

# HAND-WRITTEN NOTES

~ 2005 - 2008

ANDERS MARKVARDSSON

- PAGE 1 - 18 <sup>primarily</sup> ✓ Considerations ~~for~~ setting up MC engine
- PAGE 19 - 33 <sup>primarily</sup> ✓ Considerations for CALCULATING  
PDF, Histogram,  $S(q, \lambda)$ ,  $S(q, \omega)$

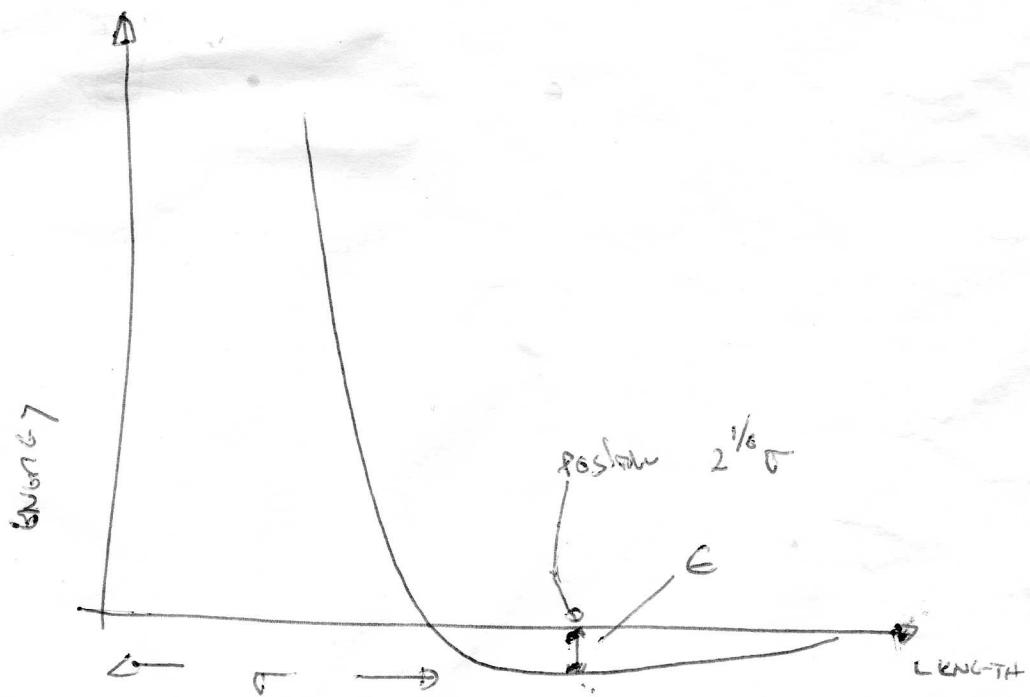
# SET UP MD PART

*Let's make  
things better*

We have some pair potential, say LJ

$$(1) \quad U(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right] & r_{ij} < r_c \\ 0 & \text{otherwise} \end{cases}$$

$r_c$  may of course be infinite, but for simplicity  
~~we~~ practical no physical reasons it might be finite.



The equation of motion becomes

Let's make  
things better! 2

$$(2) m \ddot{r}_i = \vec{f}_i = \sum_{j \neq i} \frac{48E}{r^2} \left[ \left( \frac{r}{r_j} \right)^4 - \frac{1}{2} \left( \frac{r}{r_j} \right)^8 \right] \vec{r}_j$$

Use THIS POTENTIAL RAPORT SUGGESTS ~~to~~ ~~the~~ INTRODUCE THE FOLLOWING DIMENSIONLESS VARIABLES

$$\text{LENGTH } r \rightarrow r \tau$$

$$\text{ENERGY } e \rightarrow e \epsilon$$

Time

$$t \rightarrow t \sqrt{\frac{m \tau^2}{E}}$$

HAS DIMENSIONS OF S

$$\text{SHEE ENERGY} = N \cdot \text{NM}$$

$$= \text{KG} \cdot \text{M}^2 / \text{S}^2$$

THIS EXPRESSION ~~comes from~~ IS NOT RANDOM.

INTRODUCE THESE ~~RESIZED~~ DIMENSIONLESS VARIABLES instead:

$$\text{LENGTH : } r \rightarrow \hat{r} \text{ } \text{N}_{\text{UNIT}}$$

$$\text{ENERGY : } e \rightarrow \hat{e} \text{ } \text{N}_{\text{UNIT}}$$

$$\text{MASS : } m \rightarrow \hat{m} \cdot \text{M}_{\text{UNIT}}$$

Then

$$m \ddot{r} = - \frac{\partial U}{\partial r} \rightarrow \hat{m} \cdot \text{M}_{\text{UNIT}} \cdot \text{N}_{\text{UNIT}} \hat{\ddot{r}} = - \frac{\text{L}_{\text{UNIT}}}{\text{N}_{\text{UNIT}}} \frac{\partial \hat{U}}{\partial \hat{r}}$$



$$\hat{m} \cdot \text{M}_{\text{UNIT}} \frac{\text{N}_{\text{UNIT}}^2}{\text{L}_{\text{UNIT}}} \hat{\ddot{r}} = - \frac{\partial \hat{U}}{\partial \hat{r}}$$

3  
Let's make  
things better.

FURTHER TAKE

ATMOS  $A \rightarrow \hat{A}$  UNIT

AND EQUATIONS OF HOMOLOGS READS

$$(4) \quad \hat{m} = m_{\text{UNIT}} \cdot \frac{\hat{N}_{\text{UNIT}}^2}{l_{\text{UNIT}}} - \frac{1}{A_{\text{UNIT}}} \quad \hat{A} = - \frac{\partial \hat{U}}{\partial \hat{r}}$$

IT THEREFORE MAKES SENSE TO DEFINE

$$(5) \quad l_{\text{UNIT}} = \frac{m_{\text{UNIT}} \cdot A_{\text{UNIT}}^2}{\hat{N}_{\text{UNIT}}^2}$$

IN WHICH CASE (4) SIMPLIFIES TO IT NORMAL FORM

$$m \hat{A} = - \frac{\partial U}{\partial r}$$

SAY WE WANT  $m$  TO BE MEASURED IN ATOMIC WEIGHT UNITS ( $\text{g/mole}$ )

THEN

$$m_{\text{UNIT}} = \cancel{\frac{1}{N_A}} \cdot 10^{-3} \text{ kg/mole}$$

to convert from g to SI unit  
 $\cancel{\text{kg}}$

$$N_{\text{UNIT}} = 10^{-10} \text{ m}$$

$$A_{\text{UNIT}} = 10^{-13} \text{ s}$$

THEN

$$l_{\text{UNIT}} = \frac{10^{-3} \text{ kg} \cdot 10^{-20} \text{ m}^2}{\cancel{N_A} \cdot 10^{-26} \text{ s}^2 \text{ mole}} = \frac{10^3}{\text{MOL}} \text{ N.m} = \frac{10^3}{\text{MOL}} \text{ J/MOLE}$$

WHICH E.G. IS NOT TOO DIFFERENT FROM  $E$  FOR  $A_0$

$$N_A = 6.02252 \cdot 10^{23}$$

Let's make  
things better! 4

According to Rapaport : ~~Velocity Mass~~

$$E = 120 \cdot 8.314 \text{ J/MOLE} = 120 \cdot 1.3806 \cdot 10^{-16} \text{ ERG/ATOM}$$

Kinetic energy per atom is

$$\hat{E}_{\text{kin}}^{\text{per atom}} = \frac{1}{N} \frac{1}{2} \sum_{i=1}^N \hat{m}_i \hat{v}_i^2$$

And in dimensionless units

$$\hat{E}_{\text{kin}}^{\text{per atom}} = \frac{1}{N} \frac{1}{2} \sum_{i=1}^N \hat{m}_i \hat{v}_{\text{unit}}^2 \quad \frac{\frac{N^2}{\text{unit}} \text{ unit}}{N^2 \text{ unit}} \hat{v}^2$$

$\Downarrow$

$$\hat{E}_{\text{kin}}^{\text{per atom}} = \frac{1}{N} \frac{1}{2} \sum_{i=1}^N \hat{m}_i \hat{v}_i^2$$

Take temperatures to be defined as (for simple system)

~~if~~  $E_{\text{kin}} = N \frac{d}{2} k_B T$

where  $d$  = dimension of system. Thus

$$T = \cancel{N d} \cancel{\frac{E_{\text{kin}}}{2}} \frac{2 \cdot \hat{E}_{\text{kin}}''}{N \cdot d} \frac{\text{unit}}{k_B} = \frac{\sum \hat{m}_i \hat{v}_i^2}{N d} \cdot \frac{\text{unit}}{k_B}$$

For simple systems length of cubic box, ~~is~~  
density and  $N$  is related by

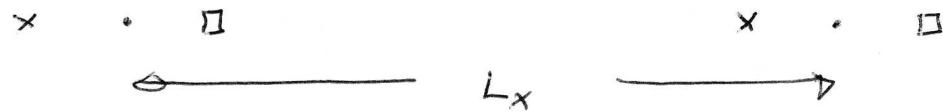
$$L = \left( \frac{V}{N} \right)^{1/3} N^{1/3}$$

*Let's make things better*<sup>5</sup>

For simple system and not long-range

interacting cubic box with periodic boundaries.

