}_1, \dots, \vec{p}_N\}$$

$$\langle A \rangle = \frac{1}{Q} \int \frac{d^3q}{(2\pi\hbar)^{3N}} \frac{d^3p}{N!} A(q^N, p^N) e^{-\beta \mathcal{H}}$$

↑
THERMODYNAMIC
AVERAGE

$$\mathcal{H} = K + U \quad K = \sum_i \frac{\vec{p}_i^2}{2m}$$

$$-U = -U(\vec{q}_1, \dots, \vec{q}_N) = \frac{1}{2} \sum_{i,j} U(\vec{q}_i - \vec{q}_j)$$

$$Q = \int \frac{d^3q}{(2\pi\hbar)^{3N}} \frac{d^3p}{N!} e^{-\beta \mathcal{H}}$$

LET'S ASSUME $A = A(q^N)$

INTEGRATE OVER p^N SO THAT

$$\langle A \rangle = \frac{\int A(q^N) e^{-\beta U} d^3q}{Z}$$

$$Z = \int e^{-\beta U} d^3q$$

IF WE DEFINE

$$X(q^N) \equiv \frac{e^{-\beta U(q^N)}}{Z} \quad \text{ONE HAS}$$

$$\langle A \rangle = \int_V X(q^N) A(q^N) d^{3N}q$$

IF WE USE A STANDARD QUADRATURE
(E.G. TRAPEZOIDAL INTEGRATION)

- WE HAVE $3N$ DIMENSIONS
- ASSUME 10 POINTS ALONG EACH DIRECTION
- ASSUME $N = 1000$ PARTICLES

WE WILL HAVE TO DO

10^{3N} OPERATIONS

IF OUR COMPUTER CAN DO EXAFLOPS, I.E.
 10^{18} FLOPS (VERY POWERFUL!)

IT WILL TAKE

$$\frac{10^{3 \cdot 1000}}{10^{18}} = 10^{3000-18} \approx 10^{3000} \text{ s}$$

TO BE COMPARED WITH HUMAN LIFE

$$3600 \times 24 \times 365 \times 100 \approx 10^9 \text{ s}$$

UNIVERSE? 10^{18} s (≈ 20 BILLION YEARS)

YET NOT ENOUGH!

BUT MC CAN DO THE JOB!

$$\begin{aligned} \langle A \rangle &\stackrel{\text{ENSEMBLE AVERAGE}}{=} \int A N(q^N) d^3q = \\ &= V^N \left(\frac{1}{V^N} \int A N(q^N) d^3q \right) = \\ &= V^N \cdot \langle A N \rangle_V \leftarrow \begin{array}{l} \text{AVERAGE} \\ \text{OF } A N \text{ WHEN} \\ \text{WE GENERATE} \\ \text{RANDOMLY POINTS} \\ \text{INSIDE VOLUME } V \end{array} \end{aligned}$$

IN PRINCIPLE IS OK

BUT IT IS INEFFICIENT SINCE

IT IS VERY LIKELY THAT

$N(q^N) \approx 0$ IF q^N IS RANDOM

NEED OF SOME IMPROVEMENT!

IMPORTANCE SAMPLING

1D CASE

"I

$$= \langle f/w \rangle_w$$

$$\int_a^b f(x) dx = \int \left(\frac{f(x)}{w(x)} \right) w(x) dx$$

WHERE

$$\int_a^b w dx = 1$$

BE

$$U = U(x)$$

$$U(x) = \int_0^x w(x') dx'$$

$$dU = w dx$$

$$U(b) = 1$$

$$U(a) = 0$$

$$= \int_0^1 \frac{f(x(u))}{w(x(u))} dU = \langle \frac{f}{w} \rangle_w$$

UNIFORM DISTRIBUTION

$$I = \frac{1}{L} \sum_{i=1}^L \frac{f(x(U_i))}{w(x(U_i))}$$

L IS THE NUMBER OF RANDOM POINTS GENERATED

$$\text{IF } g_i \equiv \frac{1}{L} \frac{f_i}{w_i} \quad \text{WHERE } f_i = f(x(U_i))$$

$$w_i = w(x(U_i))$$

$$\sigma^2(I) = \sigma^2 \left(\sum_{i=1}^L g_i \right) =$$

$$= L \sigma^2(g_i) = L \frac{1}{L^2} \sigma^2 \left(\frac{f}{w} \right)$$

I.E.

$$\sigma^2(I) = \frac{1}{\sqrt{L}} \sigma \left(\frac{f}{w} \right)$$

$$\text{IF } \frac{f}{w} \approx \text{CONSTANT}$$

$$\sigma \left(\frac{f}{w} \right) \approx 0$$

LET'S APPLY THIS TECHNIQUE TO

STATISTICAL AVERAGES $\omega = \omega(q_1, \dots, q_N)$

$$\begin{aligned} \langle A \rangle &= \int A(q^N) \frac{e^{-\beta U(q^N)}}{Z} d^3N q \\ &= \langle \underbrace{A N}_{\omega} \rangle_{\omega}^F \end{aligned}$$

WISE CHOICE IS $\omega = N(q^N)$

HENCE

$$= \langle \frac{A N}{N} \rangle_N = \frac{1}{L} \sum_i^L A(\vec{q}_1^i, \dots, \vec{q}_N^i)$$

↑
UNWEIGHTED AVERAGE!

NOW WE NEED TO FIND A

STRATEGY TO GENERATE POINTS
ACCORDING TO DISTRIBUTION N

SINCE $N = \frac{e^{-\beta U}}{Z}$ BUT

Z IS AN INTEGRAL AND WE

CAN'T CALCULATE IT EFFICIENTLY

MARKOV CHAIN

SET OF STOCHASTIC VARIABLES

$$X_t \in \{ \text{FINITE SET OF POSSIBLE VALUES} \}$$

1) $X_t = (\vec{q}_1 \dots \vec{q}_N)$ SET OF COORDS THAT ON A PC CAN ASSUME VALUES FROM A FINITE SET

2) $P(X_{t+1} = \gamma_{t+1} \mid X_t = \gamma_t)$

↑
STATE OF THE SYSTEM (E.G. POSITIONS OF ALL PARTICLES)

3) CHAIN IS ERGODIC

NOTE THAT:

$$P(X_{t+1} = \gamma_n \mid X_t = \gamma_o) = \pi_{on}$$

TRANSITION PROBABILITY



TO GO FROM OLD STATE (o)

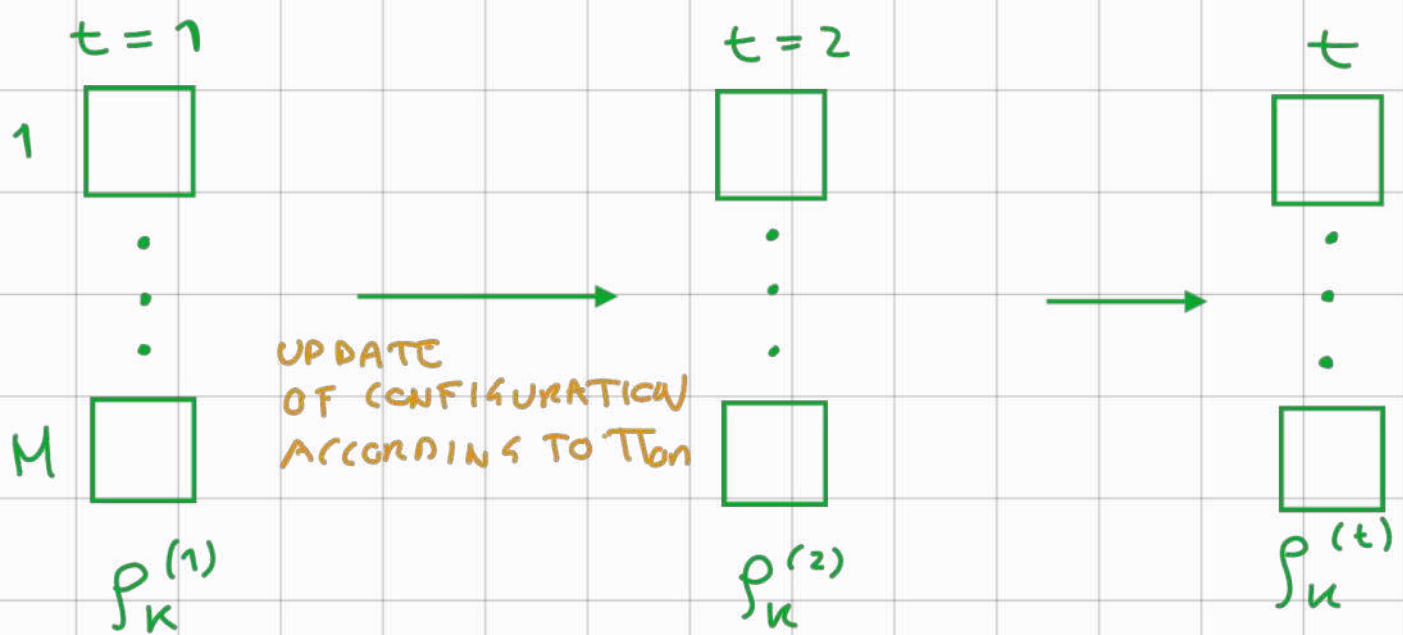
TO NEW STATE (n)

CONSIDER M SYSTEMS WHICH WE ARE SIMULATING IN PARALLEL

$\gamma_t = (\vec{x}_1^{(t)} \dots \vec{x}_N^{(t)}) \leftarrow$ POSITIONS OF N PARTICLES (STATE OF THE SYSTEM)

NOTE THAT THEY CONSTITUTE A FINITE SET

HENCE WE CAN USE AN INDEX k TO IDENTIFY THEM



$P_k^{(t)}$ IS THE PROBABILITY OF HAVING STATE k

AT $t=1$ WE WILL BE GENERALLY "OUT OF EQUILIBRIUM"

BUT IF THE MARKOV CHAIN IS ERGODIC

$\lim_{t \rightarrow +\infty} P_i^{(t)} = P_i$ SYSTEM "EQUILIBRATES" AND TENDS TO EQUILIBRIUM DISTRIBUTION P_i

IN OTHER WORDS WHEN $P_i^{(t)} = P_i$ WE CAN SAY THAT SYSTEM IS EQUILIBRATED

NOTE THAT TRANSITION MATRIX IS THE SAME FOR ALL SYSTEMS

AND WE UPDATE SYSTEM'S STATE AS DISCUSSED IN THE FOLLOWING.

