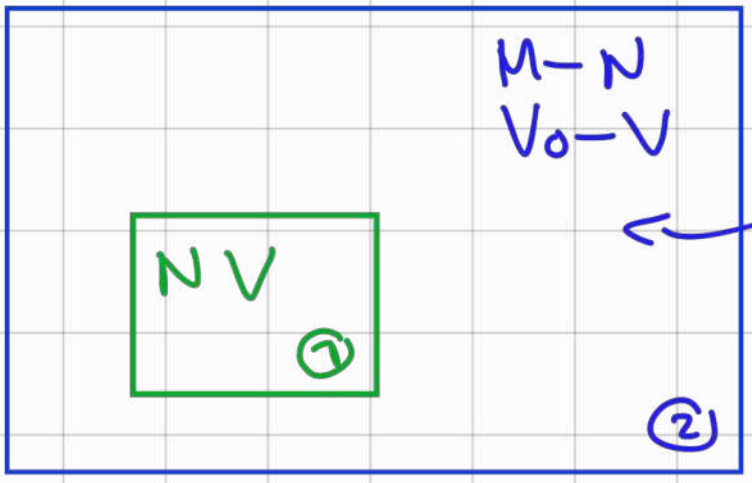
# GRAND CANONICAL ENSEMBLE ($\mu$ V T)

$\mu$ ← CHEMICAL POTENTIAL




HEAT BATH
IDEAL GAS
WITH A FIXED
CHEMICAL POTENTIAL $\mu$

$N \ll M$

$V \ll V_0$

EXCHANGE OF PARTICLES BETWEEN ① AND ②

GOAL: WRITE THE PARTITION FUNCTION OF ① + ② AND DERIVE THE CONFIGURATIONAL DISTRIBUTION FUNCTION OF ①

← SUM OVER PARTICLES NUMBER

$$Q = \sum_{N=0}^{M} \int \frac{d^{M-N}\vec{r}}{\Lambda^{3(M-N)}(M-N)!} \int \frac{e^{-\beta U_N}}{\Lambda^{3N} N!} d^N\vec{r}$$

WE USE SCALED COORDINATES AS FOR NPT, I.E.

① $\vec{r}_i = V^{1/3} \vec{s}_i \quad i \in ①$

② $\vec{r}_i = (V_0 - V)^{1/3} \vec{s}_i \quad i \in ②$

$$Q = \sum_{N=0}^{M} \underbrace{\frac{(V_0 - V)^{M-N}}{\Lambda^{3(M-N)}(M-N)!} \int d^{3(M-N)} r_s}_{\text{HEAT BATH}} \int \frac{e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{3N} r_s$$

STIRLING FORMULA

$$\ln(M-N)! \approx (M-N)\ln(M-N) - (M-N)$$

NEGLIGIBLE FOR $M \to +\infty$

I.E.

$$(M-N)! \approx (M-N)^{M-N}$$

$$Q = \sum_{N=0}^{M} \left( \frac{V_0 - V}{M-N} \right)^{M-N} \frac{1}{\Lambda^{3(M-N)}} \int \frac{e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{3N} r_s$$

BUT $\rho = \frac{M-N}{V_0 - V} \Rightarrow \frac{V_0 - V}{M-N} = \frac{1}{\rho}$

HENCE

$$Q = \sum_{N=0}^{M} \frac{1}{\rho^{M-N}} \frac{1}{\Lambda^{3(M-N)}} \int \frac{e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{3N} r_s$$

NOW REMEMBER THAT FOR ②

$$\beta \frac{F_{id}}{V} = \rho \ln(\Lambda^3 \rho) - \rho$$

$$F_{id} = \frac{V}{\beta}(\rho \ln(\Lambda^3 \rho) - \rho)$$

$$\mu \equiv \frac{\partial F_{id}}{\partial N} = \frac{1}{\beta} \ln(\Lambda^3 \rho)$$

I.E.

$$\rho = \frac{e^{\beta \mu}}{\Lambda^3}$$

$Q_N(T,V)$ = $F = -k_B T \ln\left(\frac{V^N}{\Lambda^{3N} N!}\right)$

$N! \sim N^N e^N$

$= k_B T N \ln(\Lambda^3 \rho) - N$

$= \frac{V}{\beta}(\rho \ln(\Lambda^3 \rho) - \rho)$

$$Q = \sum_{N=0}^{M} \int \frac{1}{e^{\beta\mu N}} e^{\beta\mu N} \frac{\Lambda^{3(M-N)}}{\Lambda^{3(M-N)}} \frac{e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{2N}\vec{r} =$$

CONSTANT I.E INDEPENDENT OF SYSTEM STATE

$$= \sum_{N=0}^{M} e^{\beta\mu N} \int \frac{e^{-\beta U_N}}{\Lambda^{3N} N!} d^{2N}\vec{r}$$

STATE OF THE SYSTEM : $(N, \vec{r}_1 \dots \vec{r}_N)$

PROBABILITY OF BEING IN A GIVEN STATE:

$$W(N, \vec{r}_1 \dots \vec{r}_N) \propto \frac{e^{\beta\mu N} e^{-\beta U_N}}{\Lambda^{3N} N!} V^N$$

I.E.

$$W(N, \vec{r}_1 \dots \vec{r}_N) = \frac{e^{\beta\mu N} e^{-\beta U_N}}{\Lambda^{3N} N! \; \mathcal{Q}} V^N$$

WHERE

$$\mathcal{Q} = \{\text{GRAN PARTITION FUNCTION}\} =$$

$$= \sum_{N=0}^{\infty} \int \frac{e^{\beta\mu N} e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{N}\vec{r}$$

$$\Omega = \{\text{GRAN POTENTIAL}\} = -k_B T \ln \mathcal{Q}$$

$$= -k_B T \ln \left( \sum_{N=0}^{\infty} e^{\beta\mu N} \underbrace{\int \frac{e^{-\beta U_N} V^N}{\Lambda^{3N} N!} d^{N}\vec{r}}_{Q_N(T,V)} \right) =$$

$$= -k_B T \ln \left( \underbrace{\sum_{N=0}^{\infty} e^{\beta\mu N} Q_N(T,V)}_{\text{MAIN CONTRIBUTION FROM } N = \bar{N} = \langle N \rangle} \right) =$$

$$= -k_B T \ln\left(e^{\beta\mu\bar{N}} Q_{\bar{N}}(T,V)\right) =$$

$$= -\mu\bar{N} - k_B T \ln\left(Q_{\bar{N}}(T,V)\right) =$$

$$= -\mu\bar{N} + F_{\bar{N}}(T,V)$$ ← HELMOLTZ FREE ENERGY

BUT $\mu\bar{N} = G$ ← GIBBS FREE ENERGY

HENCE

$\Omega = -G + F_{\bar{N}}$ BUT $G = F_{\bar{N}} + PV$

SO THAT

$$\Omega = -\cancel{F_{\bar{N}}} - PV + \cancel{F_{\bar{N}}} = -PV$$

$$\boxed{\Omega = -PV}$$

# IMPLEMENTATION OF MC METROPOLIS

MICROSCOPIC STATE

$(N, \vec{s}_1 \dots \vec{s}_N)$

WE NEED TWO TYPES OF MOVE

1) PARTICLE MOVE $\alpha(o \to n)$

$\vec{r}_i^{\,o} = V^{1/3} \vec{s}_i$

$\vec{r}_i^{\,n} = \vec{r}_i^{\,o} + \Delta\vec{r}$ WITH $\Delta\vec{r} = \delta \vec{\xi}$ STOCHASTIC

$\vec{\xi}_\alpha \in [-1, 1]$

$$acc(o \to n) = \min\left\{1, \frac{W(N, \vec{s}_1, \dots, \vec{s}_i', \dots, \vec{s}_N)}{W(N, \vec{s}_1, \dots, \vec{s}_i, \dots \vec{s}_N)}\right\} =$$

$$= \min\left\{1, \frac{e^{\cancel{\beta\mu N}}}{e^{\cancel{\beta\mu N}}} \frac{e^{-\beta U_N'}}{e^{-\beta U_N}} \frac{\cancel{V^N}}{\cancel{V^N}} \frac{\cancel{N!\Lambda^{3N}}}{\cancel{N!\Lambda^{3N}}}\right\}$$

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

THIS IS IDENTICAL TO PARTICLE MOVE IN A MC-NVT (CANONICAL ENSEMBLE)

2) INSERTION OR REMOVAL OF A PARTICLE

INSERTION: $o \rightarrow n$, $N \rightarrow N+1 = N'$

REMOVAL: $o \rightarrow n$, $N \rightarrow N-1 = N'$

THIS MOVE IS ATTEMPTED WITH PROBABILITY $P_{GC} \approx 5-10\%$

WHILE INSERTION AND REMOVAL CAN BE EQUALLY LIKELY

INSERTION MOVE:

$\alpha(o \rightarrow n)$:

$o$: $N$

$n$: $N+1 = N'$ PARTICLE IS INSERTED RANDOMLY IN THE SIMULATION BOX

$acc(o \rightarrow n)$:

$$W(N, \vec{r}_1 \dots \vec{r}_N) \propto \frac{z^N}{\Lambda^{3N} N!} e^{-\beta U_N} V^N$$

WHERE

$z = e^{\beta\mu} =$ {FUGACITY}

$$acc(o \rightarrow n) = \min\left\{1,\ \frac{W(N', \vec{r}_1 \dots \vec{r}_{N'})}{W(N, \vec{r}_1 \dots \vec{r}_N)}\right\} =$$

$$= \min\left\{1,\ \frac{z^{N+1} e^{-\beta U_{N+1}} V^{N+1} \Lambda^{3N} N!}{z^N e^{-\beta U_N} V^N \Lambda^{3(N+1)} (N+1)!}\right\} =$$

$$= \min\left\{1, \frac{z}{\Lambda^3}\frac{e^{-\beta\Delta U_I}V}{N+1}\right\} =$$