Say region size is  $L_x$



Because of the periodic boundary condition it's does not make sense to talk about distances between atoms  $> \frac{L_x}{2}$

Rapaport writes

"Even with periodic boundaries, finite-size effects are still present ~~asymptotically~~ ... Only detailed num. study can hope to resolve this question"

Notice THAT

$$k_B = 1.381 \cdot 10^{-16} \text{ erg/K} = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

From PAGE 3 we see also that  $\epsilon_{\text{unit}} = 10^3 \text{ J/mol}$

THIS THEN implies

$$\frac{\epsilon_{\text{unit}}}{k_B} = \frac{10^3}{8.314} \text{ K}$$

THE density OF liquid Ag

$$\rho = 0.942 \text{ g/cm}^3$$

convert THIS to

$$\frac{\text{Ag Atoms}}{\text{cm}^3}$$

$$\text{where } \sigma = 3.4 \text{ nm}$$

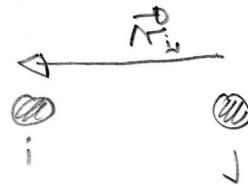
$$\rho_{\frac{\text{Ag}}{\text{cm}^3}} = 0.942 \frac{N_A}{39.95} (3.4 \cdot 10^{-8})^3$$

$$\frac{\text{Ag Atoms}}{\text{cm}^3}$$

$$\approx 0.56 \frac{\text{Ag Atoms}}{\text{cm}^3}$$

LJ - POTENTIAL RE-VISITED

Defl<sub>ij</sub>  $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$  i.e.



LJ MAY BE WRITTEN AS

$$U(r) = 4\epsilon \left( \sigma^{12} \left(\frac{1}{r^2}\right)^6 - \sigma^6 \left(\frac{1}{r^2}\right)^3 \right)$$

THE FORCE IS

$$\vec{f} = -\nabla U(r)$$

WE HAVE

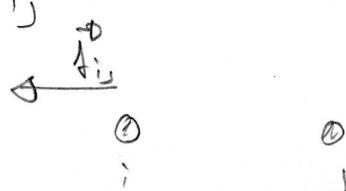
$$\begin{aligned} \frac{\partial U}{\partial r} &= \frac{\partial U}{\partial r^2} \frac{\partial r^2}{\partial r} = 2 \times 4\epsilon \left( \sigma^6 3 \left(\frac{1}{r^2}\right)^4 - \sigma^{12} 6 \left(\frac{1}{r^2}\right)^7 \right) \\ &= \frac{48\epsilon}{\sigma^2} \left( \frac{1}{2} \left(\frac{\sigma}{r}\right)^8 - \left(\frac{\sigma}{r}\right)^{14} \right) \end{aligned}$$

SO THE FORCE THAT ATOM J EXERTS ON ATOM i IS

$$\vec{f}_{ij} = \frac{48\epsilon}{\sigma^2} \left( \left(\frac{\sigma}{r_{ij}}\right)^8 - \frac{1}{2} \left(\frac{\sigma}{r_{ij}}\right)^{14} \right) \vec{r}_{ij}$$

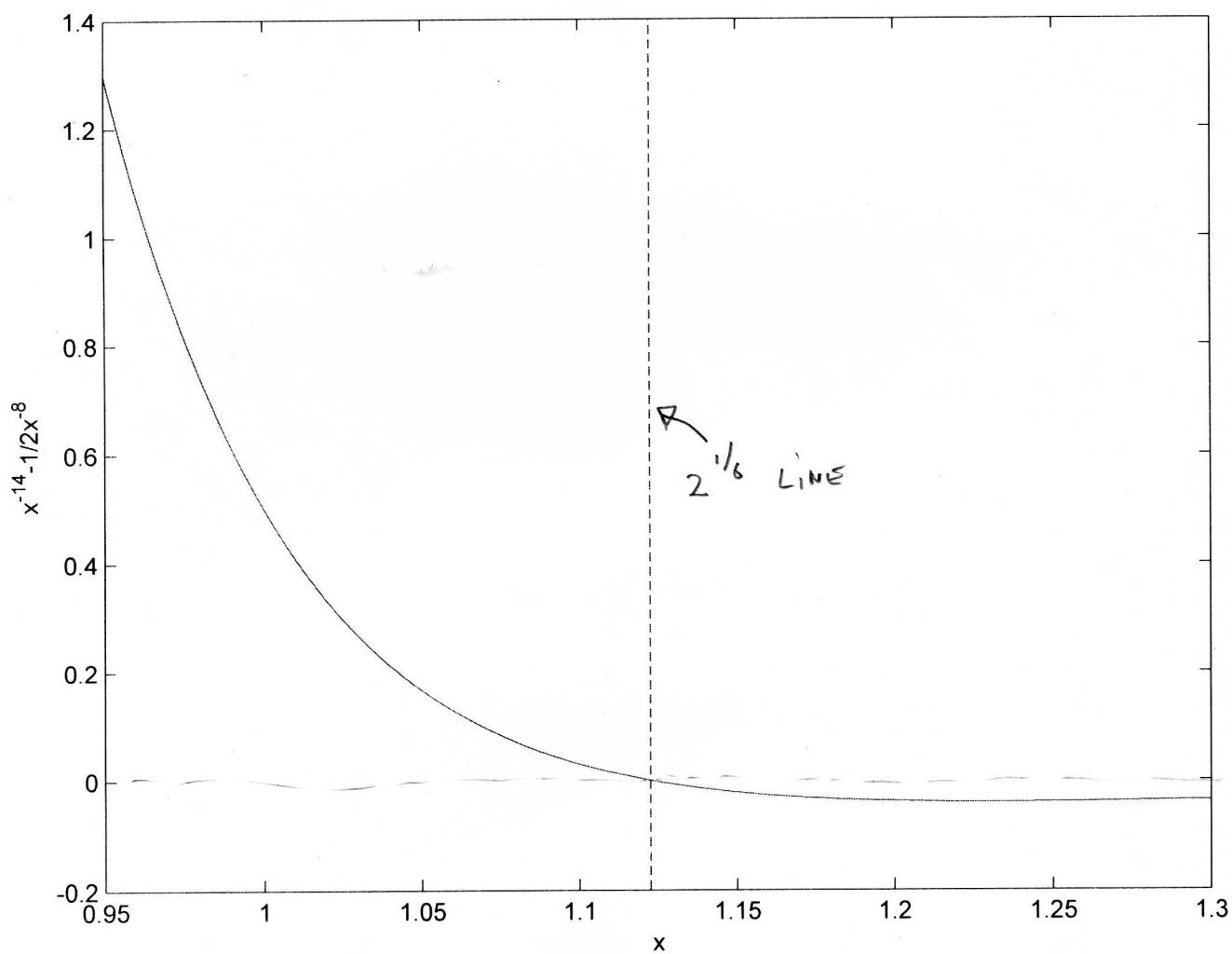
AS CAN BE SEEN FROM THE FIGURE ON THIS PAGE ~~that~~  $\vec{f}_{ij}$  IS THE FORCE THAT ATOM J EXERTS ON ATOM i MAKE SENSE

WHEN  $r_{ij} < 2^{1/6} \sigma$  ATOM J PUSHES ATOM i AWAY



WHEN  $F_{ij} > 2^{1/6} \sigma$  ATOM J ATTRACTS ATOM I

$$\sigma = 1$$



THE EXERTED ON ATOM  $i$  IS THEN

$$\vec{f}_i = \sum_{j \neq i} \vec{f}_{ij}$$

TO CALCULATE ALL THE TOTAL FORCES WE CAN  
MAKE USE OF NEWTON'S 3<sup>RD</sup> LAW.

THAT IS INSTEAD OF

$$\sum_{i=1}^N \sum_{j \neq i} \left\{ \vec{f}_i + \vec{f}_{ij} \right\}$$

WE CAN WRITE THIS DOUBLE SUMMATION AS

$$\sum_{i=1}^{N-1} \sum_{j>i} \left\{ \vec{f}_i + \vec{f}_{ij} ; \vec{f}_j - \vec{f}_{ij} \right\}$$

CALCULATING PRESSURE USE VIRIAL EQUATION OF STATE

$$PV = N k_B T + \frac{1}{d} \sum_{i=1}^N \vec{r}_i \cdot \vec{f}_i$$

WHENCE  $d$  IS EITHER 2 OR 3 FOR 2D AND  
3D SYSTEMS RESPECTIVELY. FOR PAIR POTENTIAL  
WE HAVE

$$\vec{f}_{ij} = -\frac{\partial U}{\partial r_{ij}} \vec{r}_{ij}$$

THUS FORCE

$$\sum_{i=1}^N \vec{r}_i \cdot \vec{f}_i = - \sum_{i=1}^N \vec{r}_i \sum_{j \neq i} \frac{\partial U}{\partial r_{ij}} \vec{r}_{ij}$$

NOTICE THE FOLLOWING

$$\vec{r}_i \cdot \vec{r}_{ij} + \vec{r}_j \cdot \vec{r}_{ji} = \vec{r}_{ij} (\vec{r}_i - \vec{r}_j) = r_{ij}^2$$

THEFORE

$$= - \sum_{i=1}^{N-1} \sum_{j>i} \vec{r}_{ij} \cdot \frac{\partial U}{\partial r_{ij}} \vec{r}_{ij}$$

$$= + \sum_{i=1}^{N-1} \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_{ij} = \sum_{i=1}^{N-1} \sum_{j>i} r_{ij}^2 \frac{\partial U}{\partial r_{ij}}$$

$$\text{FURTHER } \frac{d}{2} k_B N T = \frac{1}{2} \sum m_i^2 \Rightarrow k_B N T = \frac{\sum m_i^2}{d}$$

AND THE VERBAL EQUATION CAN BE WRITTEN  
AS

$$PV = \frac{1}{d} \left( \sum_i m_i v_i^2 + \sum_{i=1}^{N-1} \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_j \right)$$

Since  $V = \frac{N}{P}$

$$P = \frac{(V)^{-1}}{N \cdot d} \left( \sum_i m_i v_i^2 + \sum_{i=1}^{N-1} \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_j \right)$$

The unit of pressure is  $\frac{N}{m^2}$  THAT MEANS

In dimensionless units pressure is independent of  
of  $m_{unit}$   
~~and  $A_{unit}$~~ .