UPDATE OF SYSTEM'S STATE

CONSIDER A SYSTEM IN STATE i
TO UPDATE ITS STATE

$$T = \begin{pmatrix} \pi_{i0} & \pi_{i1} & \dots & \pi_{iN_s} \end{pmatrix} \leftarrow \text{i-th row}$$

TRANSITION MATRIX

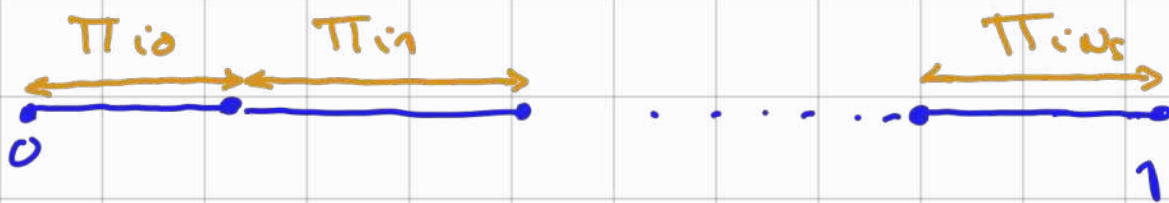
PROBABILITY TO GO FROM STATE i TO STATE k

$N_s = \{ \text{TOTAL NUMBER OF POSSIBLE STATES} \}$

NOTE THAT $\sum_k \pi_{ik} = 1$

GENERATE A UNIFORM

RANDOM NUMBER $\xi \in [0, 1]$



IF $\xi < \pi_{i0}$ THEN $i \rightarrow 0$

IF $\pi_{i0} < \xi < \pi_{i0} + \pi_{i1}$ THEN $i \rightarrow 1$

$\vdots$

WE CAN VIEW "EQUILIBRATION" FROM A
DIFFERENT PERSPECTIVE

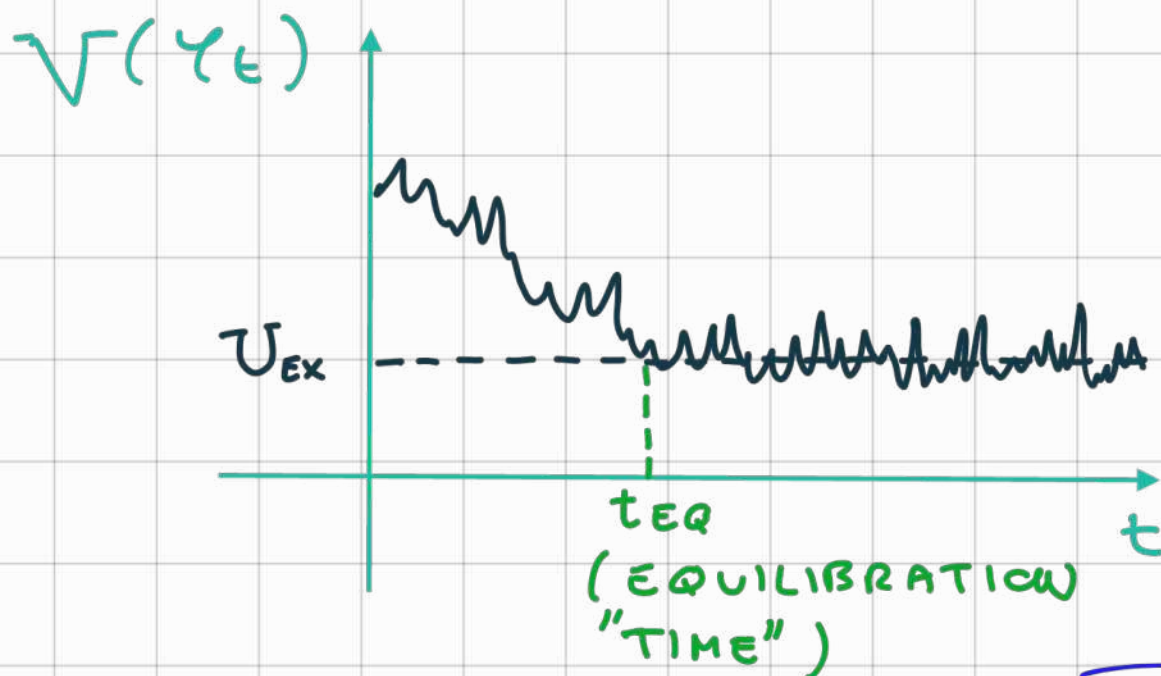
LET'S CONSIDER THE EXCESS ENERGY
DUE TO PARTICLES INTERACTIONS

$$U = \{ \text{INTERNAL ENERGY} \} = K + U_{\text{ex}}$$

WHERE K IS THE KINETIC ENERGY

AND IF $V = V(\vec{x}_1, \dots, \vec{x}_N)$ IS THE POTENTIAL ENERGY OF THE SYSTEM

$$U_{\text{ex}} = \langle V(\vec{x}_1, \dots, \vec{x}_N) \rangle$$



LET'S CONSIDER AGAIN THE M SYSTEM EVOLVING (RUNNING) IN PARALLEL

$$p_n^{(t)}, M = \{ \# \text{ OF SYSTEM IN STATE } K \}$$

$p_n^{(t+1)}$ AND $p_n^{(t)}$ CAN BE RELATED THROUGH π_{kn}

INDEED:

$$\underbrace{p_n^{(t+1)} M}_{\substack{\# \text{ OF SYSTEMS} \\ \text{IN} \\ \text{STATE } n}} = \underbrace{p_n^{(t)} M}_{\substack{\# \text{ OF SYSTEMS} \\ \text{IN} \\ \text{STATE } n}} + \underbrace{\sum_{\substack{k \\ k \neq n}} \pi_{kn} p_k^{(t)} M}_{\substack{\# \text{ SYSTEMS} \\ \text{GOING TO STATE } n}} - \underbrace{\sum_{\substack{k \\ k \neq n}} \pi_{nk} p_n^{(t)} M}_{\substack{\# \text{ SYSTEMS} \\ \text{LEAVING STATE } n \\ \text{(NOTE THE MINUS)}}}$$

BUT AT EQUILIBRIUM $p_n^{(t+1)} = p_n^{(t)} = p_n$

HENCE

$$\cancel{p_n^{(t+1)}} = \cancel{p_n^{(t)}} + \sum_{\substack{k \\ k \neq n}} \cancel{\pi_{kn}} \cancel{p_k^{(t)}} p_k - \sum_{\substack{k \\ k \neq n}} \cancel{\pi_{nk}} \cancel{p_n^{(t)}} p_k$$

THUS HAVING

$$\sum_{\substack{k \\ k \neq n}} \pi_{kn} p_k - \sum_{\substack{k \\ k \neq n}} \pi_{nk} p_k = 0$$

$$\sum_{\substack{k \\ k \neq n}} \pi_{kn} p_k + \pi_{nn} p_n = \sum_{\substack{k \\ k \neq n}} \pi_{nk} p_n + \pi_{nn} p_n$$

$$\sum_k \pi_{kn} p_k = \sum_k \pi_{nk} p_n$$

BUT $\sum_k \pi_{nk} = 1$ HENCE

$$\sum_k p_k \pi_{kn} = p_n$$

WHICH CAN BE WRITTEN IN MATRIX

FORM AS FOLLOWS

$$\vec{p} \Pi = \vec{p} \quad (1)$$

WHERE $\vec{p} = (p_1 \dots p_k \dots)$

FOR AN ERGODIC MARKOV CHAIN
WITH A FINITE SPACE OF STATES

IF WE CONSIDER $\vec{p} \Pi = \lambda \vec{p}$
 $\exists$ UNIQUE $\vec{p}$ SUCH THAT

$\lambda = 1$, Π IS NOT

GUARANTEED TO BE
DIAGONALIZABLE

AND THE OTHER
EIGENVALUES λ_k ARE SUCH

$|\lambda_k| < 1$ (THEY CAN BE
OBTAINED BY JORDAN DECOMP.)

AND Π IS A MATRIX WHOSE ELEMENTS ARE

AND $(\Pi)_{nk} = \pi_{nk}$

EQ. (1) IS CALLED BALANCE CONDITION AND IT STATES THAT VECTOR $\vec{p}$ IS AN EIGEN VECTOR OF MATRIX Π WITH EIGENVALUES 1.

EQ. (1) TELLS US THAT THE NUMBER OF SYSTEMS UNDERGOING A TRANSITION TO STATE n IS EQUAL TO THE NUMBER OF SYSTEMS LEAVING STATE n

WE CAN IMPOSE A STRONGER CONDITION

SINCE

$$\sum_k \pi_{kn} p_k = \sum_k \pi_{nk} p_n$$

THAT IS

$$\sum_k (\pi_{kn} p_k - \pi_{nk} p_n) = 0$$

WHICH IS SATISFIED IF WE REQUIRE

$$\pi_{kn} p_k = \pi_{nk} p_n \quad (2)$$

WHICH IS CALLED "DETAILED BALANCE CONDITION"

IN THIS CASE Π IS DIAGONALIZABLE WITH REAL EIGENVALUES

THIS CONDITION STATES THAT THE NUMBER OF SYSTEMS GOING FROM STATE k TO STATE n HAS TO BE EQUAL TO THE NUMBER OF SYSTEMS GOING FROM STATE n TO STATE k .

IN FOLLOWING $k \rightarrow 0$ SO THAT EQ. (2) BECOMES

$$P_0 \pi_{on} = P_n \pi_{no} \quad (3)$$

SO THAT WE CAN THINK THAT 0 STANDS FOR "OLD" AND n FOR "NEW".