$\Delta U_I = U_{N+1} - U_N$

$$= \min\left\{1, \frac{\tilde{z}}{}\frac{e^{-\beta\Delta U_I}V}{N+1}\right\}$$

WITH $\tilde{z} \equiv \frac{z}{\Lambda^3}$ ← THIS IS WHAT WE SET IN THE SIMULATION

## REMOVAL MOVE

$\alpha(o \to n)$

$o : N$

$n : N-1 = N'$

A PARTICLE IS CHOSEN RANDOMLY AND IT IS REMOVED

$acc(o \to n)$ :

$$acc(o\to n) = \min\left\{1, \frac{z^{N-1}}{z^N}\frac{e^{-\beta U_{N-1}}V^{N-1}\Lambda^{3N}N!}{e^{-\beta U_N}V^N\Lambda^{3(N-1)}(N-1)!}\right\} =$$

$$= \min\left\{1, \frac{\Lambda^3}{z^N}e^{-\beta\Delta U_R}\frac{N}{V}\right\} =$$

$\Delta U_R = U_{N-1} - U_N$

$$= \min\left\{1, \frac{1}{\tilde{z}}e^{-\beta\Delta U_R}\frac{N}{V}\right\}$$

## CALCULATION OF PRESSURE

PROBABILITY OF HAVING N PARTICLES

$$W(N) \equiv \int \mathcal{W}(N, \vec{s}_1 \dots \vec{s}_N)\, d^N\vec{s} = \frac{z^N Q_N}{\mathcal{Q}}$$

$$\bar{N} = \sum_{N=0}^{\infty} N\, W(N) = \bar{N}(\mu, T, V)$$

$$\rho = \frac{\bar{N}}{V} = \rho(\mu, T, V) \quad (1)$$

$$\Omega = -k_B T \ln \mathcal{Q} = -PV$$

HENCE $\mathcal{Q} = e^{\beta PV}$ I.E.

$$W(N) = \frac{z^N Q_N}{e^{\beta PV}}$$

LET'S CONSIDER $N = 0$

$z^0 = 1$ $\qquad Q_N = \frac{V^N}{\Lambda^{3N} N!} \int e^{-\beta U_N} d^{3N}\xi$

IF $N \leq 1$ $\qquad Q_N = \frac{V^N}{\Lambda^{3N} N!} \int_0^1 d^{3N}\xi$

HENCE

$$Q_0 = \frac{V^0}{\Lambda^{0}} \frac{1}{0!} \qquad \text{BUT } N! = \Gamma(1+N) \text{ I.E.}$$

EULER GAMMA

$0! = \Gamma(1) = 1$ SO THAT

$$Q_0 = 1$$

THEN WE HAVE

$$W(0) = \frac{1}{e^{\beta PV}} \Rightarrow P = -\frac{1}{\beta V} \ln(W(0))$$

I.E. $P = P(\mu, T, V)$ (2)

IF $T$ AND $V$ ARE FIXED AND WE VARY $\mu$, FROM (1) AND (2) WE HAVE:

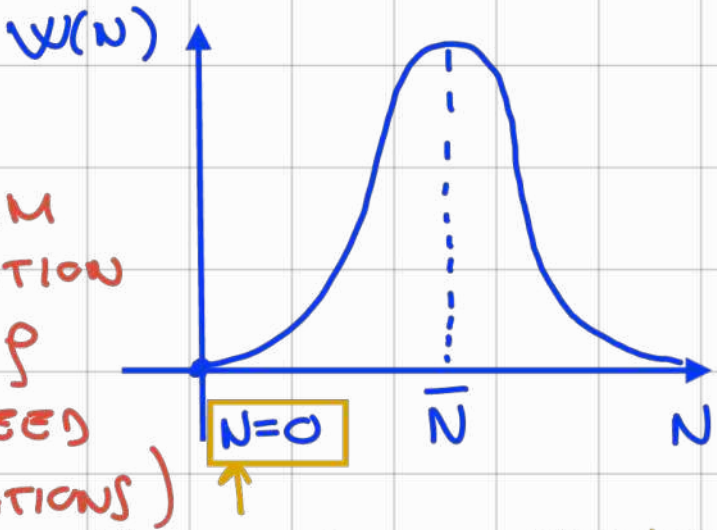
$\rho = \rho(\mu)$ AND $P = P(\mu)$

FROM WHICH WE CAN OBTAIN

$$P = P(\mu(\rho)) = P(\rho)$$

# 1.E THE EQUATION OF STATE

ANYWAY NOTE THAT




$\bar{N} \gg 0$

WE NEED TO PERFORM ONE SIMULATION FOR EACH $\beta$ (I.E. WE NEED MANY SIMULATIONS)

N=0 IS IN GENERAL VERY UNLIKELY HENCE W(0) IS RATHER NOISY

A PRACTICAL STRATEGY TO BUILD THE EQUATION OF STATE

WE WANT TO PROVE THAT

$$\beta P_N V = N \ln\left(\frac{W(N)}{W(N+1)}\right) + \ln\left(\frac{W(N)}{W(0)}\right)$$

REMEMBER THAT:

$$W(N) = \frac{z^N Q_N(T,V)}{e^{\beta PV}} \qquad \text{WHERE } z = e^{\beta M}$$

BUT $Q_N(T,V) = e^{-\beta F_N}$ HENCE

$$N \ln\left(\frac{z^N e^{-\beta F_N} e^{\beta PV}}{z^{N+1} e^{-\beta F_{N+1}} e^{\beta PV}}\right) + \ln\left(\frac{z^N e^{-\beta F_N} e^{\beta PV}}{z^0 e^{-\beta F_0} e^{\beta PV}}\right) =$$

$$= N \ln\left(\frac{1}{z} e^{\beta(F_{N+1} - F_N)}\right) + N \ln\left(z e^{-\beta F_N}\right) \quad (1)$$

NOTE THAT IF $N \gg 1$

$$F_{N+1} - F_N = \frac{F_{N+1} - F_N}{1} \approx \frac{\partial F_N}{\partial N} = \quad (2)$$

$$= \mu_N$$

GIBBS FREE ENERGY

BUT $G_N = \mu_N N = F_N + P_N V$

I.E. $$\mu_N = \frac{F_N + P_N V}{N} \quad (3)$$

AND WE HAVE BY USING EQS. (2) AND (3) IN EQ. (1):

$$= -N \ln Z + \beta F_N + \beta P_N V + N \ln Z - \beta F_N =$$

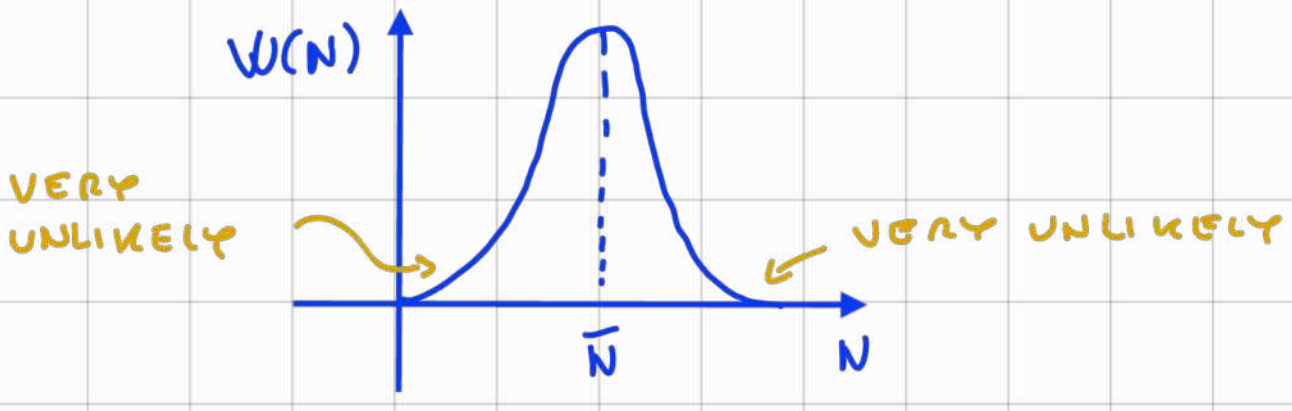
$= \beta P_N V$ WHICH IS WHAT WE HAD TO PROVE, I.E.

$$\beta P_N V = N \ln\left(\frac{W(N)}{W(N+1)}\right) + \ln\left(\frac{W(N)}{W(0)}\right)$$

NOW $P = \frac{N}{V}$ AND $V$ IS FIXED THEN

$P_N = P(\rho)$ I.E. THE EQUATION OF STATE

ANYWAY SOME N CAN BE VERY UNLIKELY FROM A MVT SIMULATION, INDEED




NEED TO IMPROVE STATISTICS

# SUCCESSIVE UMBRELLA SAMPLING (SUS)

EVEN THOUGH IT WOULD BE BETTER

CALLED PARALLEL UMBRELLA SAMPLING

(PUS ?!?)