Plan of use

$$P = \frac{1}{Vd} \left( \sum m_i v_i^2 + \sum \vec{r}_i \cdot \vec{f}_i \right)$$

In dimensional units

$$P = \hat{P} e_{press}$$

$$\checkmark \quad J = N \cdot m$$

$$= \frac{m_{unit} \cdot m_{unit}^2 / l_{unit}^2}{m_{unit}^3} = \frac{m_{unit}}{l_{unit}^2 m_{unit}^4}$$

$$= \frac{10^3 J}{MOL \cdot A_{unit}^3} = \frac{10^3}{N_A \cdot (10^{-10})^3} \quad \left( \frac{J}{m^3} \right) = \frac{N}{m^2} = P_a$$

$$= \frac{10^3}{N_A \cdot (10^{-10})^3} \quad \frac{1}{101325}$$

(ATM) = standard atmosphere

$$N_A = 6.02252 \cdot 10^{23}$$

$$\approx \frac{10^{10}}{6.02252} \quad \frac{1}{101325} \approx 1.63872 \quad \checkmark \frac{10^4}{ATM}$$

$$\approx 16387.2 \text{ ATM}$$

Notice the virial equation on page may be somewhat ~~surprised~~ ~~surprising~~, a more detailed description can be found in Goldstein or on ~~the~~ Google search "virial theorem pressure derivation". Anyway this  $\int f_i$  on page 10 refers to internal force only I believe (not from walls ...) and mathematically (two body potentials)

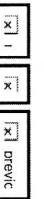
$$\sum_{i=1}^n \vec{r}_i \cdot \vec{f}_i = \sum_{i=1}^n \sum_{j>i} \vec{r}_{ij} \cdot \vec{f}_{ij}$$

However a problem appears when we have periodic boundary conditions because if the  $\vec{r}_{ij}$  are wrapped around in the above eq. then this off-expression is no longer true. In fact

only is correct!, because abs. cart. coor. are ill defined without periodic boundary cond.

(\*) where  $\vec{r}_{ij}$  are computed consistent with periodic boundary conditions.

See also <sup>PAGE</sup>  $\nabla$  118



Next: Energy fluctuations in the Up: No Title Previous: No Title

## Temperature and pressure estimators

From the classical virial theorem

$$\langle \frac{\pi_i}{\partial x_j} \frac{\partial H}{\partial x_j} \rangle = kT \delta_{ij}$$

we arrived at the equipartition theorem:

$$\left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} N kT$$

where  $\mathbf{p}_1, \dots, \mathbf{p}_N$  are the  $N$  Cartesian momenta of the  $N$  particles in a system. This says that the microscopic function of the  $N$  momenta that corresponds to the temperature, a macroscopic observable of the system, is given by

$$K(\mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i}$$

The ensemble average of  $K$  can be related directly to the temperature

$$T = \frac{2}{3Nk} \langle K(\mathbf{p}_1, \dots, \mathbf{p}_N) \rangle = \frac{2}{3mR} \langle K(\mathbf{p}_1, \dots, \mathbf{p}_3) \rangle$$

$K(\mathbf{p}_1, \dots, \mathbf{p}_N)$  is known as an *estimator* (a term taken over from the Monte Carlo literature) for the temperature. An estimator is some function of the phase space coordinates, i.e., a function of microscopic states, whose ensemble average gives rise to a physical observable.

An estimator for the pressure can be derived as well, starting from the basic thermodynamic relation:

$$P = - \left( \frac{\partial A}{\partial V} \right)_{N,T} = kT \left( \frac{\partial \ln Q(N, V, T)}{\partial V} \right)_{N,T}$$

with

$$Q(N, V, T) = C_N \int d\mathbf{x} e^{-\beta H(\mathbf{x})} = C_N \int_V d^N \mathbf{p} \int_V d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})}$$

The volume dependence of the partition function is contained in the limits of integration, since the range of integration for the coordinates is determined by the size of the physical container. For example, if the system is confined within a cubic box of volume  $V = L^3$ , with  $L$  the length of a side, then the range of each  $q$  integration will be from 0 to  $L$ . If a change of variables is made to  $\mathbf{r}_i = \mathbf{q}_i/L$ , then the range of each  $s$  integration will be from 0 to 1. The coordinates  $\mathbf{r}_i$  are known as scaled coordinates. For containers of a more general shape, a more general transformation is

$$\mathbf{s}_i = V^{-1/3} \mathbf{r}_i$$

In order to preserve the phase space volume element, however, we need to ensure that the transformation is a canonical one. Thus, the corresponding momentum transformation is

$$\pi_i = V^{1/3} p_i$$

With this coordinate/momentum transformation, the phase space volume element transforms as

$$d^N \mathbf{p} d^N \mathbf{r} = d^N \mathbf{v} d^N \mathbf{s}$$

Thus, the volume element remains the same as required. With this transformation, the Hamiltonian becomes

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \frac{V^{-2/3} \pi_i^2}{2m_i} + U(V^{1/3} \mathbf{s}_1, \dots, V^{1/3} \mathbf{s}_N)$$

and the canonical partition function becomes

$$Q(N, V, T) = C_N \int d^N \pi \int d^N \mathbf{s} \exp \left\{ -\beta \left[ \sum_{i=1}^N \frac{V^{-2/3} \pi_i^2}{2m_i} + U(V^{1/3} \mathbf{s}_1, \dots, V^{1/3} \mathbf{s}_N) \right] \right\}$$

Thus, the pressure can now be calculated by explicit differentiation with respect to the volume,  $V$ :

$$\begin{aligned} P &= kT \frac{1}{Q} \frac{\partial Q}{\partial V} \\ &= \frac{kT}{Q} C_N \int d^N \pi \int d^N \mathbf{s} \left[ \frac{2}{3} \beta V^{-5/3} \sum_{i=1}^N \frac{\pi_i^2}{2m_i} - \frac{\beta}{3} V^{-2/3} \sum_{i=1}^N \mathbf{s}_i \cdot \frac{\partial U}{\partial (V^{1/3} \mathbf{s}_i)} \right] e^{-\beta H} \\ &= \frac{kT}{Q} C_N \int d^N \mathbf{p} \int d^N \mathbf{r} \left[ \frac{\beta}{3V} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{\beta}{3V} \sum_{i=1}^N \mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} \right] e^{-\beta H(\mathbf{p}, \mathbf{r})} \\ &= \frac{1}{3V} \left\langle \sum_{i=1}^N \left( \frac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \mathbf{F}_i \right) \right\rangle \\ &= \left\langle -\frac{\partial H}{\partial V} \right\rangle \end{aligned}$$

Thus, the pressure estimator is

$$\Pi(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{r}_1, \dots, \mathbf{r}_N) = \Pi(\mathbf{x}) = \frac{1}{3V} \sum_{i=1}^N \left[ \frac{\mathbf{p}_i^2}{2m_i} + \mathbf{r}_i \cdot \mathbf{F}_i(\mathbf{x}) \right]$$

and the pressure is given by

$$P = \langle \Pi(\mathbf{x}) \rangle$$

For periodic systems, such as solids and currently used models of liquids, an absolute Cartesian coordinate  $\mathbf{q}_i$  is ill-defined. Thus, the viral part of the pressure estimator  $\sum_i q_i F_i$  must be rewritten

THE UNITS FOR ENERGY, PRESS., LENGTH AND TIME

ARE MUST SATISFY Eq (5) PAGE 3, WHICH

$$l_{\text{unit}} = \frac{M_{\text{unit}} \cdot N_{\text{unit}}^2}{t_{\text{unit}}^2}$$

ONE perhaps sensible SET OF UNITS TO USE

$$M_{\text{unit}} = \text{AMU} = 10^{-3} \text{ kg/mole}$$

$$N_{\text{unit}} = 10^{-10} \text{ m}$$

$$t_{\text{unit}} = 10^{-13} \text{ s}$$

$$l_{\text{unit}} = \frac{10^{-3} \text{ kg} \cdot 10^{-20} \text{ m}^2}{10^{-26} \text{ s}^2 \cdot \text{mole}} = \frac{10^3 \text{ N} \cdot \text{m}}{\text{mole}} = \text{KJ/mole}$$

To START WITH, ~~TRANSLATE~~ OR WHEN READING THE INPUT FILE EVERYTHING WILL BE CONVERTED INTO THESE UNITS.

From PAGE (4) WE HAVE

$$T = \frac{2 \hat{E}_{\text{kin}}}{N \cdot d} \cdot \frac{l_{\text{unit}}}{k_B}$$

So if we TEMPERATURE UNIT =  $l_{\text{temp}} = \frac{l_{\text{unit}}}{k_B}$  SO THAT

$\hat{T} = \frac{T}{l_{\text{temp}}}$  THEN THE ABOVE EQUATION BECOMES

$$\hat{T} = \frac{2 \hat{E}_{\text{kin}}}{N \cdot d} = \frac{2 \hat{E}_{\text{per atom}}}{d}$$

Notice THAT  $k_B = 1.38054 \cdot 10^{-16} \text{ erg/K} = 8.314 \frac{\text{J}}{\text{K} \cdot \text{mole}}$

THAT MEANS IN THE SUGGESTED UNITS ABOVE

$$T_{\text{UNI}} = \frac{1 \text{ kJ/mol}}{8.314 \text{ J/kmol}} = \frac{1000}{8.314} \text{ K}$$

So if temperatures input in K then to convert to temp units simply divide by  $T_{\text{unif}}$

# CALCULATING INITIAL VELOCITIES (MOMENTA)

$$\frac{1}{2} k_B T D (N-1) = \frac{1}{2} \sum_{i=1}^N m_i v_i^2 = E_{\text{kin}}$$

# Dimensions      ~~Reason:~~  
↓                    TOTAL MOMENTUM FLIES TO ZERO  
I GUESS

It is probably "microscopically" better to aim to initially fix to atoms to have the

It probably does not ~~matter~~ matter whether we aim to fix all the velocities <sup>MAGNITUDES</sup> equal to the same value instead of all the momenta magnitudes or vice versa, in this primitive initialisation.