ACCORDING TO THIS CONDITION WE CAN IMPOSE THE EQUILIBRIUM DISTRIBUTION REACHED BY THE SYSTEM BY PROVIDING A TRANSITION PROBABILITY WHICH ENFORCES EQ. (3) GIVEN A CERTAIN PROBABILITY DISTRIBUTION P_k

LET'S FIND OUT A WAY TO
PROVIDE π_{on} (MONTE CARLO
METROPOLIS)

$$\pi_{on} = \underset{\substack{\uparrow \\ \text{TRIAL MOVE}}}{\alpha(o \rightarrow n)} \underset{\substack{\uparrow \\ \text{ACCEPTANCE} \\ \text{PROBABILITY}}}{\text{acc}(o \rightarrow n)}$$

$\alpha(o \rightarrow n)$ UPDATE SYSTEM'S STATE
(I.E. PARTICLES POSITIONS)
RANDOMLY

AND WE REQUIRE

$$\text{I) } \alpha(o \rightarrow n) = \alpha(n \rightarrow o)$$

I.E. THAT IT IS SYMMETRIC
(EVEN IF IT IS NOT NECESSARY, AS WE
SHALL SEE WHEN WE WILL DISCUSS
BIASED MONTE CARLO)

$$\text{II) } \text{acc}(o \rightarrow n) = \min \left\{ 1, \frac{p_n}{p_o} \right\}$$

NOTE: IF $p = \frac{e^{-\beta V}}{Z}$ THEN

$$\frac{p_n}{p_o} = e^{-\beta(V_n - V_o)} = e^{-\beta \Delta V}$$

WHERE ΔV IS THE VARIATION
OF POTENTIAL ENERGY AFTER THE
TRIAL MOVE.

BY ENFORCING I) AND II)
DETAILED BALANCE CONDITION
IS FULLFILLED, INDEED

CASE I

CONSIDER A MOVE SUCH THAT

$$p_n < p_o \quad \text{THEN}$$

$$p_o \pi_{on} = p_n \pi_{no}$$

$$p_n \cancel{\alpha(o \rightarrow n)} \alpha(n \rightarrow o) = p_n \cancel{\alpha(n \rightarrow o)} \alpha(o \rightarrow n)$$

$$p_o \underbrace{\min\left(1, \frac{p_n}{p_o}\right)}_{= \frac{p_n}{p_o}} = p_n \underbrace{\min\left(1, \frac{p_o}{p_n}\right)}_{= 1}$$

$$\cancel{p_o} \frac{p_n}{\cancel{p_o}} = p_n \Rightarrow p_n = p_n$$

SIMILARLY ONE CAN PROCEED

BY ASSUMING $\frac{p_n}{p_o} > 1$

CASE II

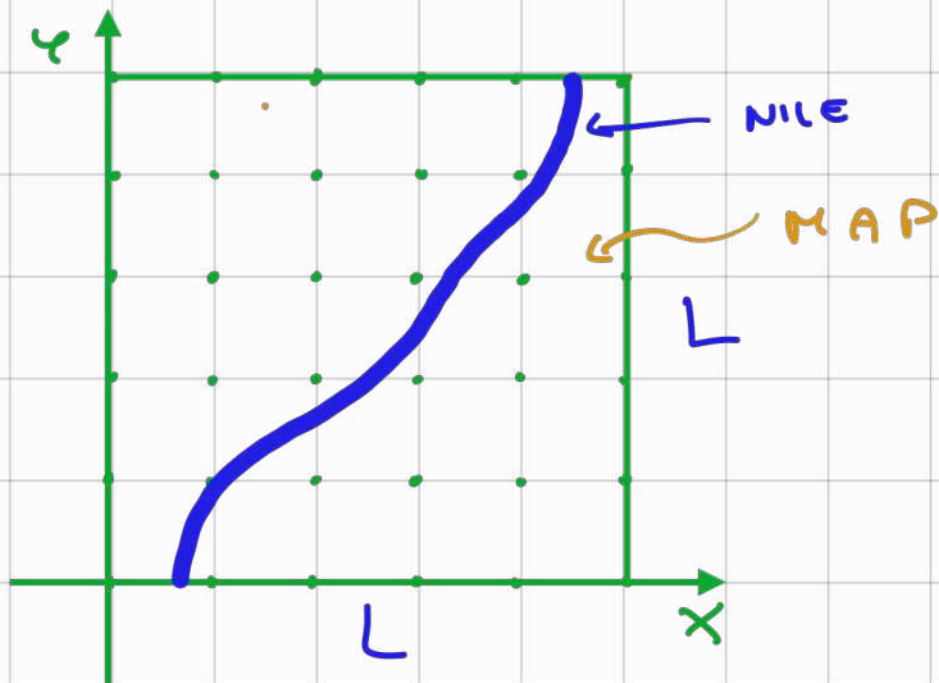
$$p_n > p_o$$

$$\rho_0 \min\left(1, \frac{\rho_n}{\rho_0}\right) = \rho_n \min\left(1, \frac{\rho_0}{\rho_n}\right)$$

$\begin{matrix} > 1 & & < 1 \\ = 1 & & = \rho_0/\rho_n \end{matrix}$

$$\rho_0 = \rho_n \frac{\rho_0}{\rho_n} \Rightarrow \rho_0 = \rho_0$$

A NEAT EXAMPLE:
CALCULATION OF AVERAGE DEPTH
OF NILE



SOME DEFINITIONS

$$A = L^2 = \{ \text{MAP AREA} \}$$

$$\Theta(x, y) = \begin{cases} 1 & \text{if } (x, y) \in \text{NILE} \\ 0 & \text{otherwise} \end{cases}$$

$$d(x, y) = \{ \text{DEPTH OF TERRAIN AT } (x, y) \}$$

↑
 NOTE THAT IT CAN BE
 ≠ 0 ALSO OUTSIDE NILE

HENCE

$$\mathcal{Z} = \int_A \Theta(x, y) dx dy = \{ \text{AREA OF NILE} \}$$

AND

$$\langle d(x, y) \rangle = \int_A \frac{d(x, y) \Theta(x, y)}{\mathcal{Z}} dx dy$$

WE CAN CALCULATE THIS INTEGRAL THROUGH A STANDARD QUADRATURE PROCEDURE (E.G. RECTANGLES METHOD)

... OR WE CAN USE A METROPOLIS MC

$\frac{\Theta(x, y)}{\mathcal{Z}}$ IS A PROBABILITY DISTRIBUTION

INDEED $\int_A \frac{\Theta(x, y)}{\mathcal{Z}} dx dy = 1$

WHERE $\mathcal{Z}$ ANALOGOUS OF PARTITION FUNCTION

AND $d(x, y)$ IS AN OBSERVABLE SO THAT

$$\int_A d(x, y) \frac{\Theta(x, y)}{\mathcal{Z}} dx dy \quad \text{CAN BE VIEWED}$$

AS A ENSEMBLE AVERAGE AND WE CAN EMPLOY A METROPOLIS MC

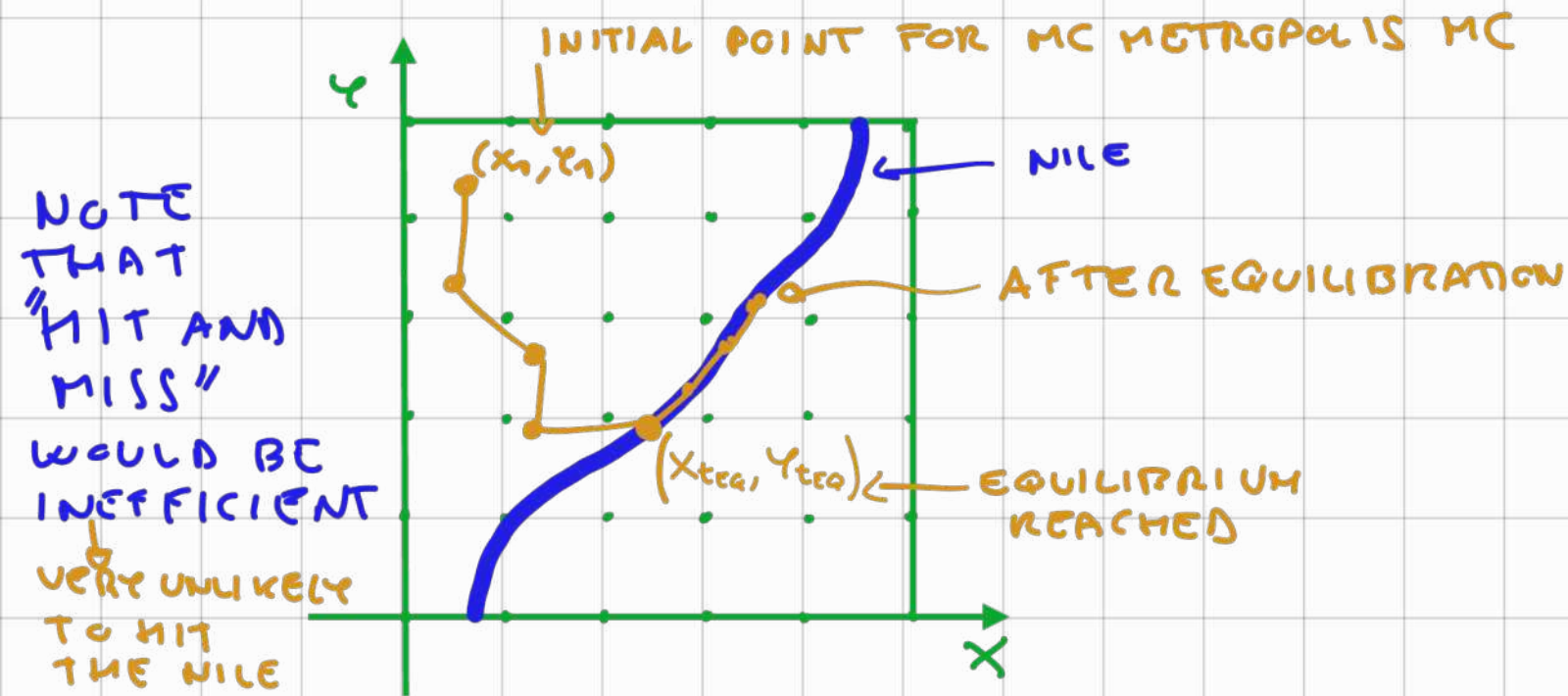
EACH TRIAL MOVE CONSISTS IN

RANDOMLY UPDATING THE POSITION OF THE CURRENT POINT (I.E.

