① radial Distribution function

$g(r)\rho$: what is

the density of finding a particle which is at distance r to your reference particle

$$\frac{\rho^{(2)}(\underline{r_1}, \underline{r_2})}{\rho^{(1)}(r_1)\,\underline{\rho^{(1)}(r_2)}} = g^{(2)}(r_1, r_2)$$

$$\rho^{(2)}(r_1, r_2) / \rho^{(1)}(r_1) = g^{(2)}(r_1, r_2) \cdot \rho(r_2)$$

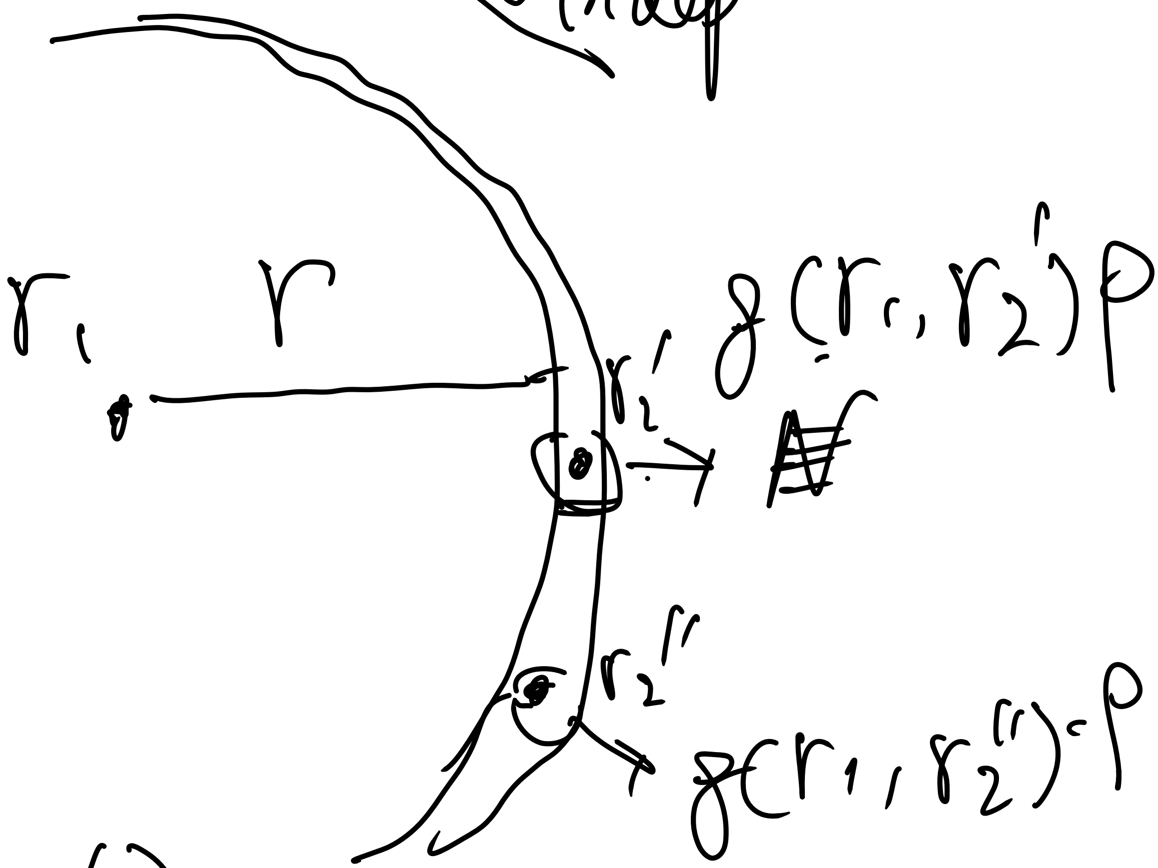
$$\rho^{(2)}(r_2 \mid r_1) = g^{(2)}(r_1, r_2)\,\rho^{(1)}(r_2)$$

dep

r

liquid: r_1 — r_2

θ indep



$$g(r_1, r_2') = g(r_1, r_2'') = g(r)$$

$$\rho(r|r_1) = \underline{g(r)} \cdot \rho$$

$$\underline{\underline{g(r)}} = \frac{\rho(\underline{\underline{r}}|\underline{\underline{r_1}})}{\rho}$$