Say we want to determine the momentum ~~a~~ magnitude, equal for all atom, for which

$$\frac{1}{2} k_B T D (N-1) = \frac{1}{2} \hat{P}_T^2 \sum_{i=1}^N \frac{1}{m_i}$$

↓

$$\hat{P}_T = \sqrt{k_B T D (N-1) / \sum_{i=1}^N \frac{1}{m_i}}$$

In ~~any~~ dimensionless unit this reads

$$\hat{\tilde{P}}_T = \sqrt{\hat{T} D (N-1) / \sum_{i=1}^N \frac{1}{m_i}}$$

\* Next CHOOSE STOP  $\checkmark$  Random direction OF motorator vector

THEN SCALE ALL THESE TO MAGNITUDE  $\hat{\vec{P}}_T$

$$\hat{\vec{P}}_T = \vec{P}_T \frac{\vec{P}_{RAN}}{|\vec{P}_{RAN}|} = \frac{\hat{\vec{P}}_T}{|\vec{P}_{RAN}|} \vec{P}_{RAN}$$

FINALLY SET

$$\hat{\vec{P}}_{JT} = \hat{\vec{P}}_T - \frac{1}{N} \sum_{i=1}^N \hat{\vec{P}}_{iT}$$

WHICH GUARANTEES THAT

$$\sum_{j=1}^N \hat{\vec{P}}_{jt} = \vec{0}$$

# RAPAPORT UNITS AND SPECIFICALLY ARGON

DATA FROM Log Venet paper

$$\text{ENERGY } E = 119.8 \times 8.314 \text{ J/mole} \approx 996.02 \text{ J/mole}$$

TEMPERATURES  $\frac{E}{\text{J/mole}} = 119.8 \text{ K}$

LENGTH  ~~$\sigma = 3.4 \text{ \AA}$~~   $\sigma = 3.4 \text{ \AA}$

MASS  $m = 39.95 \text{ g/mole}$

THIS IMPLIES THAT UNIT OF TIME

$$\text{time} \sqrt{\frac{m \text{ g}^{-1}}{E}} = \sqrt{\frac{0.03995 \cdot (3.4 \cdot 10^{-10})^2}{119.8 \cdot 8.314}} \approx 2.15 \cdot 10^{-12} \text{ s}$$

NOTICE IN DIMENSIONLESS UNITS

$$\hat{T} = \frac{2}{3} \hat{E}_{\text{kin}}^{\text{per atom}}$$

THUS

$$T = \frac{2}{3} 119.8 \text{ K} \cdot \hat{E}_{\text{kin}}^{\text{per atom}} \approx \hat{E}_{\text{kin}}^{\text{per atom}} \cdot 79.87 \text{ K}$$

UNIT per PRESSURE

$$= \frac{E}{\sigma^3} = \frac{996.02}{6.02252 \cdot 10^{23} (3.4 \cdot 10^{-10})^3} \cancel{\text{N}} \frac{1}{101325} \text{ ATM}$$

$$\approx 415.28 \text{ ATM}$$

DENSITY

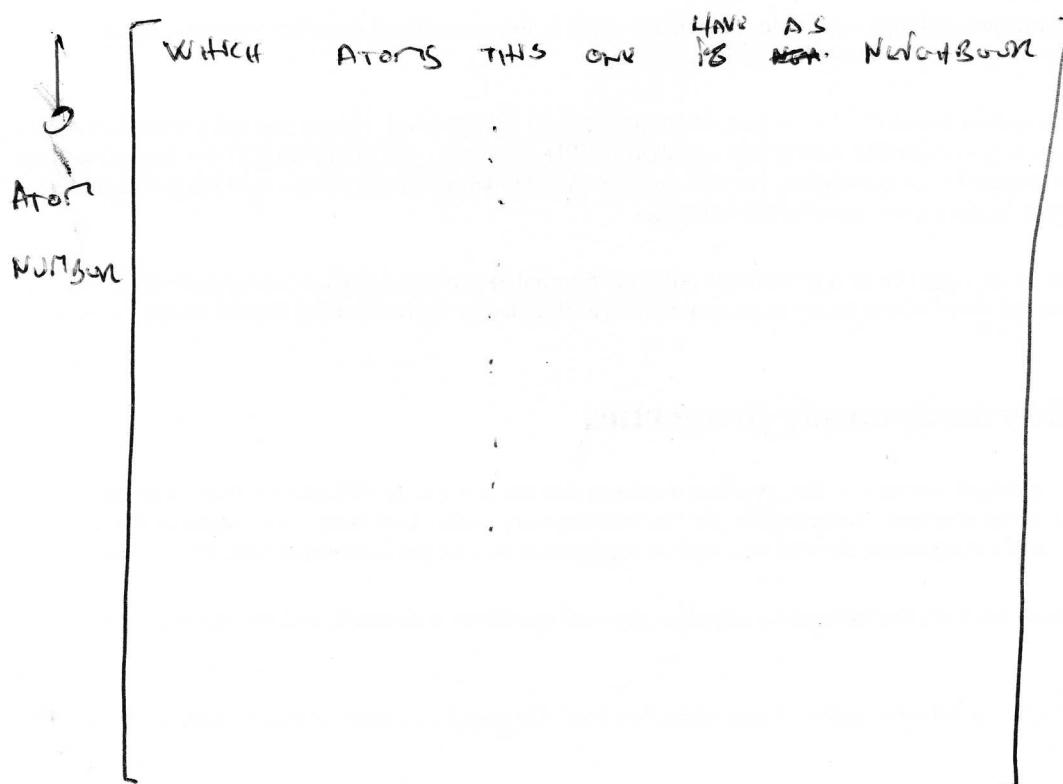
$$\rho_{\text{g/cm}^3} = \frac{39.95 \text{ g/mole}}{6.02252 \cdot 10^{23} \text{ mole}^{-1} (3.405 \cdot 10^{-10} \text{ cm})^3} \rho_{\text{atom/cm}^3} = 1.6803 \rho_{\text{atom/cm}^3}$$

## View of Nearest Neighbour Notes

Needs update when an atom moves further than  $\Delta r \approx \Delta r/2$ . The half because ~~an~~ another atom may have moved by the same distance in other directions.

As an alternative could watch how much each atom has moved - this would not cost a lot ~~more~~ more to do.

Using the following near-neighbour list



+ DISTANCES. Using this could use an algorithm which only looks at the atom which has gone further than  $\Delta r/2$  needs to update.

possible

## ✓ ADVANTAGES OF SUCH AN APPROACH

- For pure MP I AM NOT SURE  
THOSE WOULD BE MUCH SPREAD ADVANTAGES  
UNLESS FOR SOME REASNS ONLY A FEW  
OF THE ATOMS WOULD BE MOVEABLE  
A LOT
- For MC THERE COULD BE AN ADVANTAGE  
OF USING THIS APPROACH

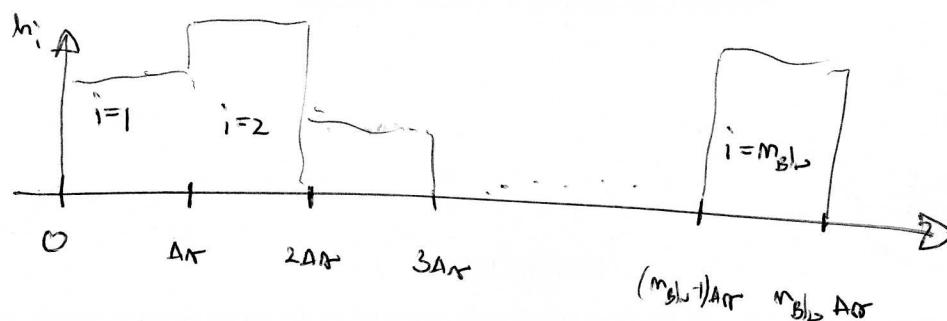
## DISADVANTAGE

- REQUIRES MORE MEMORY

# CALCULATE PDF (ROF)

19

Hence simply split  $r$ -range up in  $n_{\text{BLs}}$  intervals of length  $\Delta r = \frac{r_{\text{MAX}}}{n_{\text{BLs}}}$  starting from zero. Thus the  $i^{\text{th}}$  bin represents the number of dist. between  $(i-1)\Delta r \leq r_i < i\Delta r$  and the center of ~~each~~ & the  $i^{\text{th}}$  bin is

$$n_i = (i - \frac{1}{2}) \Delta r$$


Further calculate volume of box

$$g(r_i) = \frac{\sqrt{n_i}}{2\pi N^2 r_i^2 \Delta r} \quad i = 1, 2, \dots, n_{\text{BLs}}$$

↑  
Number of molecules

How to "derivative":

$$g(r) = \frac{2V}{N^2} \left\{ \sum_{i,j} \delta(r_i - r_j) \right\} \quad (4.3.2) \text{ Rayleigh}$$

The histogram represents the distribution of the

From Mc Grawy's Thesis 19a

$\hat{g}(r)$  (2.3.1)

~~DEFINITION~~

$$(1) \quad G(\vec{r}, 0) = \frac{1}{N} \left\langle \sum_{i,j=1}^N \delta(\vec{r} - \vec{r}_i(0) + \vec{r}_j(0)) \right\rangle$$

$$= \frac{S(\vec{r})}{V} + \rho g(r), \quad \rho = \frac{N}{V}$$

WHERE

ALSO EQUAL TO  
 $g_{\text{self}}^{(r)}(r, \Delta=0) \cdot N$

PAIR CORRELATION FUNCTION  
ALSO EQUAL TO DISTINCT

PART OF  
 $g(r, \lambda)$  WHEN  
 $\lambda=0$ . See  
PAGE 23

$$(2) \quad g(r) = \frac{V}{N^2} \left\langle \sum_{i,j} \delta(\vec{r} - \vec{r}_i(0) + \vec{r}_j(0)) \right\rangle$$

Now  $g(r)$  is ~~more~~ perhaps the standard way of defining  $g$ , but ~~it~~ (assuming here all identical atoms)  $g$  in (2) does not quite have the property that  $g(r) \rightarrow 1$  when  $r \rightarrow \infty$ , in fact (for liquids, gases)

$$(3) \quad \lim_{r \rightarrow \infty} g = \frac{V}{N^2} \cdot \frac{1}{V} N(N-1) = \frac{N-1}{N}$$

So maybe for computational reasons I might be better to store THE ~~PAIR DISTANCE FUNCTION~~ (2) in our more code as

$$(4) \quad \hat{g}(\vec{r}) = \frac{N}{N-1} g(\vec{r})$$

"NORMALIZED" PAIR CORRELATION FUNCTION

$\hat{g}(\vec{r})$  or  $g(r)$  depends only on  $r$ , hence

we use  $\hat{g}(r)$  and  $g(r)$  and in MDMC code

These are called RDF's, ALTHOUGH AS OF DATE  $\nabla^{16/2-2007}$  ~~16/2-2007~~

$\hat{g}(r) \rightarrow$  RATHER THAN THE RDF IS CALCULATED AS  $g(r)$  RATHER THAN  $\hat{g}(r)$ .