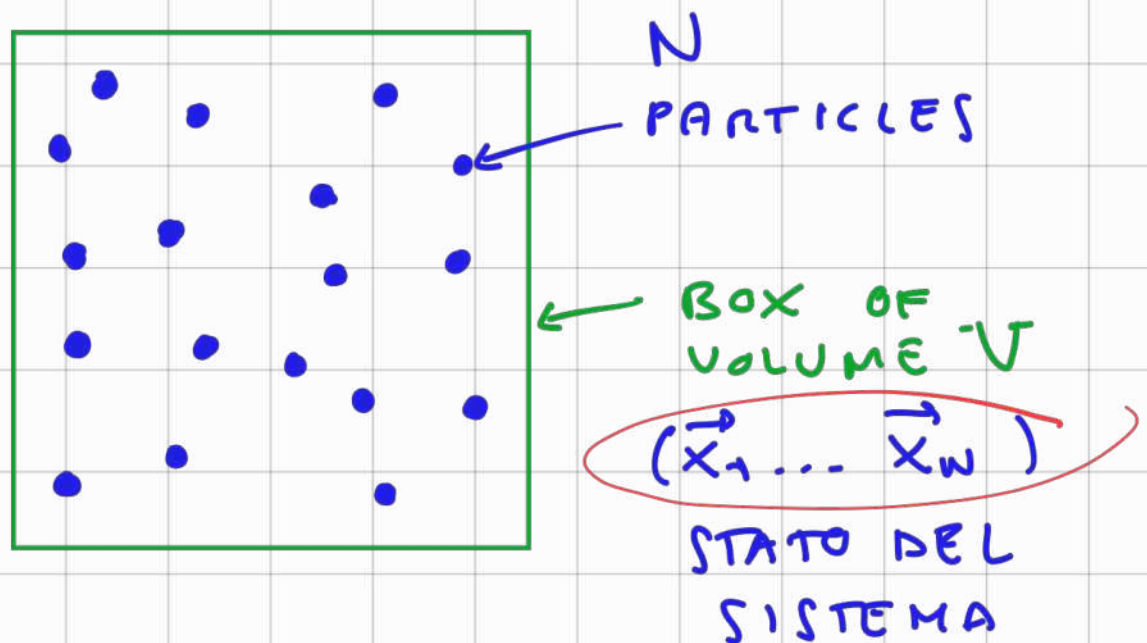
LOCATION ON THE MAP) (x_0, y_0)

TO A NEW POINT (x_n, y_n)

AND REJECTING THIS TRIAL MOVE
IF $(x_0, y_0) \in \text{NILE}$ AND $(x_n, y_n) \notin \text{NILE}$
WE WILL END UP WITH A RANDOM WALK
AS FOLLOWS :



METROPOLIS MC FOR A SYSTEM OF N PARTICLES



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

CHOOSE RANDOMLY A PARTICLE

AND DISPLACE IT BY

$$\Delta \vec{r} = (\Delta x, \Delta y, \Delta z)$$

1 MC STEP $\equiv$
N TRIAL MOVE

WHERE

ξ_α ARE RANDOM VARIABLES

$$\Delta x = \xi_x \delta$$

SUCH THAT

$$\Delta y = \xi_y \delta$$

$$-1 < \xi_\alpha < 1$$

$$\Delta z = \xi_z \delta$$

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

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

$$\alpha(0 \rightarrow n) = \min \left\{ 1, \frac{e^{-\beta U_n}}{e^{-\beta U_0}} \right\} =$$

$$= \min \left\{ 1, e^{-\beta \Delta U} \right\}$$

HENCE IF $\Delta U < 0 \Rightarrow$ ACCEPTED
OTHERWISE

ξ RANDOM VARIABLE $0 \leq \xi < 1$

IF $\xi \leq e^{-\beta \Delta U}$ ACCEPTED

$\xi > e^{-\beta \Delta U}$ REJECTED

EFFICIENCY

$$\eta = \{\text{EFFICIENCY}\} \equiv \frac{\sum_{k=1}^L \delta \Omega_k^2}{T} = \frac{\Delta \Omega^2}{T}$$

SUM OVER SINGLE PARTICLE MOVES
($\delta \Omega_k = 0$ IF REJECTED)

$\Delta \Omega^2$ QUANTIFIES THE "TOTAL DISPLACEMENT",

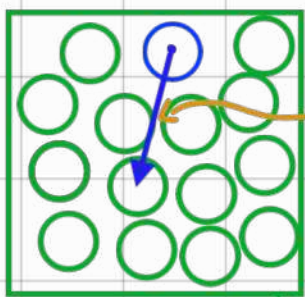
I.E. HOW MUCH THE INITIAL CONFIGURATION CHANGED

$$T = \{\text{COMPUTING TIME FOR CARRYING OUT } L \text{ TRIAL MOVES}\} = t_1 \cdot L$$

TIME NEEDED TO MOVE ONE PARTICLE (I.E. TO CALCULATE ΔU)

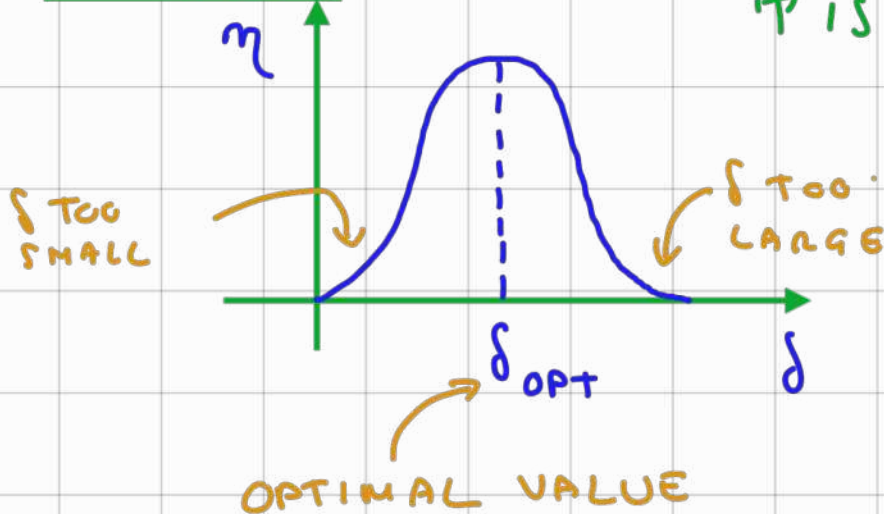
I) IF $\delta \rightarrow 0$ $\Delta \Omega^2 \rightarrow 0$ BUT $T = t_1 \cdot L$ DOES NOT $\Rightarrow \eta \rightarrow 0$

II) IF δ IS LARGE (E.G. LARGER THAN PARTICLE SIZE)



δ LARGE, IT IS VERY LIKELY TO HAVE AN OVERLAP SO THAT ENERGY IS LARGE AND MOVE IS REJECTED

HENCE $\Delta \Omega^2 \rightarrow 0$ BUT AGAIN T IS FINITE $\Rightarrow \eta \rightarrow 0$

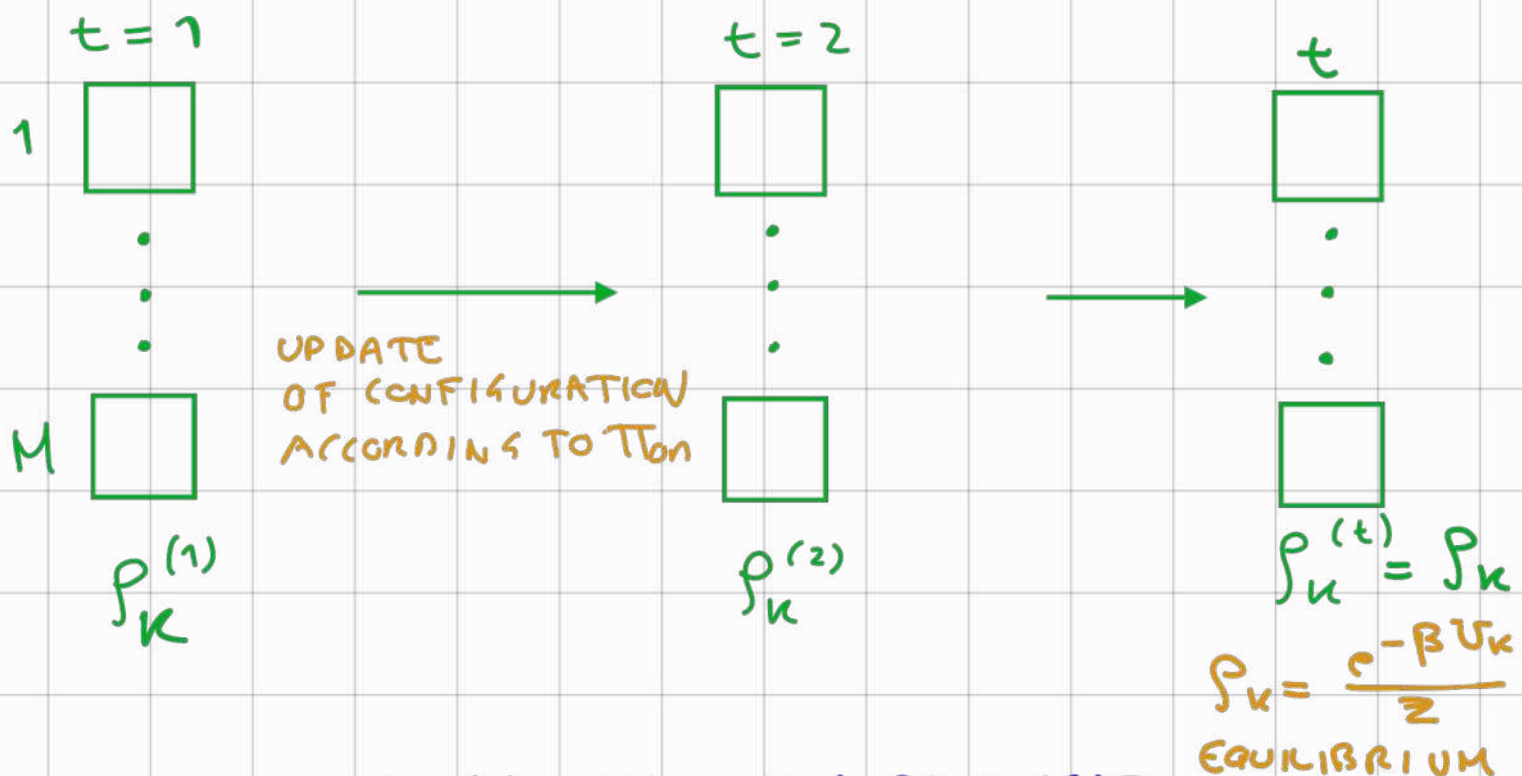


$$R = \{ \text{ACCEPTANCE RATE OF TRIAL MOVES} \} = \frac{\{ \# \text{ ACCEPTED TRIAL MOVES} \}}{\{ \# \text{ TRIAL MOVES} \}}$$

IF $0.3 < R < 0.5 \Rightarrow \mathcal{J} \approx \mathcal{J}_{\text{OPT}}$
(EMPIRICAL RULE)