$$= \frac{N(r|r_1)/4\pi r^2 \cdot dr}{\rho}$$

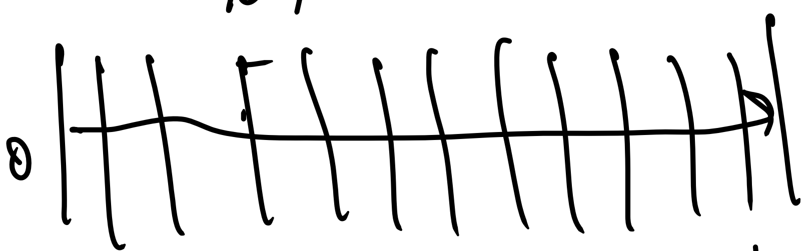
$$\text{self.rdf}[0, 1, 2, \ldots, \text{Int}(r_c / d\_rdf)]$$

$$g(r > r_c) = 1 \qquad r_c = 1.0$$

$$g(r) \quad r \leq r_c \qquad d\_rdf = 0.1$$

d_rdf

$$\text{Int}(1.0/0.1)$$



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r_c

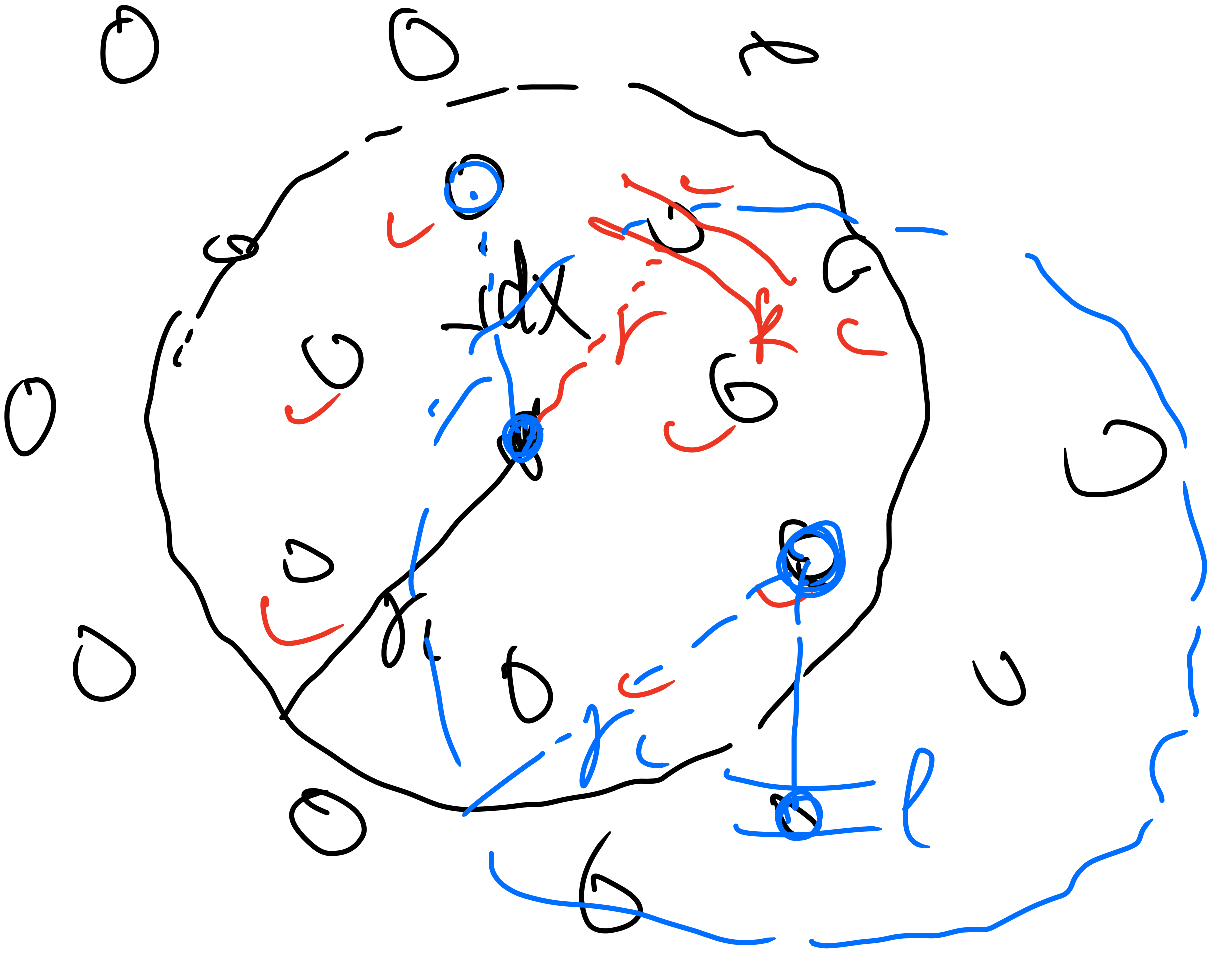
$$\text{Int}(0.77/0.1)$$

0 0.1 – 0.2 . . . . . —

0.0 0.1

$$= 7 \rightarrow 0.7 \,|\, 0.8$$

rdf[k]+=1



rdf[l]+=1

rdf.

different frames, M, rdf_n

all N particles

entire spherical shell

$N(r) = M \times N \times dV(r) \cdot g(r) \cdot \frac{n}{V}$