IN PRACTICE THE RDF IS CALCULATED BY THE USE OF A HISTOGRAM, COUNTING THE NUMBER OF DELTA FUNCTIONS  $\sum_{i+j} \delta(\vec{r} - \vec{r}_i - \vec{r}_j)$  IN SPHERICAL SHELLS WITH CENTER POSITIONS  $r_m = (m - \frac{1}{2})$ ,  $m = 1, 2, \dots, N$  AND WIDTH  $\Delta r$

$$(5) h(m_i, \Delta r) = \int_{\text{SHELL}} \sum_{i+j} \delta(\vec{r} - \vec{r}_i(o) + \vec{r}_j(o)) dr$$

SUCH TO CALCULATE  $g(r)$

$$(6) g(r_i) = \frac{\nabla h(m_i, \Delta r)}{N^2 \frac{4\pi r_i^2 \Delta r}{\text{VOLUME OF SHELL}}}$$

AND  $\hat{g}(r)$

$$(7) \hat{g}(r) = \frac{\nabla h(m_i, \Delta r)}{N(N-1) \frac{4\pi r_i^2 \Delta r}{\text{VOLUME OF SHELL}}}$$

PERHAPS BETTER TO CALCULATE  $V$  AS

$$\frac{4\pi}{3} r_i^3 (i - (i-1)^3)$$

$$i = 1, 2, \dots, N_{BL}$$

THE EXACT VOLUME OF A FINITE SPHERICAL SHELL

19

DYNAMICAL PROPERTIES OF SIMPLE FLUIDS (CHAP 5 RAPAPORT)

DIFFUSION COEFFICIENT CAN BE CAL AS

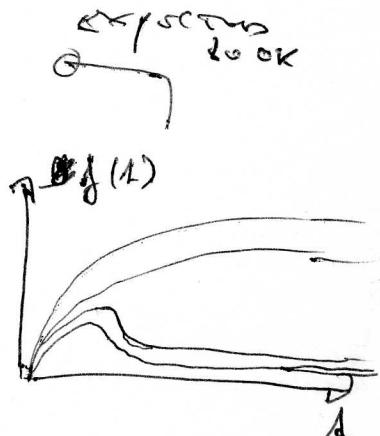
(5.2.4)  
Rapaport

$$D = \lim_{L \rightarrow \infty} \frac{1}{6N_{\text{eff}} d} \left\langle \sum_{j=1}^{N_{\text{eff}}} [\vec{r}_j(L) - \vec{r}_j(0)]^2 \right\rangle$$

$f(L)$

OR AS

$$D = \frac{1}{3N_{\text{eff}}} \int_0^\infty \left\langle \sum_{j=1}^{N_{\text{eff}}} \vec{v}_j(L) \cdot \vec{v}_j(0) \right\rangle dL$$

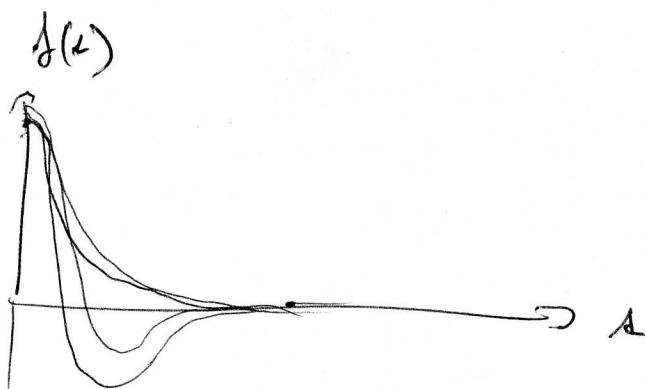


N FOR A MONOATOMIC LIQUID REFER TO THE NUMBER OF ATOMS

WHERE Rapaport REPORT THE VELOCITY AUTOCORRELATION FUNCTIONS AS

$$f(L) = \frac{\left\langle \sum_{j=0}^{N_{\text{eff}}} \vec{v}_j(L) \vec{v}_j(0) \right\rangle}{\left\langle \sum_{j=0}^{N_{\text{eff}}} |\vec{v}_j(0)|^2 \right\rangle}$$

AND  $f(L)$  IS EXPECTED TO LOOK SOMETHING LIKE



NOTE THIS WAY THIS MEAN BRACKET IS USED HERE AND IN (5.2.4) IS NOT CLEAR. IN FACT IN RAPAPORT (AND MLE, SHOW IT COPIES HIS CODE) IT REFERS TO THE AVERAGE OVER NUMBER OF BUFFERS.

To GET

$$\langle [\vec{r}_i(0) - \vec{r}_i(t)]^2 \rangle$$

Where now THE MEAN BRACKETS MEANS THE MEAN  
VALUE OF THE SQUARED DIFFERENCES BETWEEN  
ATOMS AT  $t = 0$  AND HAVE THEY HAVE MOVED  
TO AT A LATER  $t$ .

NOTE I GUESS THAT UNLESS THE WHOLE  
SAMPLE IS MOVING THAT

$$\langle [\vec{r}_i(0) - \vec{r}_i(t)] \rangle = 0$$

IF THIS IS TRUE THEN

$$\text{VAR} (\langle [\vec{r}_i(0) - \vec{r}_i(t)] \rangle) = \langle [\vec{r}_i(0) - \vec{r}_i(t)]^2 \rangle$$

Space-time correlation functions  $\langle \dots \rangle$  (ALSO CALLED VAN HOVE CORRELATION FUNCTIONS AND JUST TIME-DEPENDENT CORRELATION FUNCTION)

$$G(\vec{r}, L) = G_S(\vec{r}, L) + G_D(\vec{r}, L)$$

WHENCE

$$G_S(\vec{r}, L) = \frac{1}{N_M} \left\langle \sum \delta(\vec{r} + \vec{r}_j(0) - \vec{r}_j(L)) \right\rangle$$

$$G_D(\vec{r}, L) = \frac{1}{N_M} \left\langle \sum_{i \neq j} \delta(\vec{r} + \vec{r}_i(0) - \vec{r}_j(L)) \right\rangle$$

$$\neq \frac{2}{N_M} \left\langle \sum_{i \leq j} \delta(\vec{r} + \vec{r}_i(0) - \vec{r}_j(L)) \right\rangle$$

ACCEPT  
WHEN  
 $s=0$

ASSUME THAT BOTH  $G_S$  AND  $G_D$  ONLY DEPEND ON  $|s| = r$

$$\int G_S(\vec{r}, L) d\vec{r} \underset{\substack{\text{SHELL WITH} \\ \text{CROSS } n_i \\ \text{AREAS } \Delta r}}{\approx} \frac{1}{4\pi n_i^2 \Delta r} G_S(r_i, L) = \frac{1}{N_M} \langle h_i^S \rangle$$

WHERE

$$h_i^S = \int_{\text{SHELL}} \sum_j \delta(\vec{r} + \vec{r}_j(0) - \vec{r}_j(L)) d\vec{r}$$

THUS

$$G_S(r_i, L) = \frac{\langle h_i^S \rangle}{\frac{1}{4\pi n_i^2 \Delta r} N_M}$$

BETTER TO CALL AS

$$\frac{4\pi}{3} \Delta r^3 (i - (i-1)^3)$$

$$i = 1, 2, \dots, N_M$$

Similarly

$$\int G_d(r_i^*, l) dr^* \approx \frac{4\pi r_i^* \Delta r}{\text{SHELL}} |G_d(r_i^*, l)| = \frac{1}{N_{\text{sh}}} \langle h_i^* \rangle$$

SHELL  
CENTER  $r_i^*$   
ALONG  $\Delta r$

WHERE

$$h_i^* = \int_{\text{SHELL}} \sum_{i \neq j} \int (\vec{r} + \vec{r}_i^*(0) - \vec{r}_j^*(l)) dr^*$$

BETTER TO  
CALL AS  
 $\frac{4\pi}{3} \Delta r^3 (i^3 - (i-1)^3)$   
 $i = 1, 2, \dots, N_{\text{sh}}$

THUS

$$G_d(r_i^*, l) = \frac{\langle h_i^* \rangle}{(4\pi r_i^* \Delta r)} N_{\text{sh}}$$

So with reference to page 24 eq (1c)

$$\hat{g}^d = \frac{N}{N-1} g^d = \frac{N}{N-1} \frac{G_d}{P} N_{\text{sh}} = \frac{V}{N(N-1)} \frac{h_i^*}{(4\pi r_i^* \Delta r)}$$

AND

PAGE 28

$$\hat{g}^s = N g^s = N \frac{G_d}{P} = \frac{V}{N} \frac{h_i^s}{(4\pi r_i^* \Delta r)}$$

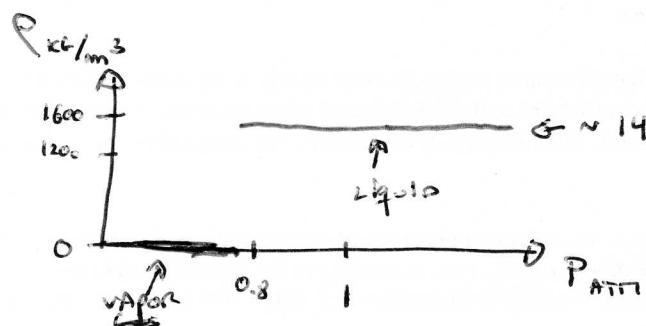
NAMES FOR THESE USED IN LITERATURE INCLUDE