CONSIDER M SIMULATIONS RUNNING IN PARALLEL

#1 [0, 1] N=0 OR N=1 PARTICLES

#2 [1, 2]

⋮

#n [n-1, n]

⋮

#M [M-1, M] N= M-1 o N=M PARTICLES

I.E. n-th SIMULATION WITH n = 1 .. M IS FORCED TO HAVE EITHER

n-1 OR n PARTICLES, THIS MEANS THAT FOR n-th SIMULATION

A) IF N = n AND INSERTION MOVE IS ATTEMPTED, THIS MOVE IS REJECTED

B) IF N = n-1 AND REMOVAL MOVE IS ATTEMPTED, THIS MOVE IS REJECTED

NOW WE OBSERVE THAT FROM EACH SIMULATION WE CAN CALCULATE:

#1: $\frac{W(1)}{W(0)}$

#2: $\frac{W(2)}{W(1)}$

⋮

#M: $\frac{W(M)}{W(M-1)}$

BUT FROM THIS QUANTITIES WE CAN HAVE:

$$\frac{W(n)}{W(0)} = \overbrace{\frac{W(n)}{W(n-1)}}^{\text{RUN \#n}} \cdot \overbrace{\frac{W(n-1)}{W(n-2)}}^{\text{RUN \#n-1}} \cdots \overbrace{\frac{W(1)}{W(0)}}^{\text{RUN \#1}}$$

$\forall\, n \in [1, M]$ WHERE

$W(0)$ IS CALCULATED BY REQUIRING

$$\sum_{n=0}^{M} W(n) = 1$$ I.E. THAT $W(n)$ IS NORMALIZED

## DETAILED DESCRIPTION OF THE PROCEDURE

FROM RUN #n WE CALCULATE

$W^{(n)}(n)$ AND $W^{(n)}(n-1)$

WHERE $W^{(n)}(\ell)$ COUNTS THE NUMBER OF TIMES SYSTEM #n HAS $\ell$ PARTICLES

AND WE DO THIS FOR ALL $n = 1 \ldots M$

NOTE THAT $W^{(n)}(n) \neq W(n)$ AND $W^{(n)}(n-1) \neq W(n-1)$

$W(n)$ IS A PROBABILITY, WHILE $W^{(n)}(n)$ IS NOT NORMALIZED

ANYWAY $$\frac{W^{(n)}(n)}{W^{(n)}(n-1)} = \frac{W(n)}{W(n-1)}$$

RATIOS DO NOT DEPEND ON NORMALIZATION

$W^{(1)}(0) \neq W(0)$

$$W(0) = W^{(1)}(0)\, K$$

RATIOS ARE CORRECT, I.E. $\frac{W^{(1)}(1)}{W^{(1)}(0)} = \frac{W(1)}{W(0)}$

$$W(1) = \frac{W^{(1)}(1)}{W^{(1)}(0)} \cdot W^{(1)}(0)\, K$$

$$W(2) = \frac{W^{(2)}(2)}{W^{(2)}(1)} \cdot W(1) = \frac{W^{(2)}(2)}{W^{(2)}(1)} \cdot \frac{W^{(1)}(1)}{W^{(1)}(0)} W^{(1)}(0)\, K$$

$\vdots$

WHERE $K$ IS UNKNOWN,

THEN WE REQUIRE THAT $K$ IS SUCH THAT

$$\sum_{n=0}^{M} W(n) = 1$$

AND AFTER HAVING DETERMINED $K$

ONE HAS:

$$W(0) = W^{(1)}(0) \cdot K$$

**REMARK FOR BUILDING $W(n)$**

IF WE ARE IN CASE A) OR B), MOVE IS REJECTED BUT HISTOGRAM FOR $W(n)$ IS UPDATED (I.E. INCREASED BY 1).

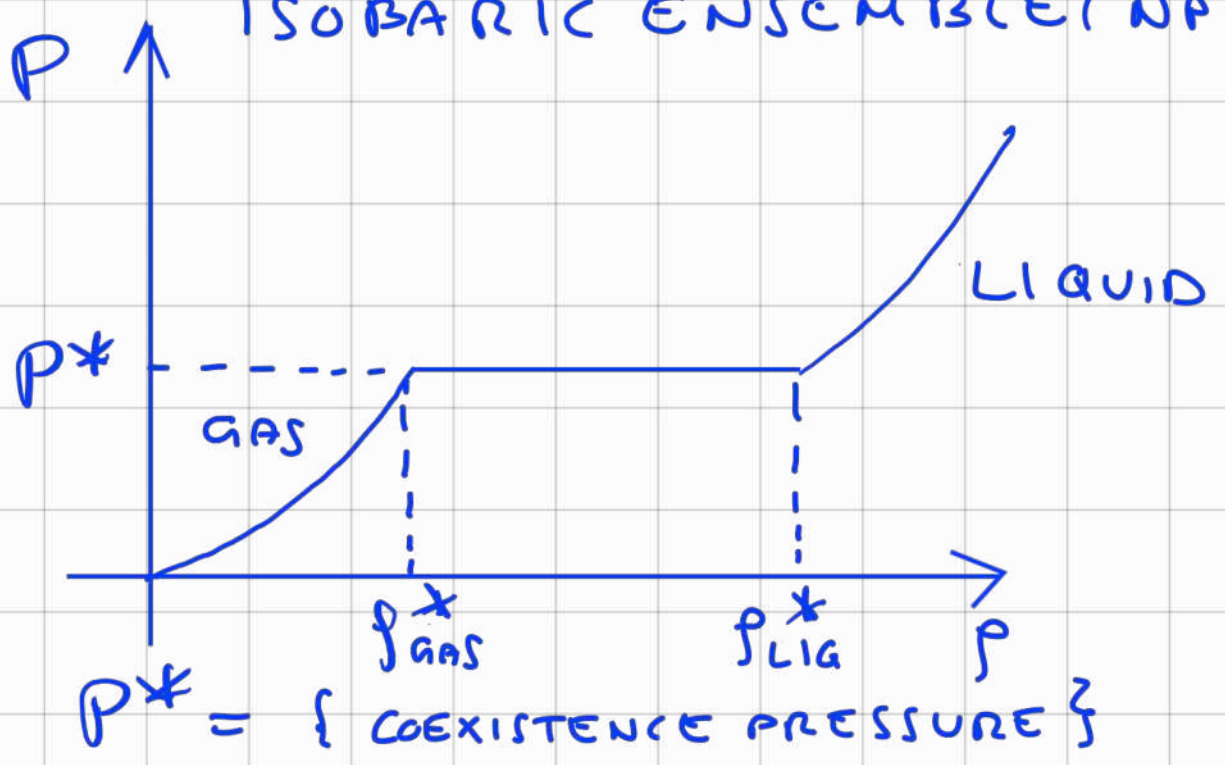
CONSIDER SIMULATION # $n$ WHERE

$N = n-1$ AND REMOVAL IS ATTEMPTED, WE HAVE TO IMAGINE THAT THE SYSTEM IN ITS RANDOM WALK IN N WILL COME BACK TO $N = n-1$ (NO MATTER THE NUMBER OF MOVES REQUIRED), HENCE WE KEEP $N=n-1$ AND WE UPDATE HISTOGRAM OF $W(n)$.

A SIMILAR REASONING CAN BE USED FOR AN INSERTION MOVE FOR $N=n$ IN THE SIMULATION # n

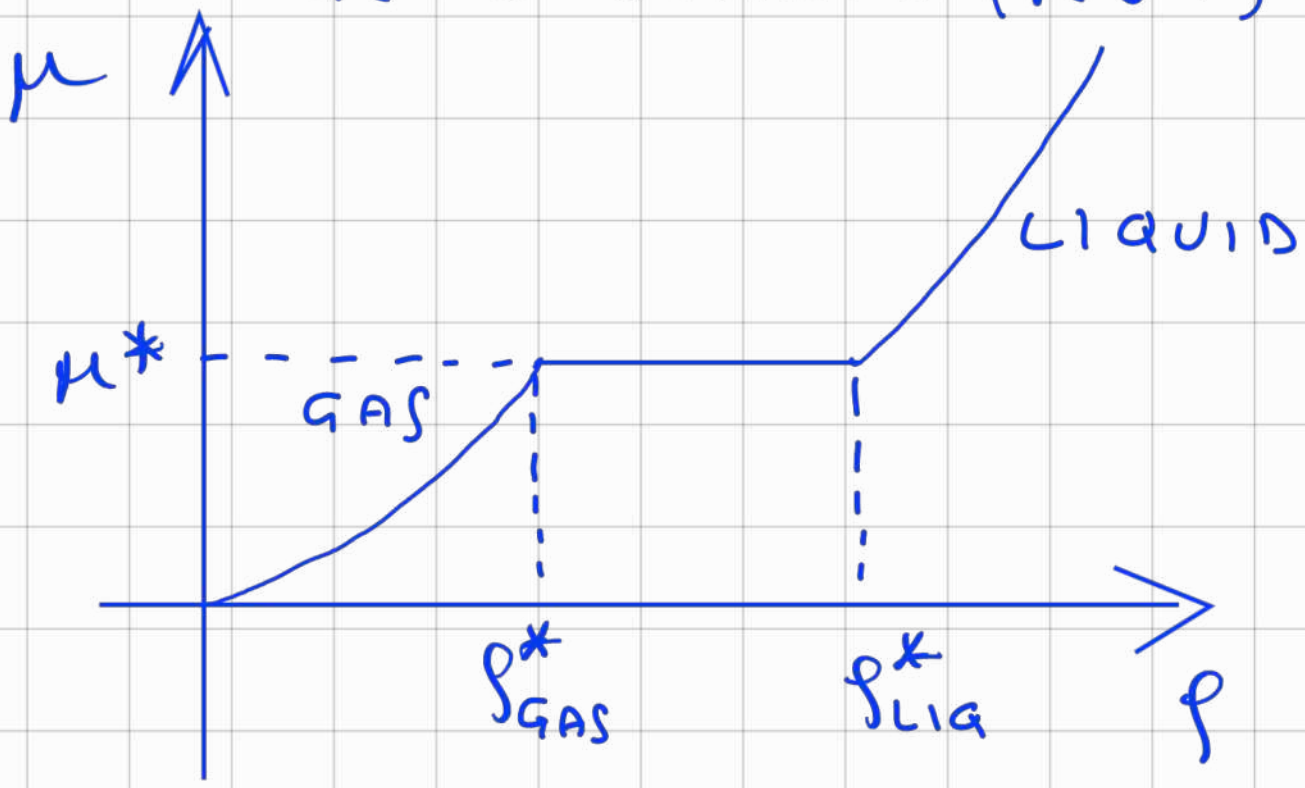
**SUS CAN BE ALSO USED TO STUDY PHASE COEXISTENCE THROUGH HISTOGRAM REWEIGHTING**

ISOBARIC ENSEMBLE (NPT)