$$g(r) = \frac{N(r)}{M\, N\, dV(r) \cdot \rho}$$

(2) F. , Pressure ;

$$P = \underbrace{\beta^{-1}\rho}_{P_K} + \frac{Vir}{V}$$

$$Vir = \frac{1}{3}\left\langle \sum_i \sum_{j>i} \vec{f}(\vec{r_{ij}}) \cdot \vec{r_{ij}} \right\rangle$$

$$\vec{f_j}(\vec{r_{ij}})$$

$$= - \left.\frac{\partial u(|\vec{r_{ij}}|)}{\partial r}\right| \cdot \hat{u}(\vec{r_{ij}})$$

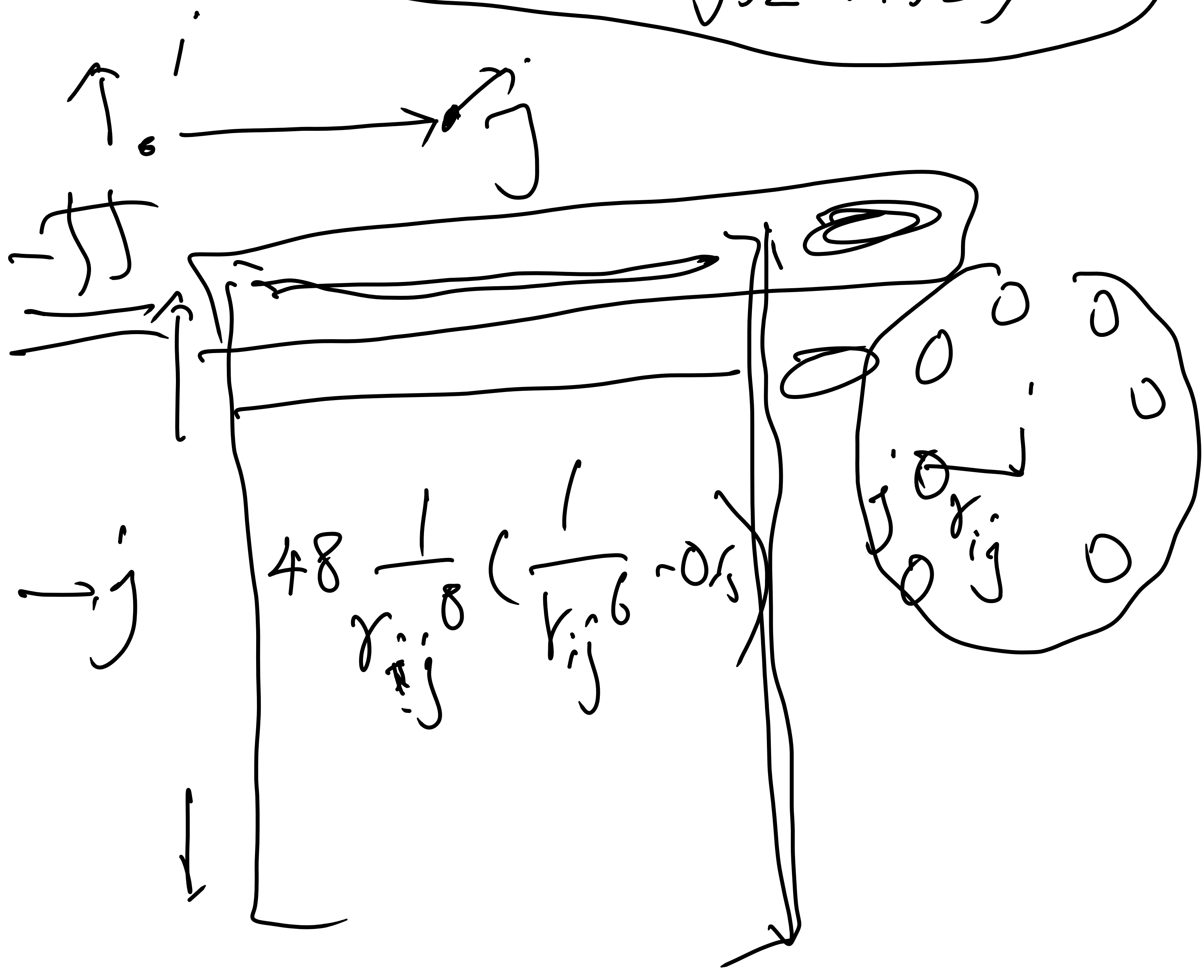
$$= - \left.\frac{\partial u(r)}{\partial r}\right|_{r=|\vec{r_{ij}}|} \cdot \left\{ \frac{r_{j,x}-r_{i,x}}{\underbrace{|\vec{r_{ij}}|}_{r}}, \frac{r_{j,y}-r_{i,y}}{|\ |}, \frac{r_{j,z}-r_{i,z}}{|\ |} \right\}$$