- SPACE-TIME PAIR CORRELATION FUNCTION
- DYNAMICAL PAIR CORRELATION FUNCTION

{ "NORMALISED" VERSIONS OF THESE USED FOR CALCULATIONS AND OTHERWISE

# Ar properties (from NIST.GOV)

Isothermal DATA  $T = 85\text{K}$



$$\rho \approx 1409.6 \text{ kg/m}^3 \quad [\Delta E_{\text{internal}} \approx -4.8 \text{ kJ/mol}]$$

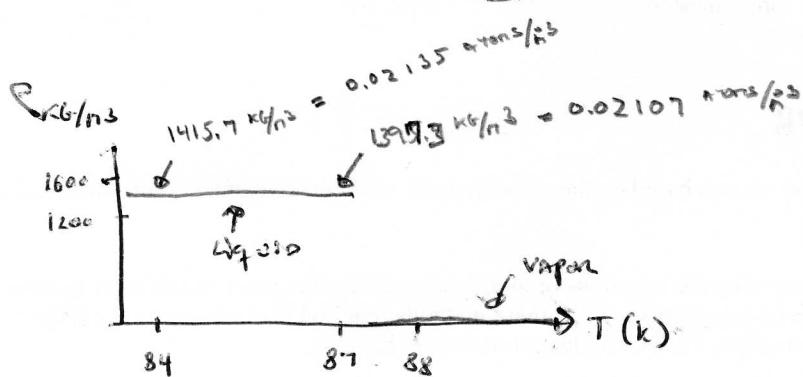
$$1.4096 \text{ g/cm}^3$$

$$1.4096 \times \frac{6.02252 \times 10^{23}}{39.95} \text{ cm}^3 \cdot (10^8 \text{ cm})^3$$

$$= 1.4096 \times 0.01508 \frac{\text{Atoms}}{\text{A}^3}$$

$$\approx 0.02125 \text{ Atoms/A}^3$$

Isothermal DATA  $P = 1 \text{ atm}$



STARTING FROM (3.3.2) THESIS

$$(1) \frac{1}{N} \frac{d^2 \sigma_c}{d\omega d\omega} = \frac{k}{k_0} \sum_{\alpha=1}^{N_a} \sum_{\beta=1}^{N_b} \bar{b}_\alpha \bar{b}_\beta S_{\alpha\beta}(\vec{q}, \omega)$$

WHERE

$$(2) S_{\alpha\beta}(\vec{q}, \omega) = \frac{1}{2\pi} \int e^{-i\omega t} S_{\alpha\beta}(\vec{q}, t) dt$$

AND

$$(3) S_{\alpha\beta}(\vec{q}, t) = \int e^{i\vec{q} \cdot \vec{r}^*} G_{\alpha\beta}(\vec{r}, t) d\vec{r}$$

WHERE

$$(4) G_{\alpha\beta}(\vec{r}, t) = \frac{1}{N} \left\langle \sum_{i_\alpha=1}^{N_a} \sum_{j_\beta=1}^{N_b} \int \delta(\vec{r} + \vec{r}_{i_\alpha}(0) - \vec{r}^*) \delta(\vec{r}^* - \vec{r}_{j_\beta}(t)) d\vec{r} \right\rangle$$

IN CLASSICAL LIMIT

$$(5) G_{\alpha\beta}^{cl}(\vec{r}, t) = \frac{1}{N} \left\langle \sum_{i_\alpha=1}^{N_a} \sum_{j_\beta=1}^{N_b} \delta(\vec{r} - \vec{r}_{j_\beta}(t) + \vec{r}_{i_\alpha}(0)) \right\rangle$$

FOR EVERY  $i_\alpha$  THE PICTURE OF THE  $\beta$  TYPE PARTICLES  
MAY LOOK THE SAME FOR A LARGE DISORDERED SYSTEM,  
IN WHICH CASE

$$(6) G_{\alpha\beta}^{cl}(\vec{r}, t) \approx \frac{N_\alpha}{N} \left\langle \sum_{j_\beta=1}^{N_b} \delta(\vec{r} - \vec{r}_{j_\beta}(t) + \vec{r}_{i_\alpha}(0)) \right\rangle$$

Consonant system or consisting of only one type of scatterer, then (1) reads

$$(7) \quad \frac{1}{N} \frac{d^2\sigma_c}{d\Omega d\omega} = \frac{k}{h_0} \bar{v}^2 S(\vec{Q}, \omega)$$

WHERE

NOTICE putting  $\hbar$  here is optional.  
IF NOT INCLUDED THEN UNIT OF  $S(\vec{Q}, \omega)$  IS  
INVERSE FREQUENCY. IF INCLUDED THEN UNIT  
IS INVERSE ENERGY.

$$(8) \quad S(\vec{Q}, \omega) = \frac{1}{2\pi c} \int e^{i(\vec{Q} \cdot \vec{r} - \omega t)} G(\vec{r}, t) d\vec{r} dt$$

CALCULATE THIS QUANTITY FOR A LIQUID IT IS  
USEFUL TO OBSERVE THAT AT  $t \rightarrow \infty$   $G \rightarrow \frac{N}{V} = \rho$   
AND AS  $t \rightarrow \infty$   $G \rightarrow \frac{N}{V} = \rho$ , THEREFORE COMPUTATION-  
NALLY IT IS EASIER TO COMPUTE

$$(9) \quad S'(\vec{Q}, \omega) = \frac{1}{2\pi} \int e^{i(\vec{Q} \cdot \vec{r} - \omega t)} [G(\vec{r}, t) - \rho] d\vec{r} dt$$

WHERE  $S$  AND  $S'$  ONLY DIFFER BY  $\propto S(\vec{Q}) S(\omega)$   
THAT IS OF NO PHYSICAL INTEREST HERE.

FURTHER FOR LIQUIDS  $G(\vec{r}, t)$  ONLY DEPENDS ON  
 $r$ , THEREFORE THEN

$$(10) \quad S'(\vec{Q}, \omega) = \frac{2\pi}{2\pi} \int_{-\infty}^{\infty} dr e^{-i\omega t} \int_0^{\infty} r^2 [G(r, t) - \rho] dr \int_{-1}^1 e^{iQr \cos \theta} d(\cos \theta)$$

use  $\int_{-\infty}^{\infty} dr e^{-i\omega t} \frac{2}{Q} \int_0^{\infty} \sin(Qr) r [G(r, t) - \rho] dr$

$$\int_{-1}^1 e^{iQr \cos \theta} dr = \frac{1}{iQr} [e^{iQr} - e^{-iQr}] = \frac{2 \sin Qr}{Qr} \text{ since } \sin x = \frac{e^x - e^{-x}}{2i}$$

SIMILAR TO PAGE 19a DEFINE  $g(r, L) = G/R$ , WHERE  
 (ALMOST)  
 $g(r, L)$  IS THE SPACE-TIME EQUIVALENT OF  $g(r)$  ON  
 PAGE 19a. To BE PRECISE  $g(r)$  ON PAGE 19a IS THE  
 OBJECT PART OF  $g(r, L)$  AT  $L=0$ , BUT WHEN NOT TIME-DEPEN-  
 DENT DATA THE "d" IN  $g^d$  IS DROPPED.  
 CLASSICALLY FROM MD SIMULATIONS  $g$  CALCULATED AS

$$(11) \quad g(r_s^L) = \frac{1}{PN} \left\langle \sum_{i,j}^N \delta(r - r_{ij}^L + r_i(0)) \right\rangle$$

For every  $i$  THE picture IS ASSUMED TO LOOK THE SAME

$$(12) \quad = \frac{1}{PN} \left\{ \left\langle \sum_i \delta(r - r_i^L + r_i(0)) \right\rangle \right.$$

$$\left. + \left\langle \sum_{i \neq j} \delta(r - r_{ij}^L + r_i(0)) \right\rangle \right\}$$

IN A MD SIMULATION THE THERMAL AVERAGE  $\langle \rangle$  IS  
 DONE BY AVERAGING OVER MANY INDEPENDENT DIFFERENT CONFIGURATIONS FOR EACH

TIME. ASSUME ONLY  $r$  DEPENDENCE  
 BOTTOM TO CALC HISTOGRAM VOLUMES AS  
 $\frac{4\pi}{3} \Delta r^3 (i^3 - (i-1)^3), i = 1, 2, \dots, N_{\Delta r}$

$$(13) = \frac{1}{PN} \left[ \frac{1}{4\pi r^2 \Delta r} \right] \left\{ \sum_{\text{SHELL}} \int \delta(r - r_i^L + r_i(0)) dr^L + \sum_{\text{SHELL}} \int \delta(r - r_{ij}^L + r_i(0)) dr^L \right\}$$

$\underbrace{\sum_{\text{SHELL}} \int \delta(r - r_i^L + r_i(0)) dr^L}_{\text{SELF-HISTOGRAM}} \quad \underbrace{\sum_{\text{SHELL}} \int \delta(r - r_{ij}^L + r_i(0)) dr^L}_{\text{DIFFERENT HISTOGRAM}}$   
 $m^s(r, \Delta r) \quad m^d(r, \Delta r)$

NOTICE FOR COMPUTATIONAL EFFICIENCY ONLY WHEN  $L=0$

$$\Rightarrow \text{sum } \sum_{i \neq j} = 2 \sum_{i < j}$$

AND FINALLY WRITE

$$(14) \quad g = g^s + g^d$$

$$\left\{ \begin{array}{l} \text{where } g^s \rightarrow \frac{1}{N} \\ g^d \rightarrow \frac{N-1}{N} \end{array} \right.$$

~~THE INTEGRAL~~

NOTICE THAT  $g \rightarrow 1$  IN LIMTS  $L \rightarrow \infty$  AND  $n \rightarrow \infty$ , BUT NOT  $g^s$  AND  $g^d$  INDIVIDUALLY. WE MAY DERIVE A

MODIFIED VERSION OF  $g^d$ , CALL IT  $\hat{g}^d$ , WHICH HAS

THE PROPERTY THAT : (FOR DISORDERS STUFF)

$$(15) \quad \hat{g}^d \rightarrow 1 \quad \text{WHEN} \quad L \rightarrow \infty \quad \text{OR} \quad n \rightarrow \infty$$

THAT IS

$$(16) \quad \begin{aligned} \hat{g}^d &= \frac{V}{N(N-1)} \left\langle \sum_{i \neq j} S(\vec{r} - \vec{r}_j(L) + \vec{r}_i(0)) \right\rangle \\ \text{"NORMALIZED" VERSO} &= \frac{N}{N-1} g^d \end{aligned}$$

FOR INSTANCE THIS QUANTITY IS CALCULATED ~~TO THE~~ BY THE RMCTT PROGRAM.