$P^*$ = { COEXISTENCE PRESSURE }

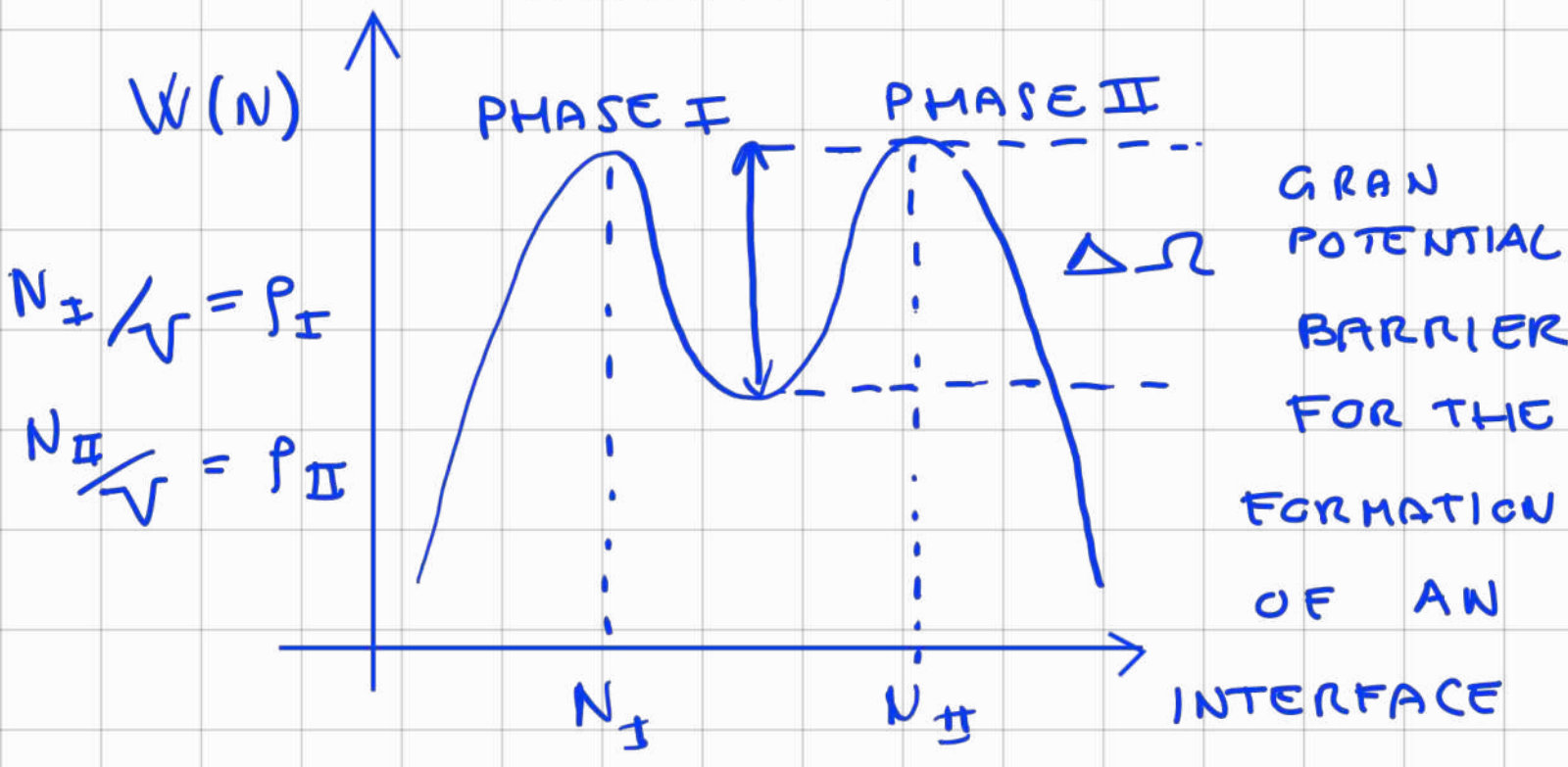
# GC ENSEMBLE ($\mu VT$)

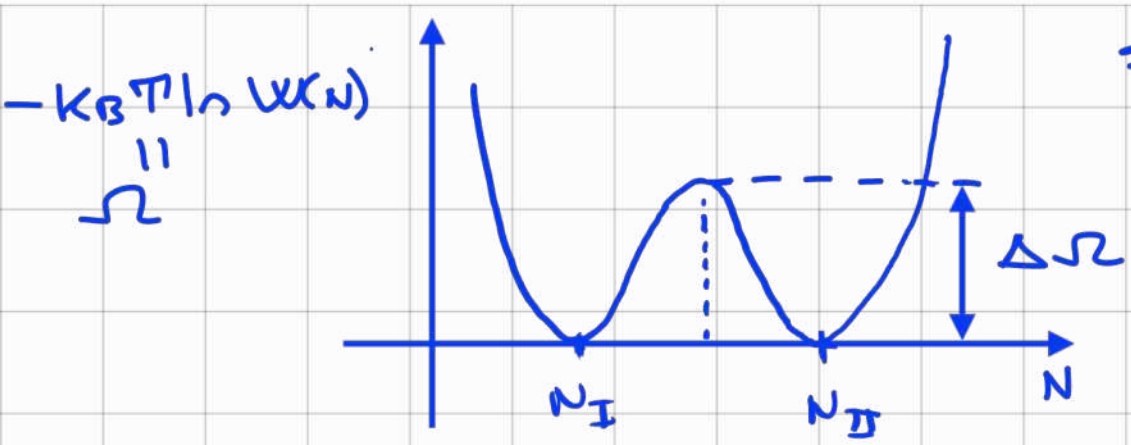



$\mu^*$ = { CHEMICAL POTENTIAL AT COEXISTENCE }

$\mu_{GAS} = \mu_{LIQ} = \mu^*$ AT COEXISTENCE

IF Z, I.E $\mu$, IS EQUAL TO THE COEXISTENCE VALUE






$z = z^*$ or $\mu = \mu^*$

$$\frac{N_I}{V} = \rho \qquad \frac{N_{II}}{V} = \rho_{II}$$

BUT IT IS NOT EASY TO HAVE $\mu = \mu^*$

⇓

HISTOGRAM REWEIGHTING

BY ASSUMING THAT $V$ AND $T$ ARE FIXED

IMAGINE THAT FROM A SUS SIMULATION AT $z = z_1$ ONE HAS CALCULATED

$$W(N, z_1) = \frac{z_1^N \, Q_N(T,V)}{\mathcal{Q}(z_1)}$$

← GRAND PARTITION FUNCTION

THEN FOR $z_2 \neq z_1$ WE HAVE

$$W(N, z_2) = \frac{z_2^N \, Q_N(T,V)}{\mathcal{Q}(z_2)}$$

HENCE DIVIDING THE TWO $W(N)$ :

$$\frac{W(N, z_2)}{W(N, z_1)} = \left(\frac{z_2}{z_1}\right)^N \frac{Q_N(T,V)}{Q_N(T,V)} \frac{\mathcal{Q}(z_1)}{\mathcal{Q}(z_2)}$$

REWEIGHTING

I.E.

$$\Omega(N, z_2) = \Omega(N, z_1) \cdot \left(\frac{z_2}{z_1}\right)^N K$$

WHERE $K = \dfrac{Q(z_1)}{Q(z_2)}$ IS A QUANTITY INDEPENDENT OF N WHICH CAN BE DETERMINED BY REQUIRING

$$\sum_{N=0}^{\infty} \Omega(N, z_2) = 1$$

NOTE THAT $\Omega(N, z_1)$ DEPENDS ON THE CALCULATIONS OF $\dfrac{\Omega(n)}{\Omega(n-1)}$ WHICH CAN BE RATHER LARGE OR SMALL, HENCE IT CAN BE CONVENIENT TO USE LOGARITHMS, I.E.

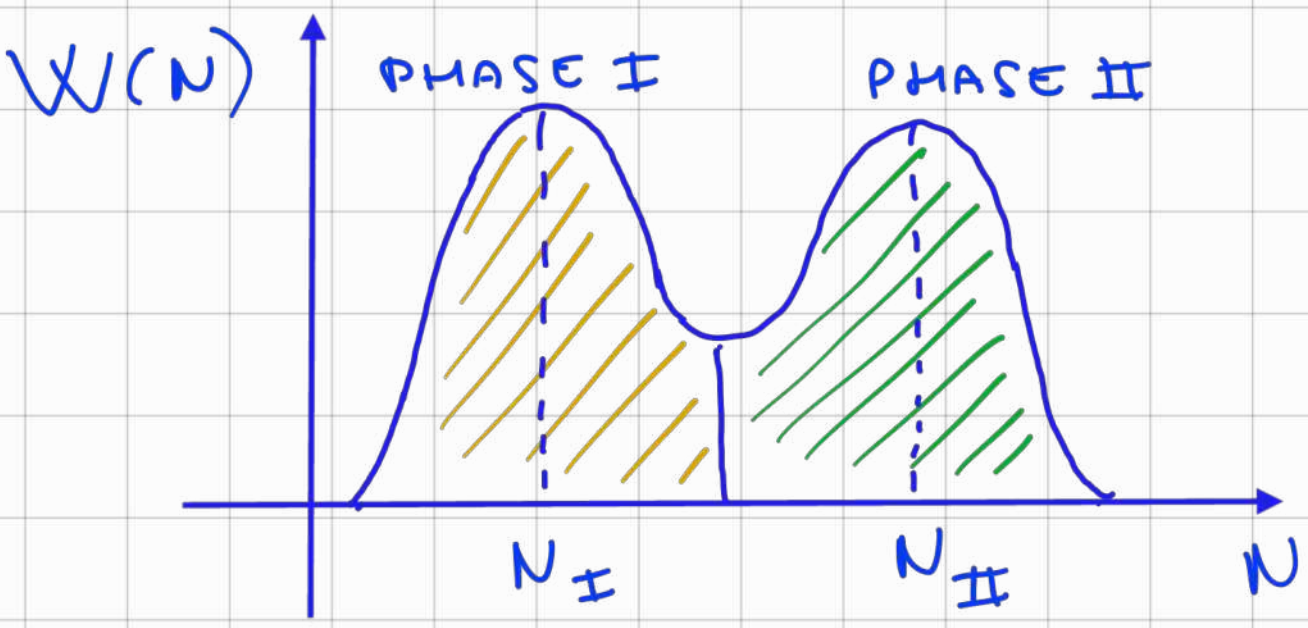
$$\ln\left(\frac{\Omega(n)}{\Omega(0)}\right) = \ln\left(\frac{\Omega(n)}{\Omega(n-1)} \cdots \frac{\Omega(1)}{\Omega(0)}\right) =$$

$$= \sum_{n=1}^{n} \ln\left(\frac{\Omega(i)}{\Omega(i-1)}\right)$$

AS DISCUSSED FOR NPT ENSEMBLE WE SEARCH THE z VALUE SUCH THAT :