$$\varepsilon^* = 1 \quad \sigma^* = 1$$

$$\underbrace{\hphantom{\varepsilon^* = 1 \quad \sigma^*}}_{r=|\ |} \hookrightarrow 4\left(\frac{1}{r^{12}} - \frac{1}{r^6}\right)$$

$$= \underbrace{48 \cdot \frac{1}{r^8}\left(\frac{1}{r^6} - 0.5\right)} \times$$

$$\underbrace{\left(r_{j,x} - r_{i,x},\ r_{j,y} - r_{i,x},\ r_{j,z} - r_{i,z}\right)}$$



$$= \frac{1}{x} ff \cdot \left(r_{j,x} - r_{i,x},\; r_{j,y} - r_{i,y},\; r_{j,z} - r_{i,z} \right)$$

$$P_u = -\frac{\rho^2}{6} \int_{\cancel{0}\; r_c}^{\infty} r\, \underline{u'(r)}\, g(r)\, 4\pi r^2\, dr$$

$$\underbrace{= \frac{16}{3} \pi \rho^2 \left(\frac{2}{3} \cdot \frac{1}{r_c^9} - \frac{1}{r_c^3} \right)}$$

$$e^{-\beta w(r_1, \ldots r_n)} \equiv g^{(n)}(r^{(n)})$$

$$\underline{r^{(n)}} \in r^{(N)}$$

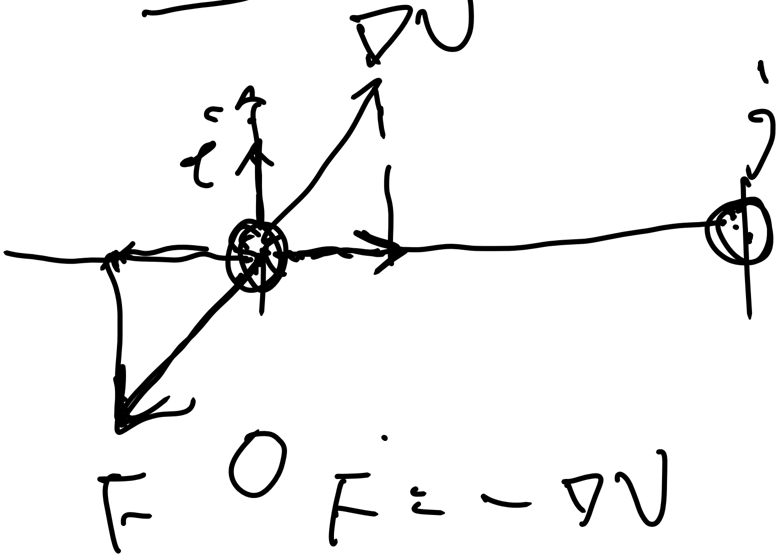
$$\nabla_2 \underbrace{w(r^{(n)})} = \underbrace{-\beta^{-1} \nabla_2 \ln g^{(n)}(\underline{r^{(n)}})}$$