SUBSTITUTE G WITH  $\hat{g}^d$  IN (10) GIVES

$$(17) \quad S(Q, \omega) = \frac{2Q}{Q} \int_{-\infty}^{\infty} dk \int_0^{\infty} dr [g(\vec{r}, L) - 1] e^{-i\omega t} \sin(Qr) r$$

WE HAVE ASSUMED  $g$  ONLY DEPENDS ON  $r$ , THEREFORE  $g(\vec{r}, L) = \hat{g}(-\vec{r}, L)$  AND  $g$  IS "PAR" WITH RESPECT TO THE CHARGE  $\vec{r} \rightarrow -\vec{r}$ . FOR FURTHER FOR A CLASSICAL TREATMENT SYSTEM  $g$  CAN BE SHOWN TO BE 100% PAR

AND THEREFORE USING  $g(\vec{r}, L) = g(\vec{r}, -L)$  IN (17) YIELDS

$$\int_{-\infty}^{\infty} dL e^{-i\omega L} = \int_{-\infty}^0 dL e^{-i\omega L} + \int_0^{\infty} dL e^{-i\omega L}$$

$\Downarrow \text{ sub } \omega L = -L$

(18)

$$- \int_{\infty}^0 dL' e^{i\omega L'} = \int_0^{\infty} dL' e^{i\omega L'}$$

Therefore

(19)

$$\int_{-\infty}^{\infty} dL e^{i\omega L} [\hat{g} - 1] = \int_0^{\infty} dL [\hat{g} - 1] (e^{-i\omega L} + e^{i\omega L})$$

$$= 2 \int_0^{\infty} dL [\hat{g} - 1] \cos(\omega L)$$

AND (10) IN THE CLASSICAL TREATMENT CAN BE CALCULATED AS

(20)

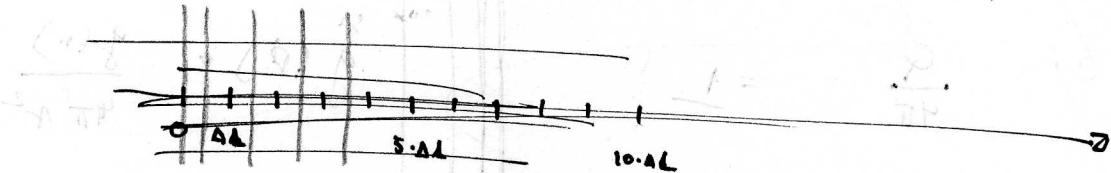
$$S^I(\vec{q}, \omega) = \frac{4\pi}{Q} \int_0^{\infty} dL \cos(\omega L) \int_0^{\infty} dr [g(r, L) - 1] \sin(qr) r$$

IN PRACTICAL APPLICATIONS CAL. (20) IN STEPS. CAL.  
1<sup>ST</sup>

$$(21) \quad S(\vec{Q}, L) = \frac{4\pi}{Q} \int_0^R dr [g(r, L) - 1] \sin(Qr) r$$

$$= R \int \exp(i\vec{Q} \cdot \vec{r}) [g(\vec{r}, L) - 1] \sin Qr d\vec{r}$$

FOR VARIOUS VALUES OF  $L$  AND  $Q$ . TAKE AND  $L$   
VALUES TO BE  $0, \pm 1, \pm 2, \dots$ :



FURTHER DO THE INTEGRATION OVER  $g^s$  AND  $g^o$   
SEPARATELY. FOR THIS IT CONSTAIN 1<sup>ST</sup>  $g^o$ .

HERE IT IS PERHAPS MORE CONVENIENT TO INTEGRATE  
OVER  $g^o$  DIRECTLY IN (16) INSTEAD OF  $g^s$  SO  
AS TO KEEP THIS ' $-1$ ', i.e.

$$(22) \quad S^o(\vec{Q}, L) = \rho \frac{N-1}{N} \frac{4\pi}{Q} \int_0^R dr [g^o(r, L) - 1] \sin(Qr) r$$

TWO " HERE  
BECAUSE  
CONSTANT HAS  
BEEN CHANGED  
AGAIN.

NOTICE WE CAN  
CHOOSE THIS VALUE  
AS WE LIKE SINCE  
IT ONLY MAKES S ID  
AND SOLELY DIFFER BY  
SOMETHING  $\propto \delta(Q)$

$\hat{g}^0$  is cal. in bls  $\Delta r$  apart, starting from 0, and  
 $\hat{g}^0$  is assumed to be constant over each bl. Denote  
each of these constant values  $\hat{g}_i^0, i=1, 2, \dots, N_r$ ,  
where e.g.  $\hat{g}_1^0$  is the constant associated with the  
interval  $[0; \Delta r]$  and so on. Under this notation  
(22) reads

$$S^0(\vec{q}, L) = P \frac{N-1}{N} \frac{4\pi}{Q} \sum_{i=1}^{N_r} \left[ \hat{g}_i^0(L) - \right] \underbrace{\int_{(i-1)\Delta r}^{i\Delta r} \sin(Qr) r dr}_{\text{area}}$$

very important to keep the -1 when doing the numerical integration

$$= P \frac{N-1}{N} \frac{4\pi}{Q} \sum_{i=1}^{N_r} \left[ \hat{g}_i^0(L) - \right] \left[ \frac{\sin(Qr)}{Q^2} - \frac{r \cos(Qr)}{Q} \right]_{(i-1)\Delta r}^{i\Delta r}$$

$$= P \frac{N-1}{N} \sum_{i=1}^{N_r} \left[ \hat{g}_i^0(L) - \right] R_i(Q)$$

WHERE

$$(24) R_i(Q) = \frac{4\pi}{Q} \left[ \frac{\sin(Qr)}{Q^2} - \frac{r \cos(Qr)}{Q} \right]_{(i-1)\Delta r}^{i\Delta r}$$

$\hat{g}^s$  is calculated over the same bl structure as  $\hat{g}^0$ ,  
but a distinction will be made between  
calculating  $S^s(\vec{q}, L)$  when  $L=0$  and  $L \neq 0$ .  
Firstly, like  $\hat{g}^0$ , introduce  $\hat{g}^s$  to have the property  
that  $\hat{g}^s \rightarrow 1$  as when  $L \rightarrow \infty$  or  $r \rightarrow \infty$ .

This MEANS

$$(25) \quad \hat{g}^s(\vec{r}, L) = \frac{V}{N} \left\langle \sum_i \delta(\vec{r} - \vec{r}_i(L) + \vec{r}_i(0)) \right\rangle = \rho N \hat{g}^s \cdot \frac{V}{N} = N \hat{g}^s$$

So AS FOR  $S^D(\vec{q}, L)$  in (22) CALCULATE

$$(26) \quad S^S(\vec{q}, L) = \underbrace{\rho}_{\frac{1}{V}} \frac{1}{N} \frac{4\pi}{Q} \int_0^\infty dr [ \hat{g}^s - 1 ] \sin(qr) r$$

AND FROM (23-24) WE SEE

NOTICE AGAIN ALL THE MODIFICATION OF THE CONSTANT IS AGAIN THE REASON FOR ALSO DISTINGUISH BETWEEN  $S^S$  AND  $S^D$ ; THEY DIFFER BY SOMETHING  $\propto \delta(Q)$

$$(26a) \quad S^S(\vec{q}, L) = \underbrace{\rho}_{\frac{1}{V}} \sum_{i=1}^{N_r} [\hat{g}^s - 1] R_i(Q), \text{ WHEN } A > 0$$

For  $L = 0$  we simply HAVE

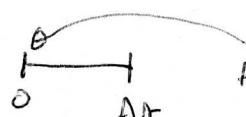
$$(27) \quad \begin{aligned} S^S(\vec{q}, 0) &= \int G^S(\vec{r}, 0) \exp(i\vec{q} \cdot \vec{r}) d\vec{r}, \quad G^S = \frac{1}{N} \sum_i \delta(\vec{r} - \vec{r}_i(0)) \exp(i\vec{q} \cdot \vec{r}_i(0)) \\ &= 1, \quad \text{WHEN } A = 0 \end{aligned}$$

MUST USE THIS EXACT EXPRESSION FOR CALCULATING  $S^S$

WHEN  $L = 0$  BECAUSE NUMERICAL & APPROXIMATES

WILL NEVER BE GOOD HERE SINCE IF CONSTRAINED

THIS HISTOGRAM WILL



ALL THE HTS WILL BE

AT  $r=0$  EXACTLY

WHICH IS THE NUMERICAL APPROXIMATION

OF ASSUMES THE HTS ARE SPREAD OUT IN THE HISTOGRAM

INTEGRATING  $S^D(\vec{Q}, L)$  AND  $S^S(\vec{Q}, L)$  OVER TIME.

WE HAVE

$$(28) \quad S(\vec{Q}, \omega) = \frac{L}{2\pi} \int_{-\infty}^{\infty} dt \exp(-i\omega t) S(\vec{Q}, t)$$

$$= \frac{1}{\pi} \int_0^{\infty} \cos(\omega t) S(\vec{Q}, t) dt$$

USING (18-20).