WE CHANGE $\zeta_1$ IN ORDER TO HAVE:

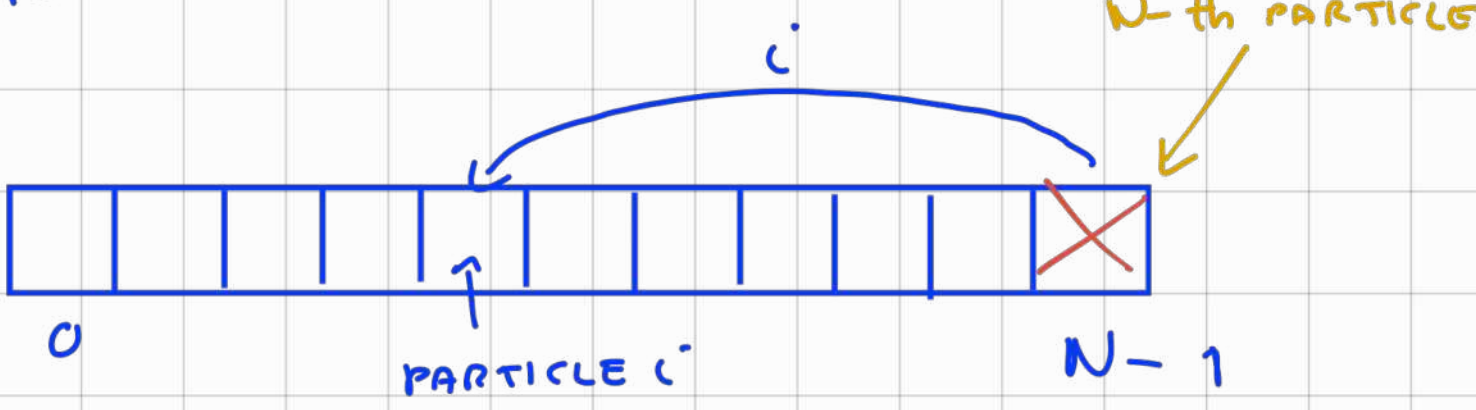
AREA I = AREA II




$$\rho_I = \frac{N_I}{V} \qquad \rho_{II} = \frac{N_{II}}{V}$$

## REMARK ON IMPLENTATION

REMOVAL OF PARTICLE




MOVE N-th PARTICLE TO i

# BIASING

$$p(o)\,\Pi(o\to n) = p(n)\,\Pi(n\to o)$$

METROPOLIS MC

$$\Pi(o\to n) = \alpha(o\to n)\,acc(o\to n)$$

IF $\alpha(o\to n) \neq \alpha(n\to o)$ BIASING

($o\to n$: TRIAL MOVE)

THEN

$$p(o)\,\alpha(o\to n)\,acc(o\to n) = p(n)\,\alpha(n\to o)\,acc(n\to o)$$

$$acc(o\to n) = \frac{\alpha(n\to o)}{\alpha(o\to n)}\,\frac{p(n)}{p(o)}\,acc(n\to o)$$

UNBIASED

$$acc(o\to n) = \min\left\{1,\ \frac{p(n)}{p(o)}\right\}$$

BIASED

$$acc(o\to n) = \min\left\{1,\ \underbrace{\frac{\alpha(n\to o)}{\alpha(o\to n)}\,\frac{p(n)}{p(o)}}_{K}\right\} =$$

$$= \min\{1, K\}$$

PROOF

$K < 1$

$$acc(o\to n) = \min\{1, K\} \overset{K<1}{=} \frac{p(n)}{p(o)}\,\frac{\alpha(n\to o)}{\alpha(o\to n)}$$

$$acc(n\to o) = \min\left\{1,\ \frac{p(o)\,\alpha(o\to n)}{p(n)\,\alpha(n\to o)}\right\} =$$

$$\min\left\{1,\ \underbrace{\frac{1}{K}}_{>1}\right\} = 1$$

HENCE

$$\pi(o)\,\alpha(o\to n)\,acc(o\to n) = \pi(n)\,\alpha(n\to o)\,acc(n\to o)$$

$$\Downarrow$$

$$\cancel{\pi(o)}\,\alpha(\cancel{o\to n})\,\frac{\cancel{\pi(n)}}{\cancel{\pi(o)}}\,\frac{\alpha(\cancel{n\to o})}{\alpha(\cancel{o\to n})} = \cancel{\pi(n)}\,\alpha(\cancel{n\to o})\,1$$

$K > 1$

$$acc(o\to n) = \min\{1, K\} = 1$$

$$acc(n\to o) = \min\left\{1, \frac{\pi(o)}{\pi(n)}\,\frac{\alpha(o\to n)}{\alpha(n\to o)}\right\} = \min\left\{1, \frac{1}{K}\right\}$$

$$= \frac{\pi(o)}{\pi(n)}\,\frac{\alpha(o\to n)}{\alpha(n\to o)}$$

$$\pi(o)\,\alpha(o\to n)\,acc(o\to n) = \pi(n)\,\alpha(n\to o)\,acc(n\to o)$$

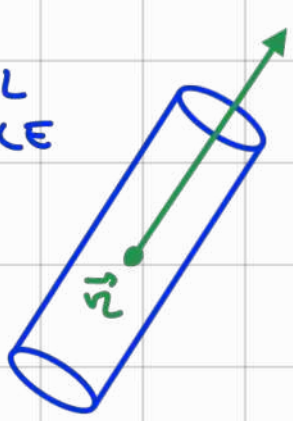
$$\Downarrow$$

$$\cancel{\pi(o)}\,\alpha(\cancel{o\to n})\,1 = \cancel{\pi(n)}\,\alpha(\cancel{n\to o})\cdot\frac{\cancel{\pi(o)}}{\cancel{\pi(n)}}\,\frac{\alpha(\cancel{o\to n})}{\alpha(\cancel{n\to o})}$$

**EXAMPLES**

## ORIENTATIONAL BIAS

UNIAXIAL PARTICLE




$(\vec{r}, \vec{u})$

IF $\alpha(o\to n) = \alpha(n\to o)$

AND WE USE A STANDARD ORIENTATIONAL MOVE (WHERE $\gamma$ OR $\Delta\theta$ ARE SMALL)

$$acc(o \to n) = \min\{1, e^{-\beta \Delta U}\}$$

IF $\beta \Delta U >> 1$

THEN $e^{-\beta \Delta U} << 1$

I.E.

$$acc(o \to n) << 1$$

I.E. IT IS VERY UNLIKELY THAT MOVE IS ACCEPTED

ORIENTATIONAL BIAS ALGORITHM

$$U = U_{POS} + U_{ROT}$$

$U_{POS}$: IT DEPENDS ONLY ON POSITIONS

$U_{ROT}$: THIS DEPENDS ON ORIENTATIONS AND POSITIONS

$$U_{POS} = U_{POS}(\vec{r}_1 \dots \vec{r}_N)$$

$$U_{ROT} = U_{ROT}(\vec{r}_1 \dots \vec{r}_N, \vec{u}_1 \dots \vec{u}_N)$$

TRIAL MOVE ($\alpha(o \to n)$)

1) CHOOSE RANDOMLY A PARTICLE $i$

2) MOVE PARTICLE $i$, I.E.

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

$\Delta\vec{r}$: RANDOM DISPLACEMENT

3) GENERATE M RANDOM ORIENTATIONS

$$\{\vec{u}_k^{(n)}\}_{k=1 \dots M}$$

(E.G. YOU CAN USE MARSAGLIA ALGORITHM)

4) CALCULATE THE SO CALLED ROSENBLUTH FACTOR, I.E. :

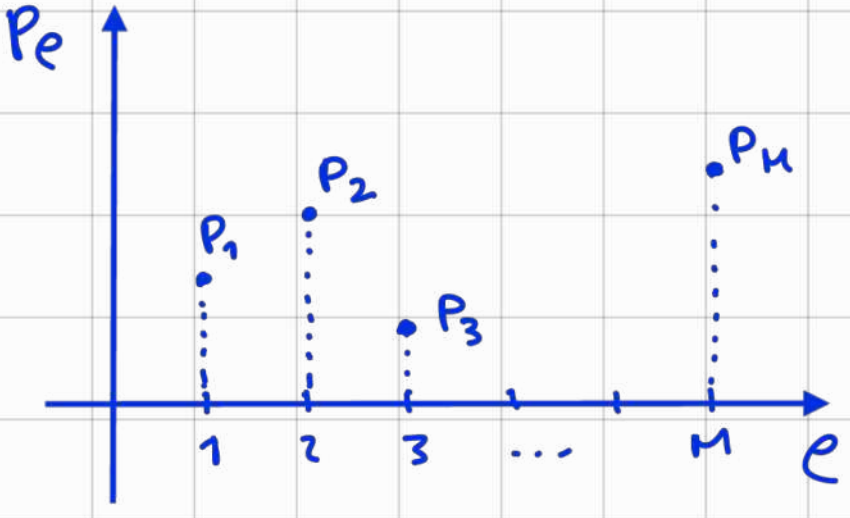
$$W(n) = \sum_{k=1}^{M} e^{-\beta U_{ROT}(\vec{U}_k^{(n)})}$$