$$= \underbrace{\left\langle \nabla_2 U \right\rangle_{r^{(n)}}}$$

$$\left\langle \nabla_2 U \right\rangle_{r^{(2)}} = -\beta^{-1} \nabla_2 \ln \underbrace{g^{(2)}(r_1, r_2)}$$

$$\underbrace{\left\langle \nabla_{r_{ij}} \underline{\underline{U}} \right\rangle_{\underline{r}}} = \underbrace{-\beta^{-1} \nabla_{r_{ij}} \ln g(r)}$$

$$\langle \nabla_r U \cdot \hat{r}_{ij\parallel} \rangle \gg \underbrace{\langle \nabla_r U \cdot \hat{r}_{ij\perp} \rangle}_{0}$$

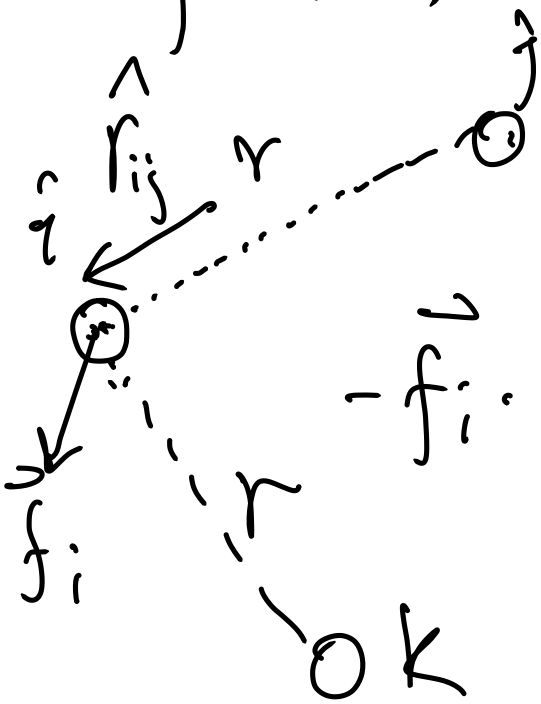


$F = -\nabla V$

$$\boxed{\langle \nabla_r U \cdot \hat{r}_{ij\parallel} \rangle_v = -\beta^{-1} \nabla_{r_{ij}} \ln g(r)}$$

$$(\ln g(r))(-\beta^{-1}) = f(r)$$

$$f'(r)$$



$$-\vec{f}_i \cdot \hat{r}_{j\to i} \quad (r)$$

$$-\vec{f}_i \cdot r_{j-k} \quad (r)$$

$$\left\langle -\vec{f}_i \cdot \hat{r}_{ij} \right\rangle_r$$

NVT, MC

Isothermal - Isobaric MC

NPT. → V : change

$$\underline{P}(\cancel{\#}\ \vec{q}^{(N)}, \underline{V})$$

$$\frac{\sum_V \sum_E \Omega(N,V,E)\, e^{-\beta E} e^{-\beta PV} = \Delta}{}$$

$$P(\vec{q}^{(N)}, V) = \frac{1}{\Delta} e^{-\beta E} e^{-\beta PV}$$

$$\Delta = \int_0^\infty dV\, e^{-\beta PV} \cdot Q(N,V,T)$$

$$Q(N,V,T) = \frac{1}{\Lambda^{3N} N!} \int_V d\vec{q}^{(N)} \cdot e^{-\beta U(\vec{q}^{(N)})}$$

$$\underline{P(\vec{q}^{(N)}, V)} \propto \underline{e^{-\beta PV}} \cdot \underline{Q(N,V,T)}$$

$$L^3 = V \qquad L = V^{1/3}$$

$$\vec{s}^{(N)} = \vec{q}^{(N)} / L$$

$$Q = \frac{1}{\Lambda^{3N} N!} \cdot V^N \int_0^1 d\vec{s}^{(N)}\, e^{-\beta U(\vec{s}^{(N)}, V)}$$

$$\underline{P(\vec{s}^{(N)}, V) \propto V^N \cdot e^{-\beta PV} \cdot e^{-\beta U(\vec{s}^{(N)}, V)}}$$

