

10. Systems of interacting particles

canonical partition function

distribution functions

pair correlation functions

the assumption of pair potentials

the Lennard-Jones fluid

ensemble averages of dynamical

variables and molecular

properties

more on intermolecular potentials

phase transformations

Recall:

Perfect gas in the Canonical Ensemble

Example: 3 non-interacting particles only (a, b, c) each particle has energy levels

$$\epsilon_1, \epsilon_2, \epsilon_3, \dots, \epsilon_i, \dots$$

and wavefunctions

$$\phi_1, \phi_2, \phi_3, \dots, \phi_i, \dots$$

The system wavefunction

$$\Psi_{ijk} = \phi_i(a) \cdot \phi_j(b) \cdot \phi_k(c)$$

energy of this system quantum state

$$\text{is } E_{ijk} = \epsilon_i + \epsilon_j + \epsilon_k$$

The canonical partition function is $Q = \sum_J e^{-\beta E_J}$

where J denotes one set of quantum numbers ijk for example

The molecular partition function

$$\text{is } q = \sum_i e^{-\beta \epsilon_i}$$

$$Q = \sum_{ijk} e^{-\beta(\epsilon_i + \epsilon_j + \epsilon_k)} = \left(\sum_i e^{-\beta \epsilon_i} \right) \left(\sum_j e^{-\beta \epsilon_j} \right) \left(\sum_k e^{-\beta \epsilon_k} \right) = q^3$$

Particles _{a,b,c} can be permuted among the states ijk and there are $3!$ ways of doing this.

general: So the correct expression is $Q = \frac{q^N}{N!}$

where no internal structure (rare gas atoms):

$$q = \left(\frac{2\pi m kT}{h^2} \right)^{3/2} \cdot V$$

$$Q = \frac{1}{N!} \left(\frac{2\pi m kT}{h^2} \right)^{\frac{3N}{2}} \cdot V^N$$

SYSTEMS OF INTERACTING PARTICLES

The Configuration Integral and the Canonical Partition Function

Consider a fluid

consisting of N identical molecules or atoms

The coordinates of the N particles in space are specified by the N vectors

$$\vec{r}_1, \vec{r}_2, \vec{r}_3 \dots \vec{r}_N$$

Let the vector momentum of the i th particle be \vec{p}_i

Let the potential energy of interaction between the N molecules be represented by

$$U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Assume that the set of internal energy levels of each atom or molecule are unaffected by the other molecules

$$q = q_{\text{int}} = \sum_k e^{-E_k/k_B T} \quad \left\{ \begin{array}{l} \text{internal energies} \\ \text{only} \end{array} \right.$$

The canonical partition function is

$$Q = \sum_j e^{-E_j/k_B T}$$

The energy of the j th system quantum state

$$E_j = \underbrace{\sum_i \epsilon_{k_i}}_{\substack{\text{q-mechanical} \\ \text{internal}}} + \underbrace{\sum_i \frac{p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2}{2m}}_{\substack{\text{K.E.} \\ \text{translation}}} + U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \quad \left. \vphantom{\sum_i} \right\} \text{P.E. of interacting molecules}$$

$$Q = \sum_j e^{-E_j/k_B T} = \sum_j \underbrace{\left(e^{-\sum_{i=1}^N \epsilon_{ai}/k_B T} \right)}_{(q_{\text{int}})^N} \underbrace{\left(e^{-\frac{1}{k_B T} \sum_i \frac{p_{xi}^2 + p_{yi}^2 + p_{zi}^2}{2m}} \right)}_{\text{replace sums by a classical integral}} \left(e^{-\frac{U(\vec{r}_1, \dots)}{k_B T}} \right)$$

$$Q \approx (q_{\text{int}})^N \cdot \frac{1}{N! h^{3N}} \int \dots \int e^{-\frac{1}{k_B T} \sum_i \frac{(p_{xi}^2 + \dots)}{2m}} e^{-\frac{U(\vec{r}_1, \dots)}{k_B T}} d^3 p_1 \dots d^3 r_1 \dots d^3 r_N$$

Since $\int_{-\infty}^{\infty} e^{-p_x^2/2mk_B T} dp_x = (2\pi mk_B T)^{1/2}$

means $dx, dy, dz,$

recall $q_{\text{transl}} = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} \cdot V$