5) SELECT RANDOMLY AN ORIENTATION $\vec{U}_c^{(n)}$ WITH PROBABILITY :

$$p_k = \frac{e^{-\beta U_{ROT}(\vec{U}_k^{(n)})}}{W(n)}$$

YOU CAN USE ONE OF THE TWO FOLLOWING STRATEGIES:

STRATEGY # 1



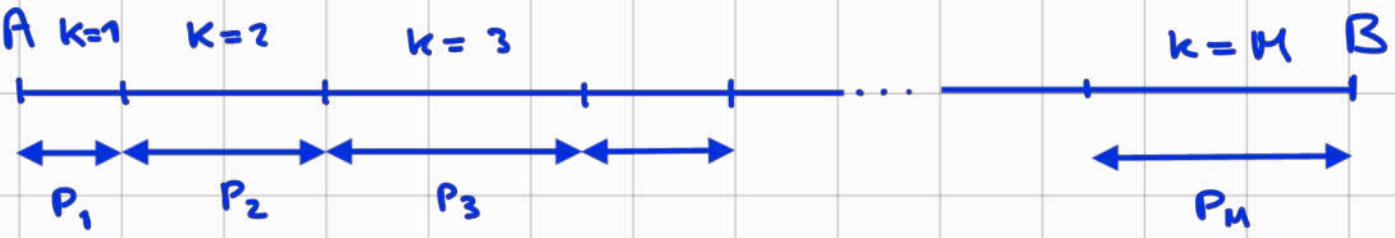

a) GENERATE A RANDOM NUMBER $e \in \{1, 2, .. M\}$

b) GENERATE RANDOMLY $\xi \in [0, p_{MAX}]$ WHERE $p_{MAX} = \max_k \{p_k\}$

c) IF $\xi < p_e$ THEN CHOOSE ORIENTATION $e$

# STRATEGY # 2

CONSIDER M INTERVALS AS FOLLOWS




$$\overline{AB} = \sum_{k}^{M} P_k = 1$$

CHOOSE RANDOMLY $\xi \in [0,1]$

IF $\xi \in$ k-th INTERVAL CHOOSE $\vec{U}_k^{(n)}$

6) GENERATE M-1 ORIENTATIONS RANDOMLY (E.G. BY MARSAGLIA)

$$\{ \vec{U}_k^{(0)} \}_{k=1 \dots M-1}$$

7) CALCULATE

$$W(0) = e^{-\beta U_{ROT}(\vec{U}_i)} + \sum_{k=1}^{M-1} e^{-\beta U_{ROT}(\vec{U}_k^{(0)})}$$

BY THIS TRIAL MOVE

$$\underbrace{U_{POS}(0)}_{U_{POS}(\dots \vec{r}_i \dots)} \rightarrow \underbrace{U_{POS}(n)}_{U_{POS}(\dots \vec{r}_i^{\,n} \dots)}$$

$$\underbrace{U_{ROT}(\dots \vec{r}_i \dots \vec{U}_i)}_{U_{ROT}(0)} \rightarrow \underbrace{U_{ROT}(\dots \vec{r}_i^{\,n} \dots \vec{U}_i^{\,n} \dots)}_{U_{ROT}(n)}$$

HENCE

$\Delta U = \Delta U_{POS} + \Delta U_{ROT}$ WITH

$\Delta U_{POS} = U_{POS}(n) - U_{POS}(0)$ AND

$$\Delta U_{ROT} = U_{ROT}(n) - U_{ROT}(o)$$

ACCEPTANCE MOVE ( $acc(o \to n)$ )

WE CAN PROVE THAT

$$acc(o \to n) = \min\left\{1, \frac{W(n)}{W(o)} e^{-\beta \Delta U_{POS}}\right\}$$

CONCERNING $\alpha(o \to n)$

INDEED CONSIDER ALL THE STEPS ABOVE

IN STEP 1)

$P_R$ = { PROBABILITY OF CHOOSING PARTICLE $i$ } =

$$= \frac{1}{N}$$

IN STEP 2)

$P_T(o \to n)$ = { PROBABILITY OF SELECTING A NEW POSITION }

$\vec{r}_i \to \vec{r}_i + \Delta\vec{r}$ ← RANDOM DISPLACEMENT

IN STEP 3)

$\tilde{p}(n)$ = { PROBABILITY TO GET ORIENTATION $\vec{v}_i^{(n)}$ AMONG THE M RANDOMLY GENERATED }

NUMBER OF POSSIBLE ORIENTATIONS IS FINITE

HENCE IS LIKE ROLLING A DICE WITH 6 FACES M TIMES AND CALCULATING THE PROBABILITY OF GETTING A SPECIFIC NUMBER.

THIS PROBABILITY AFTER TWO ROLLS IS

$$\frac{6 \cdot 6 - 5 \cdot 5}{6 \cdot 6} = \frac{6^2 - 5^2}{6^2}$$

AFTER M ROLLS THE PROBABILITY IS

$$\frac{6^M - 5^M}{6^M}$$

HENCE IT DEPENDS ONLY ON M

THIS MEANS THAT

$$\tilde{P}(n) = \frac{N_{OR}^M - (N_{OR}-1)^M}{N_{OR}^M}$$

WHERE $N_{OR}$ IS THE NUMBER OF POSSIBLE ORIENTATIONS

IN STEP 5)

$$P(n) = P_K = \frac{e^{-\beta U_{ROT}(n)}}{W(n)}$$

SO THAT OVERALL WE HAVE

$$\alpha(o \to n) = \frac{1}{N} P_T(o \to n) \cdot \tilde{P}(n) \cdot P(n)$$

NOW CONSIDER $\alpha(n \to o)$

$$\alpha(n \to o) = \frac{1}{N} P_T(n \to o) \cdot \tilde{P}(o) \cdot P(o)$$

BUT NOTE THAT $P_T(o \to n) = P_T(n \to o)$

AND THAT

$$\tilde{P}(n) = \frac{N_{OR}^M - (N_{OR}-1)^M}{N_{OR}^M} = \tilde{P}(o)$$

AND FINALLY

$$P(o) = \frac{e^{-\beta U_{ROT}(o)}}{W(o)}$$

NOW LET'S CALCULATE THE ACCEPTANCE PROBABILITY

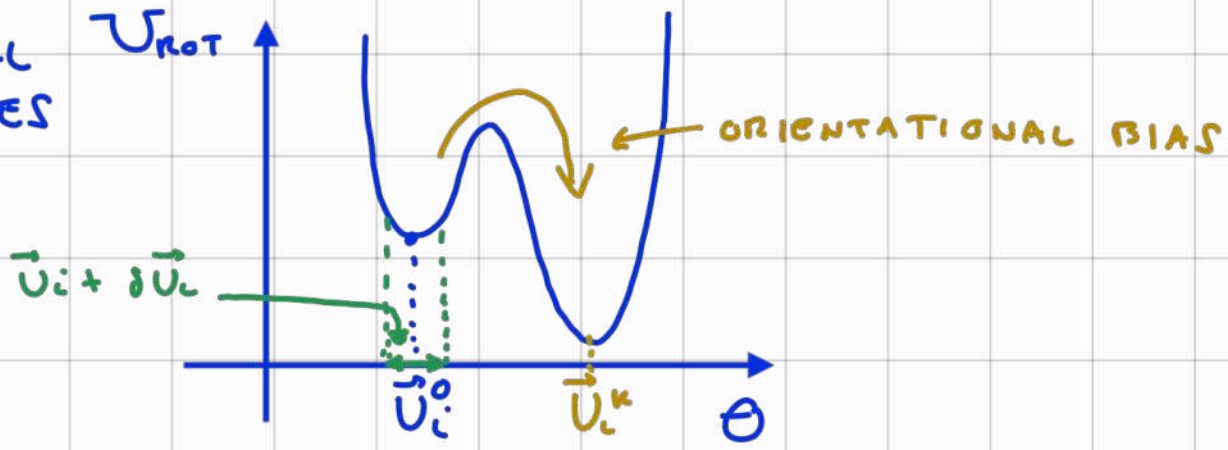
$$acc(o \to n) = \min\left\{1, \frac{\alpha(n \to o)}{\alpha(o \to n)} \frac{e^{-\beta U(n)}}{e^{-\beta U(o)}}\right\}$$

$$= \min\left\{1, \frac{\frac{1}{N} P_T(n \to o)\, \tilde{\beta}(o)\, p(o)}{\frac{1}{N} P_T(o \to n)\, \tilde{\beta}(n)\, p(n)} \frac{e^{-\beta U(n)}}{e^{-\beta U(o)}}\right\} =$$

$$= \min\left\{1, \frac{e^{-\beta U_{ROT}(o)}}{e^{-\beta U_{ROT}(n)}} \frac{W(n)}{W(o)} \frac{e^{-\beta(U_{ROT}(n) + U_{POS}(n))}}{e^{-\beta(U_{ROT}(o) + U_{POS}(o))}}\right\} =$$

$$= \min\left\{1, \frac{W(n)}{W(o)} e^{-\beta \Delta U_{POS}}\right\}$$

UNIAXIAL PARTICLES




WITH A STANDARD ORIENTATIONAL MOVE

$$\vec{U}_i^n = \frac{\vec{U}_i^o + \gamma \Delta\vec{U}}{\| \vec{U}_i^o + \gamma \Delta\vec{U} \|} = \vec{U}_i^o + \delta\vec{U}_i^o$$

WHERE $$\delta\vec{U}_i = \frac{\vec{U}_i^o + \gamma \Delta\vec{U}}{\| \vec{U}_i^o + \gamma \Delta\vec{U} \|} - \vec{U}_i^o$$

WHICH IS SMALL SINCE $\gamma$ IS SMALL, I.E.

$$\| \delta\vec{U}_i \| \ll \| \vec{U}_i \|$$

↑ TO HAVE A GOOD ACCEPTANCE RATE

WITHOUT BIASING ONE HAS

$$acc(o \to n) = \min\left\{1, e^{-\beta \Delta U_{ROT}} e^{-\beta \Delta U_{POS}}\right\}$$