$$P(V, \vec{S}^{(N)})\,\pi\big((V,S) \to (V, S+\Delta S)\big)$$

$$= P(V, S+\Delta S)\,\pi\big((V, S+\Delta S) \to (V,S)\big)$$

N, V, T ~~TIT~~ the same vs NVT MC

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change V

$$P(V, \vec{S}^{(N)})\,\pi(V, S \to V+\Delta V, S)$$

$$= P(V+\Delta V, S^{N})\,\pi(V+\Delta V, S \to V, S)$$

$$\frac{\mathrm{acc}(V \xrightarrow{S} V+\Delta V^{S})}{\mathrm{acc}(V+\Delta V^{S} \to V^{S})} = \frac{P(V+\Delta V, \vec{S}^{(N)})}{P(V, \vec{S}^{(N)})}$$

$$= \frac{(V+\Delta V)^{N} e^{-\beta P(V+\Delta V)}}{V^{N} e^{-\beta P V}} \frac{e^{-\beta U(\underline{\vec{S}^{(N)}}, \underline{V+\Delta V})}}{e^{-\beta U(\vec{S}^{(N)}, V)}}$$

$$\left(\frac{V+\Delta V}{V}\right)^N = e^{x} \quad x = N\ln\frac{V+\Delta V}{V}$$

$$\hookrightarrow \; e^{N\ln\frac{V+\Delta V}{V}}$$

$$= e^{-\beta\left(\underbrace{\mathcal{U}(\vec{s}^{(N)}, V+\Delta V) - \mathcal{U}(\vec{s}^{(N)}, V) + P\Delta V}_{} - N\beta^{-1}\ln\frac{V+\Delta V}{V}\right)}$$

[ ]

$$\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}$$

$$\mathcal{U} = \sum_{n=1}^{m} \sum_{i>j} \underline{\epsilon_n} \cdot \left(\frac{\sigma_n}{r_{ij}}\right)^n = \sum_{n=1}^{M} \mathcal{U}_n(\vec{s}^{(N)}, V)$$

$$V \to V', \quad q^{(N)'} = \vec{s}^{(N)} \cdot L'$$

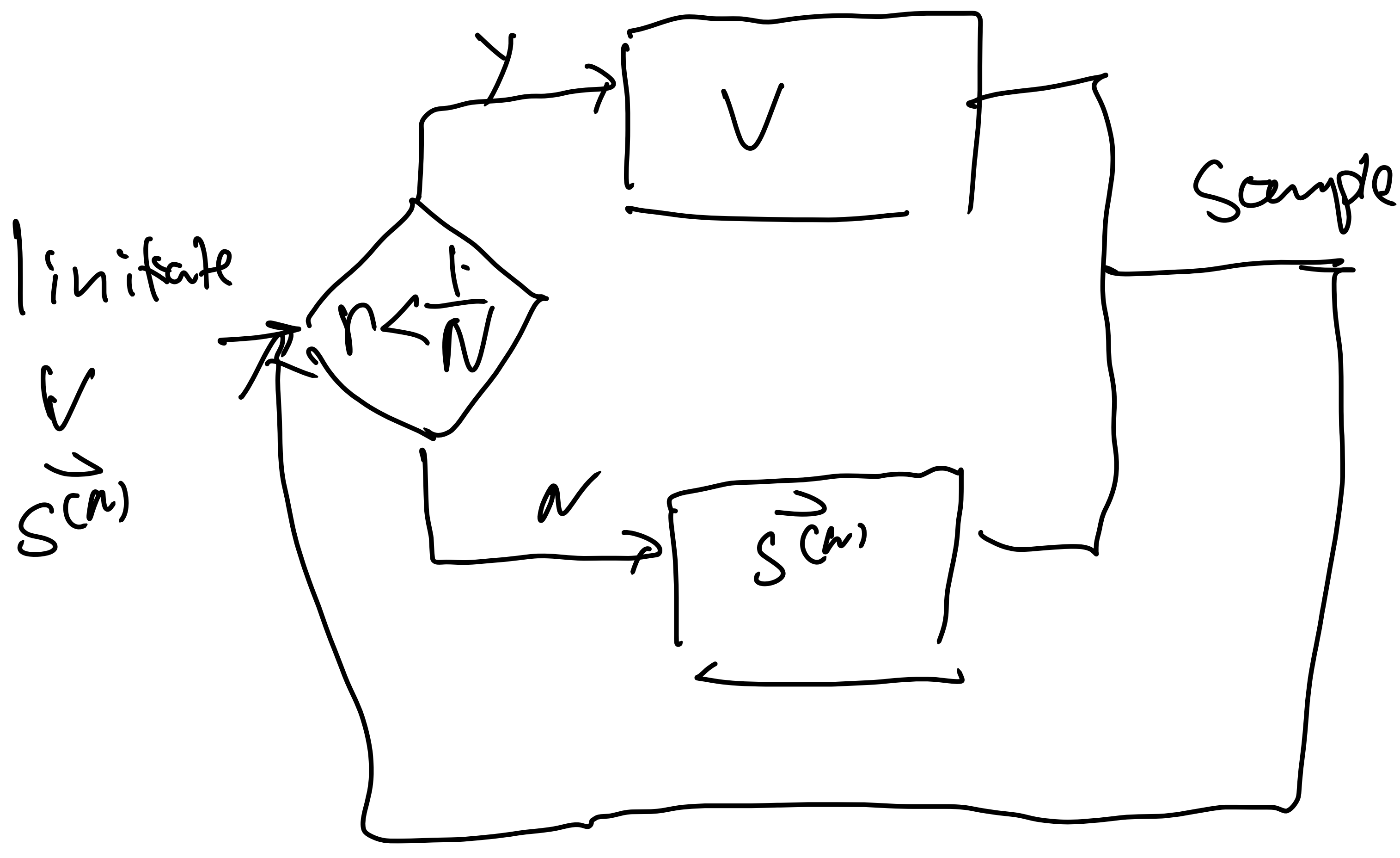
$$L \to L' \quad q^{(N)} = \vec{s}^{(N)} \cdot L$$