(OR  $N_L - 1$   
HERE ...)

$S(\vec{Q}, t)$  IS CALCULATED AT  $t = 0, \Delta t, \dots, N_L \Delta t$ .

NUMERICALLY (28) COULD BE CALCULATED IN ~~ANY~~ 1000 OF DIFFERENT WAYS, INCLUDING FFT ....

From PAGE 23 Eq. 15 AND PAGE 24 Eq. 16 WE SEE

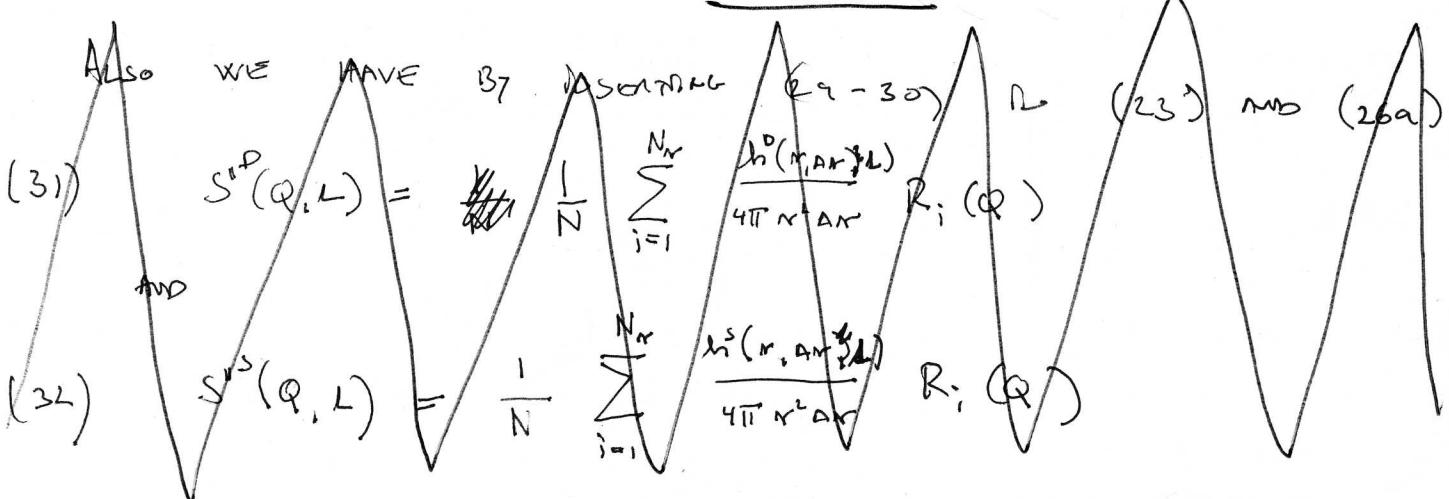
IN PRACTICE  $\hat{g}^D$  IS CALCULATED

$$(29) \quad \hat{g}^D(r, \lambda) = \frac{V}{N(N-1)} \frac{h^D(r, \Delta r, \lambda)}{[4\pi r^2 \Delta r]}$$

AND

$$(30) \quad \hat{g}^S(r, \lambda) = \frac{V}{N} \frac{h^S(r, \Delta r, \lambda)}{[4\pi r^2 \Delta r]}$$

BETTER TO  
CAL AS  
 $\frac{4\pi}{3} \Delta r^3 (i - (i-1)^3)$ ,  
 $i = 1, 2, \dots, N_{\Delta r}$



Notice THAT

$$S''(\vec{q}, L) = S''^D(\vec{q}, L) + S''^S(\vec{q}, L)$$

NOTE  
DATA  
FUNCTION  
NOT S

$$\mathcal{D}(\vec{q})$$

WHENCE  $S''$  ONLY VARY FROM  $S'$  AND  $S$  BY CONST  $\propto \mathcal{D}(\vec{q})$

IN THE IDEAL WORLD WHERE  $\hat{g}^0, \hat{g}^S \rightarrow 1$  AS WHEN  $N \rightarrow \infty$ ,

THIS IS IN PARTICULAR A PROBLEM FOR  $\hat{g}^S$  SHOCK FOR

$A > 0$   $\hat{g}^S > 0$   $N \neq 0$  AND FOR  $A$  NOT TOO MUCH BIGGER

THAN ZERO, THE ATOMS WILL NOT HAVE MOVED TO

FAR FROM EACH OTHER RELATIVE TO THE BOX LENGTH, TO

GIVE A NON-ZERO  $\checkmark$  FOR  $\hat{g}^S$  FOR LARGER  $N$ -VALUES.

THIS MIGHT HAVE IMPLICATIONS ~~WITH INTEGER~~, SINCE IT

MIGHT HAVE THE FOLLOWING EFFECT:



$$(3) \quad \int_0^{R_{\max}} (f(r) + c) \underbrace{\sin(Qr)}_{\text{SH}} \, dr \approx \int_0^{R_{\max}} r \cos(Qr) \, dr = \left[ \frac{\sin(Qr)}{Q^2} - \frac{r \cos(Qr)}{Q} \right]_0^{R_{\max}} = \frac{\sin(QR_{\max})}{Q^2} - \frac{R_{\max} \cos(QR_{\max})}{Q}$$

WHICH MIGHT HAVE NON-ZERO CONTRIBUTIONS ~~TO~~

FOR  $Q \neq 0$  WHICH ARE SEEN TO BE  $\propto C$  !!

BASICALLY THE A  $\left[ \frac{\sin(Qr)}{Q^2} - \frac{r \cos(Qr)}{Q} \right]_0^{R_{\max}}$  IS UNPREDICTABLE AND

SHOULD BE AVOIDED BY HAVING  $f(r) \rightarrow c$  FOR  $r \rightarrow \infty$ .

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METHOD 1 OF CALCULATION  $\frac{1}{\pi} \int_0^\infty \cos(\omega L) S(\vec{Q}, L) dL$

$$= \frac{1}{\pi} \left[ \frac{1}{2} \Delta L S(\vec{Q}, 0) + \sum_{m=1}^{n-\text{thre}-1} \Delta L \cos(\omega m \Delta L) S(\vec{Q}, m \Delta L) \right]$$

WHERE IT IS REQUIRED THAT  $\omega \Delta L \ll \pi$  IN SOME WAY.

METHOD 2 OF CALCULATION  $\frac{1}{\pi} \int_0^\infty \cos(\omega L) S(\vec{Q}, L) dL$

$$= \frac{1}{\pi \omega} \left\{ S(\vec{Q}, 0) \left[ \sin(\omega L) \right]_0^{\frac{1}{2} \Delta L} + \sum_{m=1}^{n-\text{thre}-1} S(\vec{Q}, m \Delta L) \left[ \sin(\omega L) \right]_{(m-\frac{1}{2}) \Delta L}^{(m+\frac{1}{2}) \Delta L} \right\}$$

WHERE AGAIN IT IS REQUIRED THAT  $\omega \Delta L \ll \pi$  IN SOME WAY.

Note CANNOT USE METHOD 2 WHEN  $\omega = 0$ .

OBSERVATIONS ABOUT  $g_0(r, L)$ ,  $g_s(r, L)$ ,  $S_0(q, L)$   
 $S_s(q, L)$ ,  $S^0(q, \omega)$  AND  $S_s(q, \omega)$

1) IT MAKE SENSE TO KEEP A COPY OF BOTH  
 $g_0(r, L)$  AND  $g_s(r, L)$  BECAUSE FOR ~~THE~~ TWO  
 REASONS

- a) PLOTTING REASONS. IF YOU PLOTTED  
 $g_0 + g_s$  THE LATTER WOULD COMPLETELY  
 SWAMP THE FORMER.
- b) MORE IMPORTANT  $g_s$  IS NEEDED  
 FOR THE INCOHERENT CROSS SECTIONS.

2) IT ONLY MAKES SENSE TO ~~STOKE~~ STORE AND  
 CALCULATE

$$\text{a)} \quad \text{SUM} \int (g_0 + g_s) \exp(i\vec{r} \cdot \vec{q}) d\vec{r} = S^{\text{coh}}(q, L)$$

$$\text{b)} \quad \int g_s \exp(i\vec{r} \cdot \vec{q}) d\vec{r} = S^{\text{incoh}}(q, L)$$

IN PRACTICE YOU SEEM TO BE ABLE TO GET  
 AWAY WITH CALCULATING  $S^s(q, L)$  AND  $S^0(q, L)$   
 SEPARATELY AND ADDING THESE TOGETHER.

BBM

## UNITS OF $S(Q, \omega)$ , $S(Q, L)$ AND ETC

$G(r, L)$  HAS UNIT OF INVERSE VOLUME. SINCE  
THE UNIT OF LENGTH IS  $10^{-10} \text{ m} = 1 \text{ \AA}$  THEN  
UNIT OF  $G(r, L)$  IS  $\text{\AA}^{-3}$ .

$$g(r, L) = G(r, L) / \rho = G(r, L) * \frac{V}{N} \text{ IS DIMENSIONLESS,}$$

~~Since Eqn (8) page 22~~ UNITS OF  
Since TIME IS MEASURED IN  $10^{-13} \text{ s} = 0.1 \text{ ps}$   
THEN FROM EQ (8) PAGE 22 IT FOLLOWS THAT  
THE UNIT OF  $S(Q, \omega)$  IS  $10^{-13} \text{ s} = \frac{1}{10^{13} \text{ s}^{-1}}$   
I.E A UNIT OF INVERSE FREQUENCY AS ~~TIME~~  
WELL AS A UNIT OF TIME.

NOTE IN VAN WELL THESIS HE USES PS AS UNIT  
FOR  $S(Q, \omega)$ .

FROM EQ (3) PAGE 21 IT FOLLOWS THAT THE  
INTERMEDIATE SCATTERING FUNCTION  $S(Q, L)$  IS  
DIMENSIONLESS.