Q. WHAT R DO WE HAVE IF WE MOVE N PARTICLES AT A TIME?

CONSIDER AGAIN M IDENTICAL SYSTEMS BEING SIMULATED IN THE NTV ENSEMBLE (CANONICAL ENSEMBLE)



AFTER A TRIAL MOVE OF 1 PARTICLE

$$\langle \Delta U \rangle = \left\langle \sum_{\alpha} \frac{\partial U}{\partial \eta_i^{\alpha}} \delta \eta_i^{\alpha} + \frac{1}{2} \sum_{\alpha, \beta} \frac{\partial^2 U}{\partial \eta_i^{\alpha} \partial \eta_i^{\beta}} \delta \eta_i^{\alpha} \delta \eta_i^{\beta} \right\rangle =$$

WHERE $\langle \dots \rangle$ IS OVER ALL M SYSTEMS
 ↓ AVERAGE OVER TRIAL MOVES

$$= \left\langle \sum_{\alpha} \frac{\partial U}{\partial \eta_i^{\alpha}} \right\rangle \overline{\delta \eta_i^{\alpha}} + \left\langle \frac{1}{2} \sum_{\alpha \beta} \frac{\partial^2 U}{\partial \eta_i^{\alpha} \partial \eta_i^{\beta}} \right\rangle \overline{\delta \eta_i^{\alpha} \delta \eta_i^{\beta}}$$

↑ AVERAGE OVER M RUNS

WE SPLITTED THE AVERAGE SINCE AVERAGE OVER TRIAL MOVES ($\overline{}$) IS INDEPENDENT OF AVERAGE OVER M SYSTEMS ($\langle \rangle$)

BUT $\overline{\delta \eta_i^{\alpha}} = 0$ AND

$$\overline{\delta \eta_i^{\alpha} \delta \eta_i^{\beta}} = 0 \quad \text{IF } \alpha \neq \beta$$

AND $\overline{(\delta \eta_i^x)^2} = \overline{(\delta \eta_i^y)^2} = \overline{(\delta \eta_i^z)^2} = \overline{\delta \eta^2}$

MOREOVER $\frac{1}{2} \sum_{\alpha} \frac{\partial^2 U}{\partial \eta_i^{\alpha} \partial \eta_i^{\alpha}} \equiv f(U)$

HENCE WE ARE LEFT WITH

$$= f(U) \overline{\delta \eta^2}$$

A MOVE IS LIKELY ACCEPTED IF

$$\langle \Delta U \rangle \simeq k_B T \quad \text{THUS HAVING}$$

$$f(U) \overline{\delta \eta^2} = k_B T \Rightarrow \overline{\delta \eta^2} = \frac{k_B T}{f(U)}$$

THAT IS IF WE MOVE 1 PARTICLE AT A TIME L TIMES:

$$\tau_1 = \frac{L \overline{\delta \eta^2}}{L \tau_1} = \frac{\overline{\delta \eta^2}}{\tau_1} = \frac{k_B T}{\tau_1 f(U)}$$

IF WE ATTEMPT TO MOVE N
PARTICLES AT A TIME

$$\langle \Delta U \rangle = f(U) \overline{\delta \eta^2} N$$

SINCE WE HAVE CONTRIBUTIONS FROM N PARTICLES
(NOT JUST i -TH PARTICLE AS BEFORE)

HENCE:

$$\overline{\delta \eta^2} = \frac{k_B T}{N f(U)}$$

→ AVERAGE DISPLACEMENT OF A SINGLE PARTICLE AFTER A TRIAL MOVE

NOTE THAT $\eta = \frac{\sum_k \delta \eta_k^2}{N}$

$\sum_k \delta \eta_k^2$ IS NOW A SUM OVER ALL
PARTICLE DISPLACEMENTS AFTER
 L TRIAL MOVES, I.E.:

$$\sum_k \delta \eta_k^2 = L \cdot N \cdot \overline{\delta \eta^2}$$

HENCE THE EFFICIENCY η_N OF MOVING SIMULTANEOUSLY
 N PARTICLES AFTER L TRIAL MOVES IS

$$\eta_N = \frac{\overline{\delta \eta^2} \cancel{N}}{t_1 \cancel{N}} = \frac{k_B T}{N t_1 f(U)}$$

← η_1

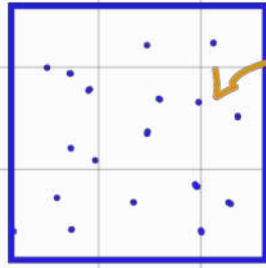
SO THAT

$$\eta_N = \frac{\eta_1}{N}$$

I.E. η_N IS N TIMES SMALLER
THAN η_1 !

INTERACTION POTENTIALS

SIMULATION
BOX
 $V = L^3$



N INTERACTING
PARTICLES

2 BODY INTERACTIONS

$$U = \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_i, \vec{r}_j) + \sum_{i < j < k} U_3(\vec{r}_i, \vec{r}_j, \vec{r}_k)$$

$$= \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_{i,j}) \quad \vec{r}_{i,j} = \vec{r}_i - \vec{r}_j$$

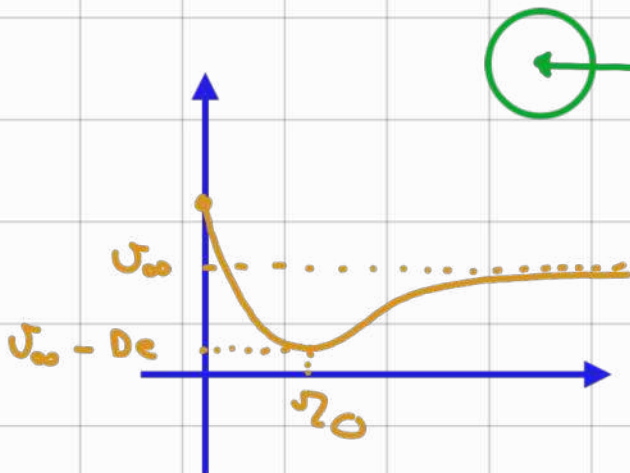
3 BODY
INTERACTIONS

NOTE THAT

$$U = \frac{1}{2} \sum_{i \neq j} U_2(\vec{r}_{i,j}) = \sum_{i < j} U_2(\vec{r}_{i,j})$$

MORSE POTENTIAL (BIATOMIC MOLECULE)

$$U_2(r) = U_M(r) = U_\infty + D_e \{ [1 - e^{-\alpha(r-r_0)}]^2 - 1 \}$$

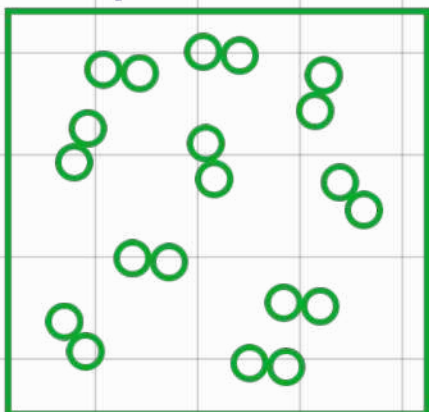


INTERACTION
BETWEEN TWO
ATOMS BELONGING
TO A BIATOMIC
MOLECULE

$$\left. \frac{dU_M}{dr} \right|_{r=r_0} = 0$$

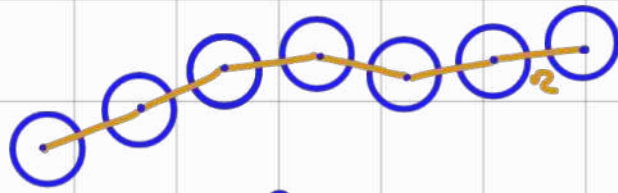
AND

$$U_M(r_0) = U_\infty - D_e$$



INTERACTION OF
PAIR OF PARTICLES
BELONGING TO A
BIATOMIC MOLECULE

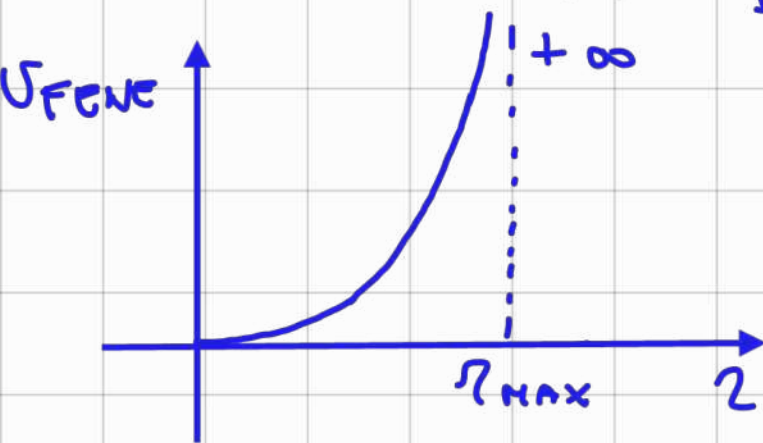
POLYMERS



$$U_{FENE}(r) = \begin{cases} -\frac{1}{2} r_{\text{MAX}}^2 \ln \left[1 - \left(\frac{r}{r_{\text{MAX}}} \right)^2 \right] & r \leq r_{\text{MAX}} \\ \infty & r > r_{\text{MAX}} \end{cases}$$

INTERACTIONS OF TWO SUCCESSIVE PARTICLES BELONGING TO A POLYMER

FENE = { FINITE EXTENSIBLE NON LINEAR ELASTIC }



IF $r \ll r_{\text{MAX}}$

$$U_{FENE} \approx \epsilon \frac{r^2}{2}$$

HENCE ϵ IS THE ELASTIC CONSTANT OF SMALL OSCILLATIONS

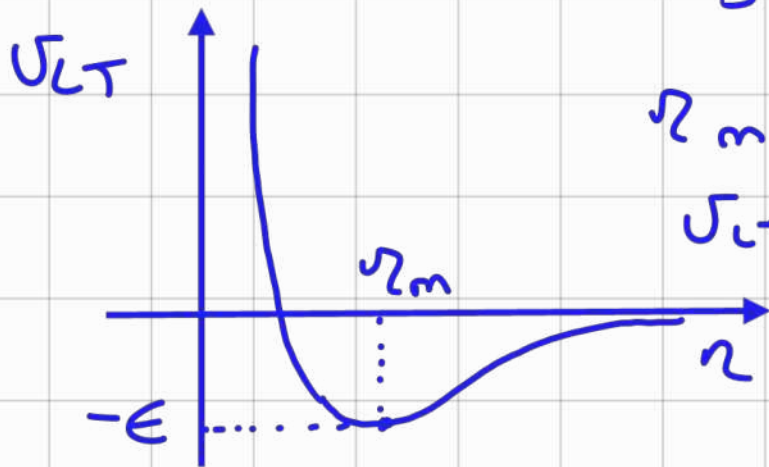
LENNARD-JONES

(NOBLE GASES SUCH AS ARGON, NEON, XENON OR RADON)