HENCE IF $e^{-\beta U_{ROT}} << 1$ AS IN THE ABOVE EXAMPLE $acc(o \to n) << 1$

ANYWAY WITH ORIENTATIONAL BIAS WE HAVE

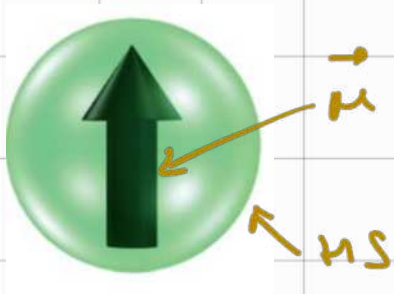
$$acc(o \to n) = \min\left\{1, \frac{W(n)}{W(o)} e^{-\beta \Delta U_{POS}}\right\}$$

BUT $\frac{W(n)}{W(o)} \approx 1$ HENCE

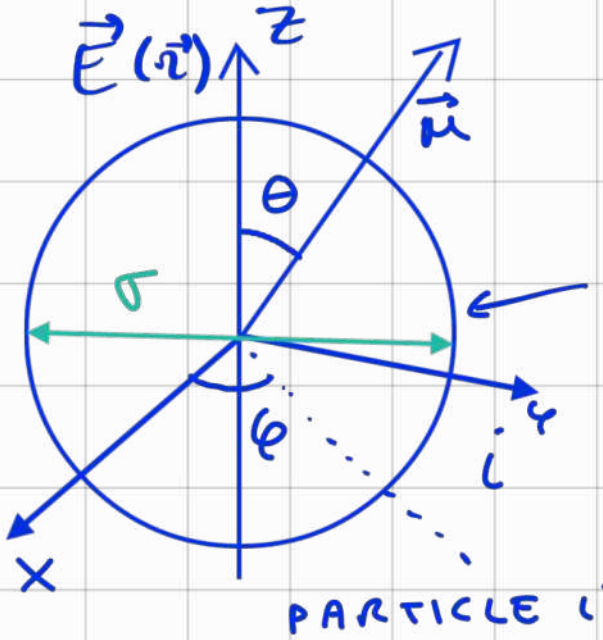
$$\frac{W(n)}{W(o)} >> e^{-\beta \Delta U_{ROT}}$$

IN PRACTICE BY ORIENTATIONAL BIAS LARGE ORIENTATIONAL DISPLACEMENT ARE ALLOWED

# APPLICATION OF ORIENTATIONAL BIAS: DIPOLAR HARD SPHERES




$\vec{\mu}$ IS THE DIPOLE MOMENT OF THE PARTICLE




$\vec{E} = \vec{E}(\vec{r})$

↑ ELECTRIC FIELD INDUCED BY THE OTHER DIPOLAR HS

$$U = U_{POS} + U_{ROT}$$

$$U_{POS} = \sum_{ij} U_{HS}(r_{ij})$$

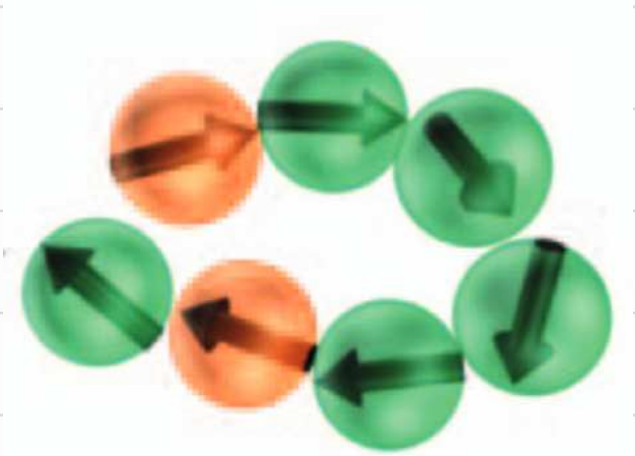



$$U_{ROT} = \sum_i U_{ROT}(\vec{r}_i, \vec{\mu}_i) = \sum_i U^i_{ROT}$$

$$U^i_{ROT} = \vec{\mu}_i \cdot \vec{E}(\vec{r}_i) = \mu E(\vec{r}_i) \cos\theta_i$$

$$E(\vec{r}_i) = \| \vec{E}(\vec{r}_i) \|$$



MINI SNAPSHOT

FOR THIS SYSTEM WE CAN GENERATE $\vec{\mu}$ OVER THE WHOLE SOLID ANGLE WITH PROBABILITY $P(r,\theta,\varphi) = \frac{e^{-\beta\mu E(\vec{r})\cos\theta}}{W(\vec{r})}$

SINCE WE CAN CALCULATE EXACTLY THE ROSENBLUTH FACTOR, I.E.

$$W(n) = \int e^{-\beta\mu E(\vec{r}_i^{\,n})\cos\theta} \sin\theta\, d\theta\, d\varphi =$$

$$= 2\pi \int_{-1}^{1} e^{-\beta\mu \vec{E}(\vec{r}_i^{\,n})\cos\theta}\, d(\cos\theta) =$$

NEW POSITION

$$= \frac{2\pi}{-\beta\mu E(\vec{r}_i^{\,n})}\left[ e^{-\beta\mu E(\vec{r}_i^{\,n})} - e^{+\beta\mu E(\vec{r}_i^{\,n})}\right]$$

AND SIMILARLY

$$W(o) = \frac{2\pi}{-\beta\mu E(\vec{r}_i^{\,o})}\left[ e^{-\beta\mu E(\vec{r}_i^{\,o})} - e^{+\beta\mu E(\vec{r}_i^{\,o})}\right]$$

OLD POSITION

HENCE

$$acc(o\to n) = \min\left\{1, \frac{W(n)}{W(o)}\, e^{-\beta U_{pos}}\right\} =$$

IF HS OVERLAP, MOVE IS REJECTED

$$= \min\left\{1, \frac{E(\vec{r}_i^{\,o})}{E(\vec{r}_i^{\,n})}\, \frac{e^{-\beta\mu E(\vec{r}_i^{\,n})} - e^{+\beta\mu E(\vec{r}_i^{\,n})}}{e^{-\beta\mu E(\vec{r}_i^{\,o})} - e^{+\beta\mu E(\vec{r}_i^{\,o})}}\, e^{-\beta U_{pos}}\right\}$$

(*)

$$P(r,\theta,\varphi)\sin\theta\, d\theta\, d\varphi = -\frac{e^{-\beta\mu \vec{E}(\vec{r}_i^{\,o})\cos\theta}}{W(o)}\, d(\cos\theta)\, d\varphi$$

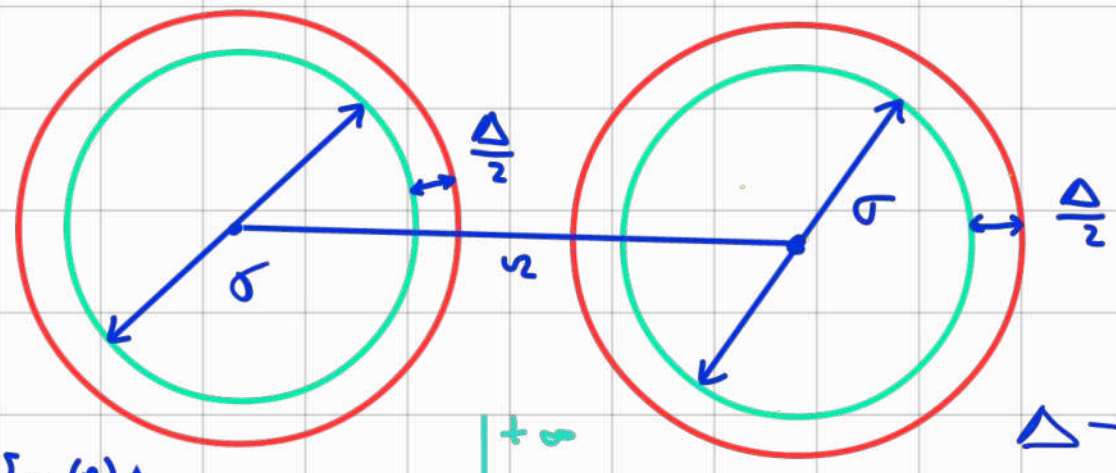
SETTING $\cos\theta = -\frac{1}{\beta\mu E(\vec{r}_i^{\,o})}\ln\xi$ ONE HAS

$\propto \xi\,\frac{1}{\xi}\, d\xi\, d\varphi$ WHICH IS A UNIFORM DISTR. IN $\xi$ AND $\varphi$