$$r_{ij}' = \frac{L'}{L} \cdot r_{ij}$$

$$U_n(V') = \left(\frac{L}{L'}\right)^n \cdot U_n(L)$$

$$U(V') = \sum_{n=1}^{m} \left(\frac{L}{L'}\right)^n \cdot U_n(\vec{S}^{(n)}, V)$$

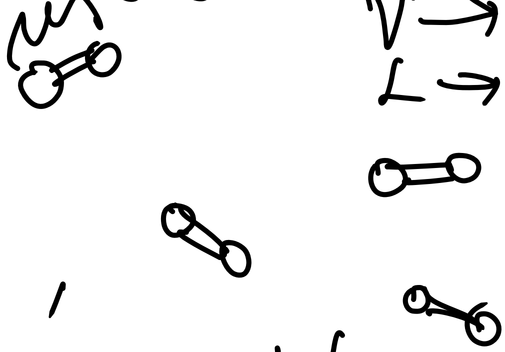
$\vec{q}^{(n)}$, V



$\vec{q}^{(N)} = \vec{s}^{(N)} \cdot L$ $\quad b_{o-o}$ $\quad L \propto V^{1/3}$

$V \to V'$,

$L \to L'$



$$b'_{o-o} = \frac{L'}{L} b_{o-o}$$

$$U(\vec{s}^{(N)}, V)$$

$$r_{ki} = \underbrace{R_i}_{V} + \underbrace{\Theta_{i,k}}_{X}$$

$$V \to V' = V + \Delta V$$

$[-\delta, \delta]$

$$r \to r \cdot \frac{L'}{L}$$

If)

$$\Delta r = r\left(\frac{L'}{L} - L\right) = r \cdot \frac{\Delta L}{L}$$

$$= r - \frac{(\delta)}{L}$$

$$r + \underset{\sim}{\Delta r} \in [-\delta, \delta]$$

$$\left(\frac{\Delta V}{V}\right) \in [-\delta, \delta]$$

$$\Delta = C \cdot \int \left(\frac{dV}{V}\right) V^{N+1} e^{-\beta P V} \cdot Q(\vec{s}^{(N)}, V, T)$$

$$= C \cdot \int d\underline{\ln V} \cdot \underset{\sim}{V^{N+1} \cdot e^{-\beta P V} Q} \cdots$$

$$P(V, \vec{s}^{(N)}) \propto V^{N+1} e^{-\beta P V} e^{-\beta U(s, V)}$$

$$\frac{\Delta V}{V} = \delta$$

$$\frac{P(V + \Delta V, \vec{s}^{(N)})}{P(V, \vec{s}^{(N)})} = e^{-\beta(U(\vec{s}^{(N)}, V(1+\delta)) - U(\vec{s}^{(N)}, V))}$$

$$+ \rho \cdot \delta \cdot V - (n+1)\beta^{-1} \ln(1+\delta) \Big]$$