↑
MONOATOMIC
GASES

[1964 RAMAN AND
1969 VERLET AND HANSEN]

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



$$r_m = 2^{1/6} \sigma \approx 1.12 \sigma$$

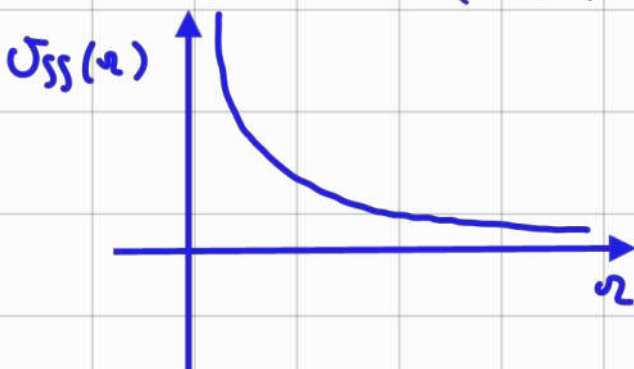
$$V_{LJ}(r_m) = -\epsilon$$

THIS POTENTIAL WELL DESCRIBES
INTERACTION BETWEEN UNCHARGED
ATOMS

SOFT SPHERE POTENTIAL

$$V_{SS}(r) = \epsilon \left(\frac{\sigma}{r} \right)^n$$

n QUANTIFIES [SOFTNESS]
OF PARTICLES



SCALING LAWS OF SOFT-SPHERE FLUID

$$F = -k_B T \ln Z \quad Z = \int_V e^{-\beta U_{ss}} d^3N$$

$$U_{ss} = \epsilon \sum_{i < j} \left(\frac{\sigma}{r_{ij}} \right)^n \quad r_{ij} = |\vec{r}_{ij}|$$

$$Z = \int_V e^{-\beta \epsilon \sum_{i < j} \left(\frac{\sigma}{r_{ij}} \right)^n} d^3N$$

$$\vec{r}_i = V^{1/3} \vec{\xi}_i \quad \text{SCALED COORDINATES}$$

$$= \int_V e^{-\beta \epsilon \frac{\sigma^n}{V^{n/3}} \sum_{i < j} \left(\frac{1}{\xi_{ij}} \right)^n} V^N d^3N_{\xi}$$

$$\text{CONSIDER } \frac{\beta \epsilon \sigma^n}{V^{n/3}} = \left[(\beta \epsilon)^{3/n} \sigma^3 \frac{N}{V} \right]^{n/3} \frac{1}{N^{n/3}}$$

$$\text{IF WE DEFINE } \Gamma = (\beta \epsilon)^{3/n} \sigma^3 \rho = \Gamma(T, \rho)$$

WE HAVE

$$Z = V^N \int e^{-\left(\frac{\Gamma}{N}\right)^{n/3} \sum_{i < j} \left(\frac{1}{\xi_{ij}} \right)^n} d^3N_{\xi}$$

$$= Z_{ID} \cdot Z_{EX}(\Gamma)$$

$$\text{WHERE } Z_{ID} = V^N \quad \text{AND}$$

$$Z_{EX}(\Gamma) = \int e^{-\left(\frac{\Gamma}{N}\right)^{n/3} \sum_{i < j} \left(\frac{1}{\xi_{ij}} \right)^n} d^3N_{\xi}$$

$$U = U_{ID} + U_{EX} \quad U_{ID} = \langle U \rangle = \frac{3}{2} N k_B T$$

$$\begin{aligned} \beta U_{EX} &= \beta \langle U_{ss} \rangle = \beta \int U_{ss} \frac{e^{-\beta U_{ss}}}{Z} d^3N_{\xi} = \\ &= \int \beta U_{ss} \frac{e^{-\beta U_{ss}}}{V^N Z_{EX}(\Gamma)} V^N d^3N_{\xi} \end{aligned}$$

$$\overline{\beta U_{ss}} = \left(\frac{\Gamma}{N} \right)^{n/3} \sum_{i=1}^N \left(\frac{1}{F_{i,5}} \right)^n = f(\Gamma)$$

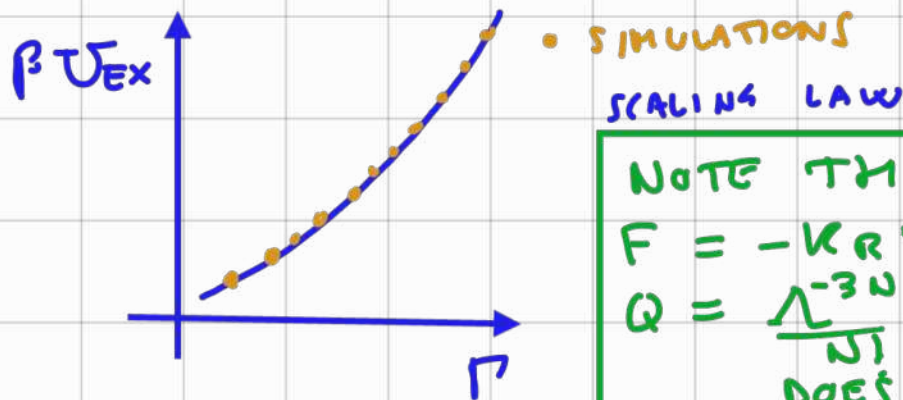
↑ FOR FIXED N

HENCE

$$\beta U_{ex} = F(\Gamma)$$

SIMULATIONS WITH SAME $\Gamma = \Gamma(T, P)$
(EVEN IF T AND P ARE DIFFERENT)

WILL YIELD SAME VALUE OF βU_{ex} , I.E.



NOTE THAT:

$$F = -k_B T \ln Q \quad \text{BUT} \\ Q = \frac{\Lambda^{-3N}}{N!} Z \quad \text{AND} \quad \frac{\Lambda^{-3N}}{N!} \text{ DOES NOT DEPEND ON } V$$

SIMILAR SCALING FOR PRESSURE

$$P = - \frac{\partial F}{\partial V} = \frac{\partial (k_B T \ln Z)}{\partial V} \quad \text{BUT } Z = Z_{id} \cdot Z_{ex} \quad V^N$$

$$= \underbrace{\frac{\partial}{\partial V} [k_B T N \ln V]}_{P_{id}} + \underbrace{k_B T \frac{1}{Z_{ex}} \frac{\partial Z_{ex}}{\partial V}}_{P_{ex}}$$

$$P = P_{id} + P_{ex} = \frac{P}{\beta} + P_{ex}$$

$$P_{id} = \rho k_B T$$

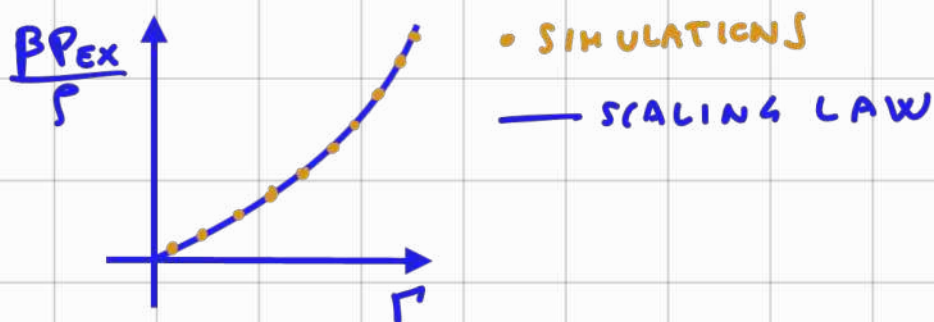
$$P_{ex} = k_B T \frac{1}{Z_{ex}} \frac{\partial Z_{ex}}{\partial V} = k_B T \frac{1}{Z_{ex}} \frac{\partial Z_{ex}}{\partial \Gamma} \frac{\partial \Gamma}{\partial V}$$

$$\text{BUT } \frac{\partial \Gamma}{\partial V} = -(\beta \epsilon)^{3/2} \frac{N}{V^2} \sigma^3 = \Gamma \frac{\rho}{N}$$

$$= \rho k_B T \underbrace{\frac{\Gamma/N}{Z_{\text{ex}}(\Gamma)} \frac{\partial Z_{\text{ex}}}{\partial \Gamma}}_{G(\Gamma) \leftarrow \text{FOR FIXED } N}$$

$$\frac{\beta P_{\text{ex}}}{\rho} = G(\Gamma) \quad \text{SCALING LAW}$$

IF ONE PERFORMS SIMULATIONS CHANGING T AND ρ
BUT AT FIXED Γ ONE HAS TO GET



COULOMB INTERACTIONS

$$U_C(r) = \frac{1}{4\pi \epsilon_r \epsilon_0} \frac{q_1 q_2}{r}$$

SCREENED INTERACTIONS [DEBYE-HÜCKEL THEORY]

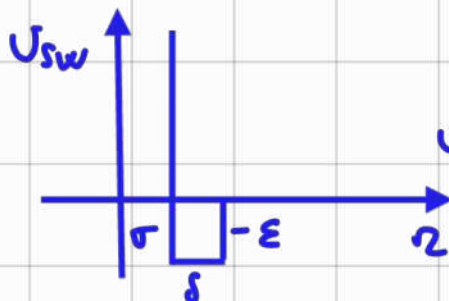
$$U_{\text{sc}}(r) = A \frac{q_1 q_2}{r} e^{-r/\lambda}$$

λ IS THE DEBYE SCREENING LENGTH

λ DEPENDS ON CHARGE IN SOLUTION

HARD SPHERES (ALREADY DISCUSSED)

SQUARE WELL



$$U_{\text{sw}} = \begin{cases} +\infty & r < \sigma \\ -\epsilon & \sigma < r < \sigma + \delta \\ 0 & r > \sigma + \delta \end{cases}$$

TRUNCATION, SHIFT AND SMOOTHING OF INTERACTION POTENTIALS

INTERACTION POTENTIALS MAY EXTEND TO INFINITE DISTANCE (E.G. LENNARD-JONES), HENCE NEED OF TRUNCATION

$$U_{LT}^C(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] & r \leq r_c \\ 0 & r > r_c \end{cases}$$