WITH $\xi \in [e^{-\beta\mu E}, e^{\beta\mu E}]$ AND $\varphi \in [0, 2\pi]$

# AGGREGATION VOLUME BIAS MONTE CARLO (AVB MC)

## SQUARE-WELL SYSTEM



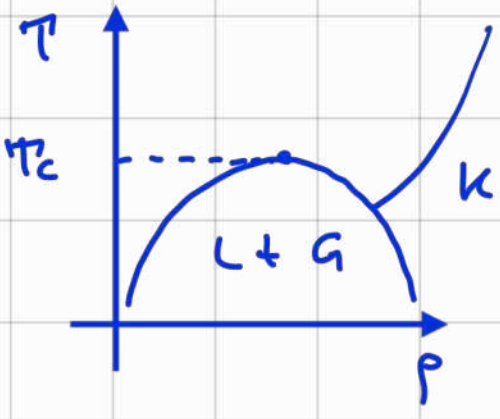




$\Delta \to 0$

$U_0 \to +\infty$

BAXTER MODEL



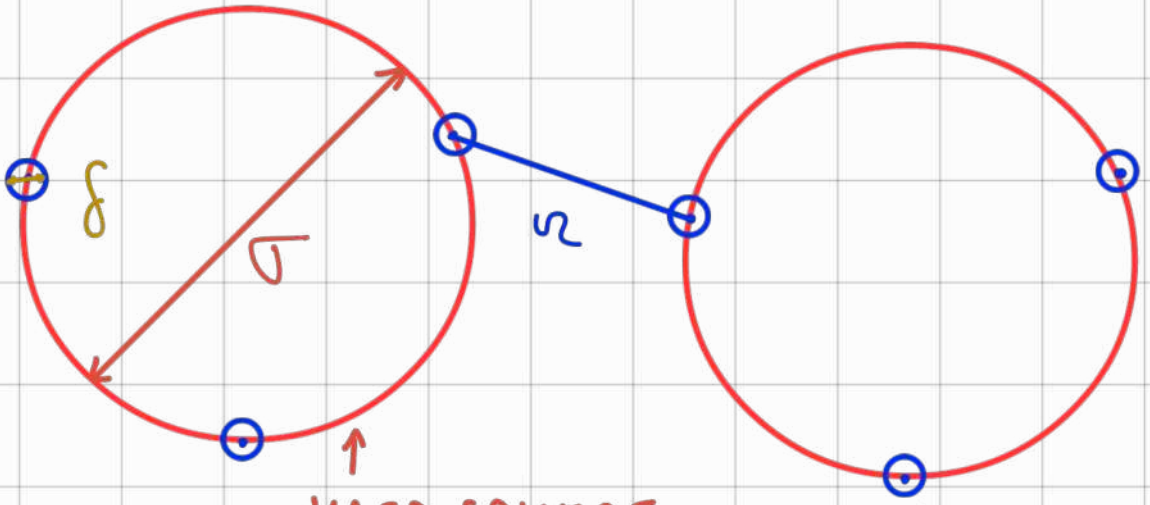

SKETCH OF PHASE DIAGRAM WHICH IS SIMILAR TO THAT OF LENNARD-JONES

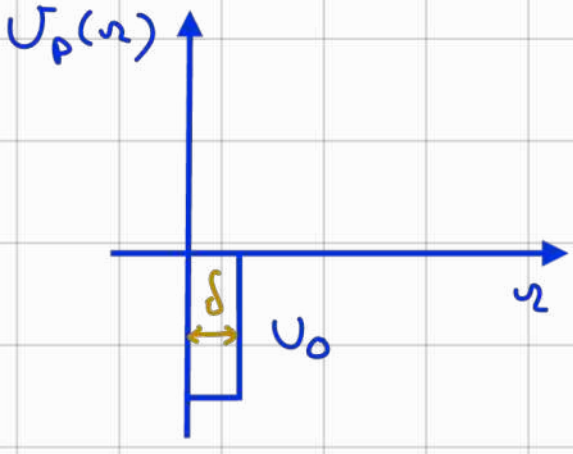
IF $\Delta \ll \sigma$ $\quad \beta_c = \frac{1}{k_B T_c}$ $\quad \beta_c U_0 \gtrsim 20$

HENCE $\quad e^{-\beta_c U_0} \approx 10^{-8}$

I.E PROBABILITY OF BREAKING A BOND CAN BE VERY SMALL

# PATCHY HARD SPHERES



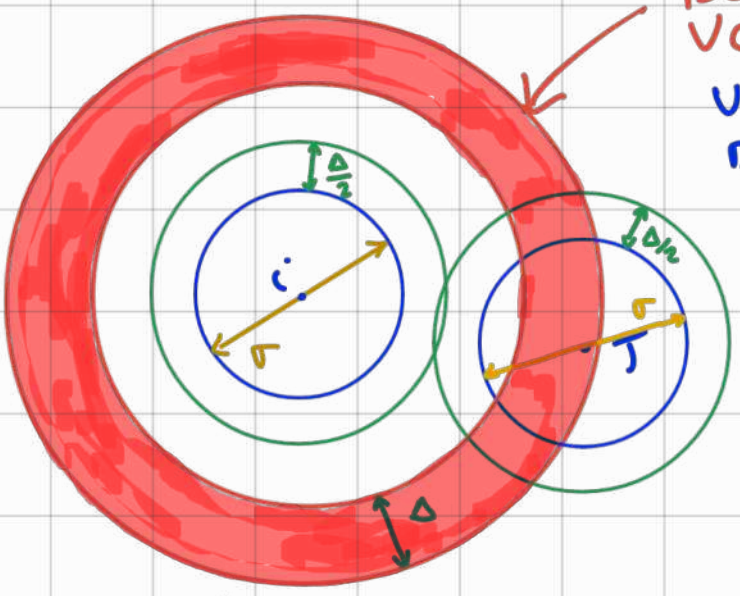




$\delta << \sigma$

IN THIS CASE WE ALSO HAVE THAT

$$\beta_c U_0 >> 1 \Rightarrow e^{-\beta_c U_0} << 1$$

# BONDING VOLUME OF SW PARTICLES




VOLUME FORMED BY POSITION OF PARTICLE j WHEN BONDED TO i

PARTICLES ARE BONDED IF THEIR DISTANCE $\vec{r}_{ij}$ IS SUCH THAT:

$$\sigma < \|\vec{r}_{ij}\| < \sigma + \Delta$$

IN THIS CASE $V_b$ IS THE VOLUME OF THE RED SPHERICAL CORONA OF THICKNESS $\Delta$

## AGGREGATION VOLUME BIASED ALGORITHM

### TRIAL MOVES

WE CONSIDER TWO POSSIBLE BIAS MOVES

OUT → IN AND IN → OUT WITH EQUAL PROBABILITY

OUT → IN MOVE

1) CHOOSE RANDOMLY A PARTICLE i
2) IF $N_{IN}$ = {NUMBER OF PARTICLES BONDED TO i}

   $N_{OUT} \equiv N - N_{IN} - 1$ = {NUMBER OF PARTICLES NOT BONDED TO i}

   CHOOSE RANDOMLY A PARTICLE j AMONG THE $N_{OUT}$ PARTICLES
3) MOVE j RANDOMLY IN THE BONDING VOLUME $V_b$ OF i

IN → OUT MOVE

1) CHOOSE RANDOMLY A PARTICLE $i$

2) IF $N_{IN} = \{$ NUMBER OF PARTICLES BONDED TO $i\}$
CHOOSE RANDOMLY A PARTICLE $j$
AMONG THE $N_{IN}$ PARTICLES

3) IF $V_{OUT} = V - V_b$
MOVE $j$ RANDOMLY IN $V_{OUT}$

## ACCEPTANCE

OUT → IN

$$acc(o \to n) = \min\left\{1, \frac{\alpha(n \to o)}{\alpha(o \to n)} \frac{\rho(n)}{\rho(o)}\right\} =$$

$$= \min\left\{1, \frac{\alpha(IN \to OUT)}{\alpha(OUT \to IN)} \frac{\rho(IN)}{\rho(OUT)}\right\}$$

BY CONSIDERING THE PROBABILITY OF 3 STEPS DISCUSSED ABOVE WE HAVE: $V_{IN} = V_b$

$$\alpha(o \to n) = \alpha(OUT \to IN) = \frac{1}{N} \cdot \frac{1}{N_{OUT}} \cdot \frac{1}{V_{IN}}$$

AND

$$\alpha(n \to o) = \alpha(IN \to OUT) = \frac{1}{N} \cdot \frac{1}{N_{IN}^{(n)}} \cdot \frac{1}{V_{OUT}}$$

WHERE $N_{IN}^{(n)}$ IS THE NUMBER OF PARTICLES BONDED TO $i$ IN THE $n$ STATE, THEREFORE $N_{IN}^{(n)} = N_{IN} + 1$

THUS HAVING

$$\alpha(IN \to OUT) = \frac{1}{N} \cdot \frac{1}{N_{IN}+1} \cdot \frac{1}{V_{OUT}}$$

HENCE

$$acc(OUT \to IN) = \min\left\{1, \frac{\cancel{\frac{1}{N}} \cdot \frac{1}{N_{IN}+1} \frac{1}{V_{OUT}}}{\cancel{\frac{1}{N}} \cdot \frac{1}{N_{OUT}} \cdot \frac{1}{V_{IN}}} e^{-\beta \Delta U}\right\} =$$

$$= \min\left\{1, \frac{N_{OUT} \cdot V_{IN}}{(N_{IN}+1) V_{OUT}} e^{-\beta \Delta U}\right\}$$

IN → OUT

$$acc(o \to n) = \min\left\{1, \frac{\alpha(n \to o)}{\alpha(o \to n)} \frac{p(n)}{p(o)}\right\} =$$

$$= \min\left\{1, \frac{\alpha(OUT \to IN)}{\alpha(IN \to OUT)} \frac{p(OUT)}{p(IN)}\right\}$$

BY CONSIDERING THE PROBABILITY OF 3 STEPS DISCUSSED ABOVE WE HAVE:

$$\alpha(o \to n) = \alpha(IN \to OUT) = \frac{1}{N} \cdot \frac{1}{N_{IN}} \cdot \frac{1}{V_{OUT}}$$

AND

$$\alpha(n \to o) = \alpha(OUT \to IN) = \frac{1}{N} \cdot \frac{1}{N_{OUT}^{(n)}} \frac{1}{V_{IN}}$$

WHERE $N_{OUT}^{(n)}$ IS THE NUMBER OF PARTICLES NOT BONDED TO $i$ IN THE $n$ STATE, I.E

$N_{OUT}^{(n)} = N_{OUT} + 1$ SO THAT

$$\alpha(OUT \to IN) = \frac{1}{N} \frac{1}{N_{OUT}+1} \frac{1}{V_{IN}}$$

HENCE:

$$acc(IN \to OUT) = \min\left\{1, \frac{\frac{1}{N}\cdot\frac{1}{N_{OUT}+1}\cdot\frac{1}{V_{IN}}}{\frac{1}{N}\cdot\frac{1}{N_{IN}}\cdot\frac{1}{V_{OUT}}} e^{-\beta\Delta U}\right\} =$$

$$= \min\left\{1, \underbrace{\frac{N_{IN}\cdot V_{OUT}}{(N_{OUT}+1)V_{IN}}}_{\text{THIS FACTOR CAN BE LARGE } (V_{OUT} \gg V_{IN}) \text{ AND COMPENSATE FOR THE SMALL } e^{-\beta\Delta U}} e^{-\beta\Delta U}\right\}$$