WHERE r_c IS THE CUTOFF RADIUS
(IN OLD LITERATURE $r_c = 2.5\sigma$)

AT $r = r_c$ WE HAVE A DISCONTINUITY
(BAD FOR MD SIMULATIONS AS WE SHALL SEE)
HENCE SHIFT OF POTENTIAL, I.E.

$$U_{LT}^{CS}(r) = \begin{cases} U_{LT}(r) - U_{LT}(r_c) & r \leq r_c \\ 0 & r > r_c \end{cases}$$

NOTE THAT FOR MC SIMULATIONS
SHIFT IS NOT NEEDED

MODIFIED LT

TO HAVE ALSO SECOND DERIVATIVE
CONTINUOUS

$$U_{LT}^M = \begin{cases} U_{LT}(r) + a \cdot r + b & r \leq r_c \\ 0 & r > r_c \end{cases}$$

WHERE a AND b ARE SUCH THAT

$$U_{LT}(r_c) + a \cdot r_c + b = 0$$

$$\left. \frac{dU_{LT}^M}{dr} \right|_{r=r_c} = \left. \frac{dU_{LT}(r)}{dr} \right|_{r=r_c} + a = 0$$

SO THAT

$$a = - \left. \frac{dU_{LT}}{dr} \right|_{r=r_c}$$

$$b = - U_{LT}(r_c) - a r_c$$

TYPICALLY

$$2.5 \sigma \leq r_c \leq 5 \sigma$$

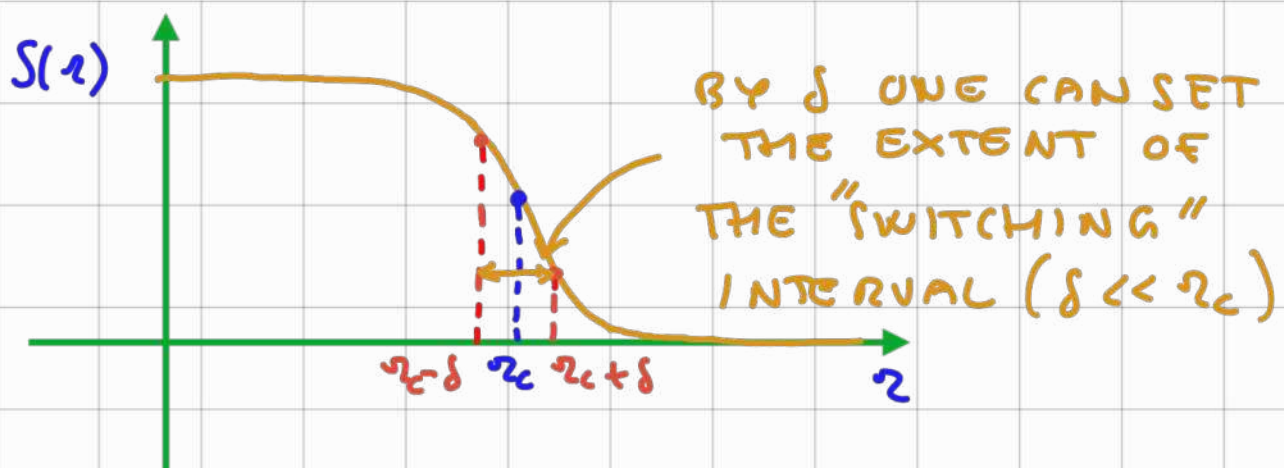
SWITCH FUNCTION

$$U_{LT}^S(r) = U_{LT}(r) \cdot S(r)$$

WHERE

$$S(r) = 0.5 \left[1 + \tanh\left(\frac{r_c - r}{\delta}\right) \right]$$

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad \text{WITH } \delta \ll r_c$$



LENNARD-JONES POTENTIAL FROM FIRST PRINCIPLES (SEE SLIDES)

EXAMPLE SIMULATION OF A POLYMER MELT (KREMER-GREST MODEL)

INTRAMOLECULAR

$$U_{LT}^{CS} (r_c = 2.5\sigma)$$

POLYMER #1
(A MONOMER)

INTERMOLECULAR
NON-CONSECUTIVE

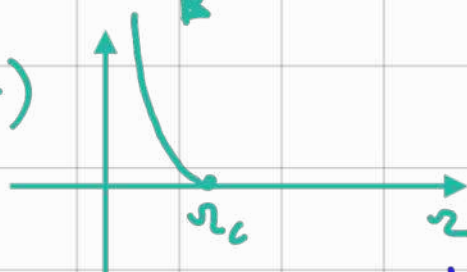
$$U_{LT}^{CS} (r_c = 2.5\sigma)$$

INTERMOLECULAR
CONSECUTIVE

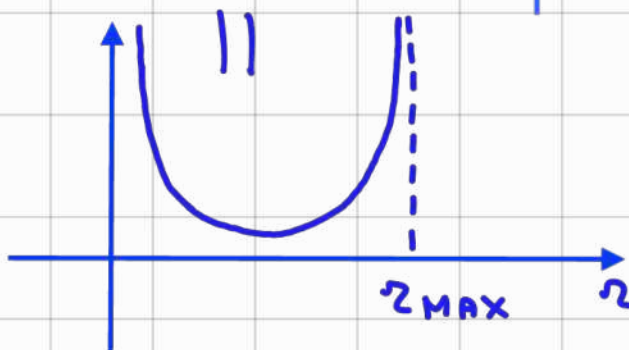
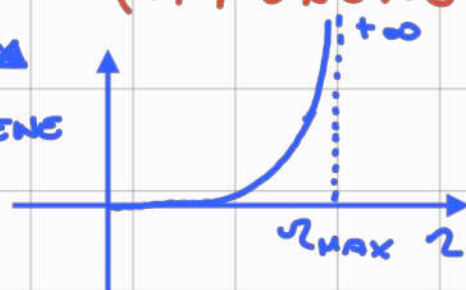
$$U_{LT}^{CS} (r_c = 2^{1/6}\sigma) + U_{FENE}$$

POLYMER #2
(A MONOMER)

$$U_{LT}^{CS} (r_c = 2^{1/6}\sigma)$$



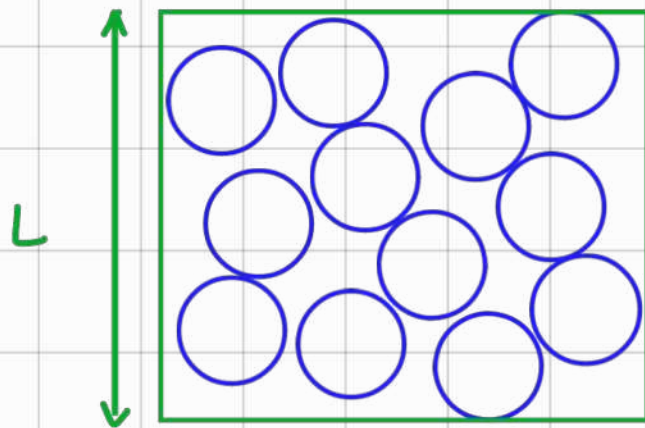
+ U_{FENE}



MC ON LATTICE (E.G. ISING MODEL)

EACH MC CONSISTS IN UPDATING
STATE OF A LATTICE SITE

SURFACE EFFECTS



$$V = L^3$$

N PARTICLES

$$\rho = \frac{N}{V}$$

$$F = F_{\text{SURF}} + F_{\text{BULK}}$$

$$F_{\text{SURF}} = \gamma \overset{\text{AREA}}{\sigma} = 6\gamma L^2$$

$$F_{\text{BULK}} = \overset{\text{CONSTANT}}{k} \cdot N = k \rho V = k \rho L^3$$

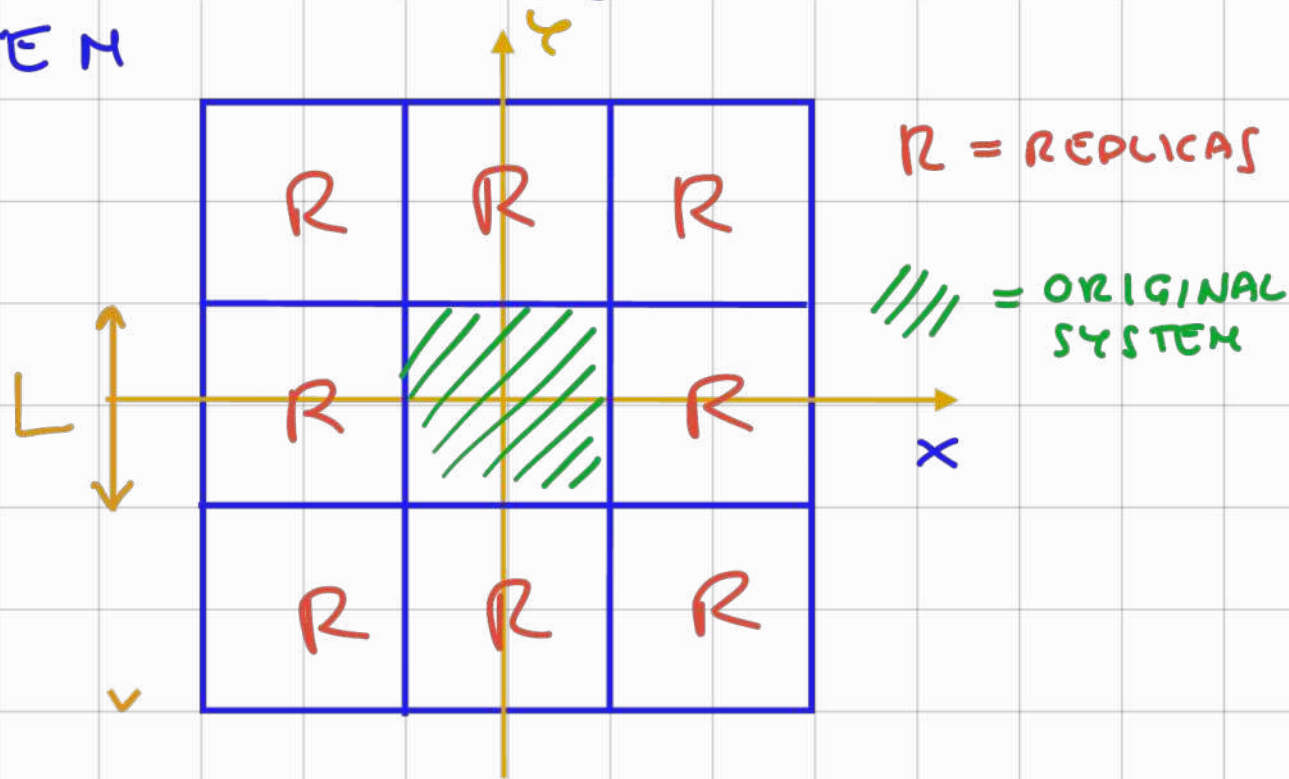
HENCE

$$\frac{F_{\text{SURF}}}{F_{\text{BULK}}} \sim \frac{1}{L}$$

I.E. F_{SURF} IS NOT NEGLIGIBLE FOR SIMULATED SYSTEMS,
SINCE BOX SIZE IS RATHER SMALL

NEED TO GET RID OF
SURFACE EFFECTS TO COMPARE
WITH EXPERIMENTAL RESULTS

INFINITE REPLICAS OF THE SYSTEM



$$U = \frac{1}{2} \sum_{i,j} U_2(\vec{r}_{ij})$$

↑
POTENTIAL ENERGY

$$U = \frac{1}{2} \sum_{\substack{i,j,\vec{n} \\ i \neq j, \vec{n} \neq 0}} U_2(\vec{r}_i - (\vec{r}_j + L\vec{n}))$$

↓
PAIR POTENTIAL

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

n_d SIGNED INTEGER $d = x, y, z$

PROBLEM: INFINITE TERMS IN CALCULATION OF ENERGY

↓
MINIMUM IMAGE CONVENTION

WHEN WE MOVE A PARTICLE i IN A MC SIMULATION WE NEED TO CALCULATE THE VARIATION OF U , I.E.

$$\Delta U_i = U_i' - U_i \quad \vec{r}_i \rightarrow \vec{r}_i'$$

WHERE

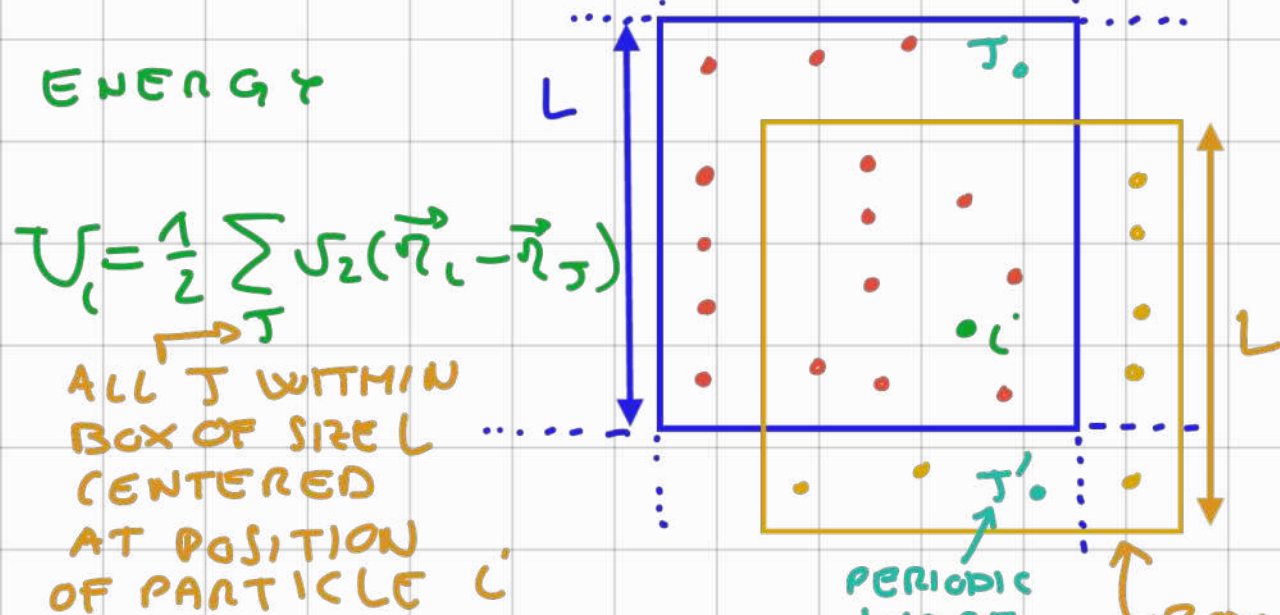
$$U_i' = \sum_j U_2(\vec{r}_i' - \vec{r}_j)$$

$$U_i = \sum_j U_2(\vec{r}_i - \vec{r}_j)$$

↑
NEW STATE

TO CALCULATE U_i AND U_i' WE EMPLOY THE MINIMUM IMAGE CONVENTION

ENERGY



ALL j WITHIN
BOX OF SIZE L
CENTERED
AT POSITION
OF PARTICLE i

PERIODIC
IMAGE
OF j

BOX CENTERED
AT POSITION
OF PARTICLE i

WHERE WE
REQUIRE $r_c < \frac{L}{2}$

↑
SO THAT WE ARE NOT
MISSING CONTRIBUTIONS

$$U_i = \sum_j U_2(\vec{r}_i - \vec{r}_j) = \sum_j U_2(\vec{r}_{i,j})$$

IF j IS NOT INSIDE MINIMUM IMAGE
WE NEED TO CONSIDER IS PERIODIC
IMAGE, I.E.

ELEMENT-WISE DIVISION,

$$U_2(\vec{r}_{1,T}) \rightarrow U_2\left(\vec{r}_{1,T} - L \cdot \pi \pi \left(\frac{\vec{z}_{1,T}}{L}\right)\right) (*)$$

WHERE IF $\vec{u} = (u_x, u_y, u_z)$

$$\text{RINT}(\vec{v}) \equiv \text{RINT} \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \equiv \begin{pmatrix} \text{RINT}(v_x) \\ \text{RINT}(v_y) \\ \text{RINT}(v_z) \end{pmatrix}$$

WHERE $R_{INT}(x) = \{ \text{INTEGER NEAREST TO } x \}$

EXAMPLES $\text{RINT}(0.6) = 1$

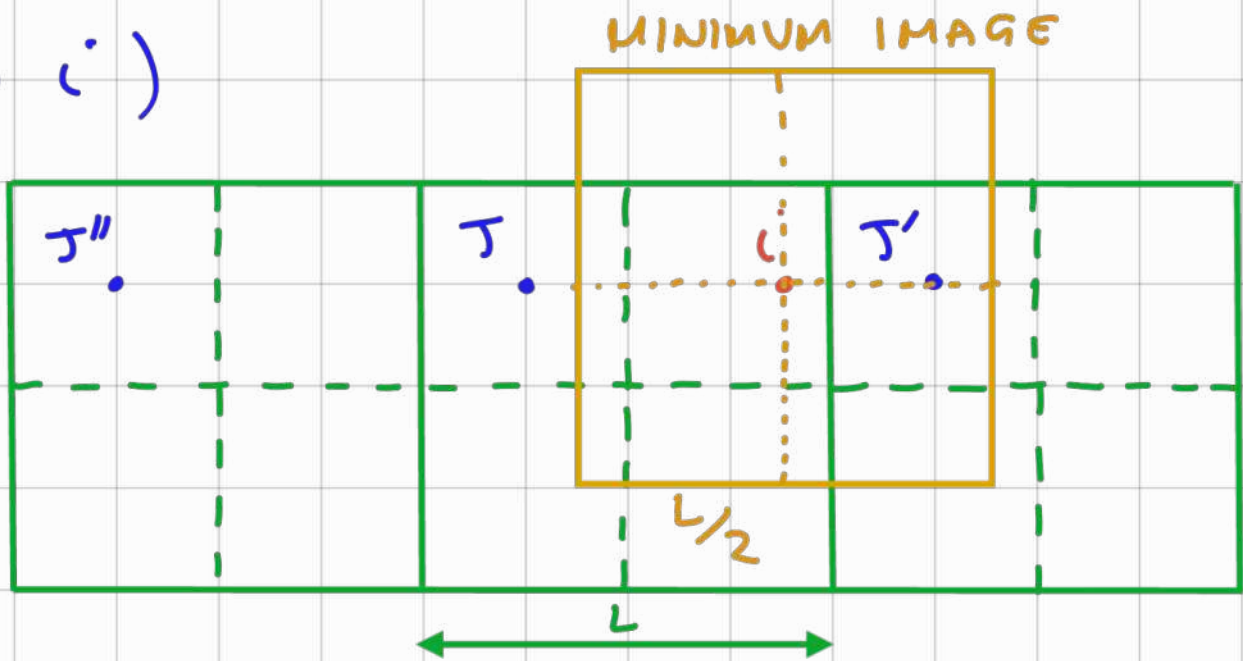
$$\text{rint}(0.2) = 0$$

$$\pi_{NT}(-0.7) = -1$$

LET'S SHOW THAT (*) PROVIDES

THE CORRECT MINIMUM IMAGE PARTICLE
(I.E. THE PARTICLE γ IN THE

PERIODIC SYSTEM WHICH IS CLOSER
TO (i) MINIMUM IMAGE



$$\vec{r}_i = (x_i, y_i) \quad \vec{r}_j = (x_j, y_j)$$

$$\vec{r}_i - \vec{r}_j - L \text{ RINT} \left(\frac{\vec{r}_i - \vec{r}_j}{L} \right) =$$

$$\text{BUT } L \text{ RINT} \left(\frac{\vec{r}_i - \vec{r}_j}{L} \right) = L \text{ RINT} \left(\begin{array}{c} \frac{x_i - x_j}{L} \\ \frac{y_i - y_j}{L} \end{array} \right) =$$

$$= L \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} L \\ 0 \end{pmatrix}$$

ELEMENT
WISE DIVISION

HENCE

$$\begin{pmatrix} x_i - x_j - L \\ y_i - y_j \end{pmatrix} = \begin{pmatrix} x_i - (x_j + L) \\ y_i - y_j \end{pmatrix} =$$

$$= \begin{pmatrix} x_i - x_{j'} \\ y_i - y_j \end{pmatrix} = \vec{r}_i - \vec{r}_{j'}$$

↑
CLOSEST PERIODIC
IMAGE OF J

FINAL REMARK :

ADJUSTMENT OF DISTANCES BETWEEN
PARTICLES (EQ. (*)) MUST BE APPLIED
EVERY TIME ONE HAS TO CALCULATE
DISTANCES FOR CALCULATION OF INTERACTION
POTENTIAL