This is why h^{3N} factor needs to be introduced when using classical mechanics

$$Q_{\text{inter-acting}} = \frac{(q_{\text{int}})^N}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} \cdot \underbrace{\int \dots \int e^{-U(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)/k_B T} d^3 r_1, \dots}_{3N \text{ integrations altogether}}$$

call this $Z(T, V)$

"CONFIGURATION INTEGRAL"

When $U=0$ this equals V^N as it should for non-interacting particles

$$Q_{\text{non-interacting particles}} = \frac{(q_{\text{int}})^N}{N!} \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3N}{2}} \cdot V^N$$

configuration integral replaces V^N

The fundamental equation in the CANONICAL ensemble is $A = -k_B T \ln Q$,

$$A = -Nk_B T \left[\ln \left(\frac{q_{\text{int}}}{N} \right) + 1 \right] - \frac{3Nk_B T}{2} \ln \left(\frac{2\pi m k_B T}{h^2} \right) - k_B T \ln \underbrace{Z(T, V)}_{\text{CONFIGURATION INTEGRAL}}$$

The pressure is $P \equiv -\left(\frac{\partial A}{\partial V}\right)_T$

$$= k_B T \left[\frac{\partial \ln Z(T, V)}{\partial V} \right]_T$$

reduces to $\frac{N}{V}$ for non-interacting

Note that q_{int} does not affect PVT behavior and is omitted. \rightarrow due to the assumption that the internal energy levels are unaffected by interactions. The above says that the interaction potential determines the equation of state.

Distribution Functions

[Occupation numbers of internal energy levels are normally part of the definition of "distribution" Since we are omitting q_{int} from this discussion the distribution will be specified by specifying only the POSITIONS of the particles in space]

The probability of observing the system in the system quantum state of energy E_j is

$$P_j = \frac{e^{-E_j/kT}}{Q}$$

The probability of observing the system with particle 1 in the volume element $d^3\vec{r}_1$ at \vec{r}_1 , particle i in the volume element $d^3\vec{r}_i$ at \vec{r}_i etc. ..., irrespective of the kinetic energy of the particles is

$$P(\vec{r}_1, \dots, \vec{r}_N) d^3\vec{r}_1 \dots d^3\vec{r}_N = \frac{e^{-U(\vec{r}_1, \dots, \vec{r}_N)/k_B T}}{Z(T, V)} d^3\vec{r}_1 \dots d^3\vec{r}_N$$

specific distribution functions:

$$P^{(1)}(\vec{r}_1) = \frac{\int_{\vec{r}_2} \dots \int_{\vec{r}_N} e^{-U(\vec{r}_1, \dots, \vec{r}_N)/k_B T} d^3\vec{r}_2 \dots d^3\vec{r}_N}{Z(T, V)} = \frac{1}{V} \text{ for an isotropic fluid}$$

This is the probability of finding particle 1 at \vec{r}_1 , averaged over all possible configurations of the remaining $N-1$ particles.

Since there are N ways of choosing the first particle,

generic distribution function:

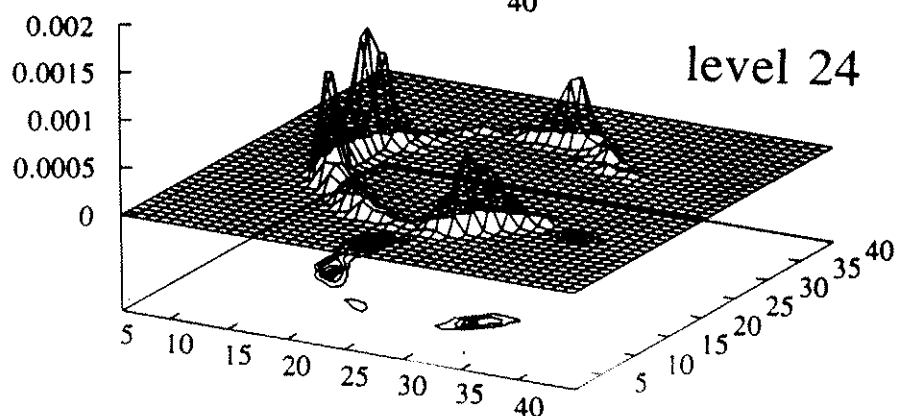
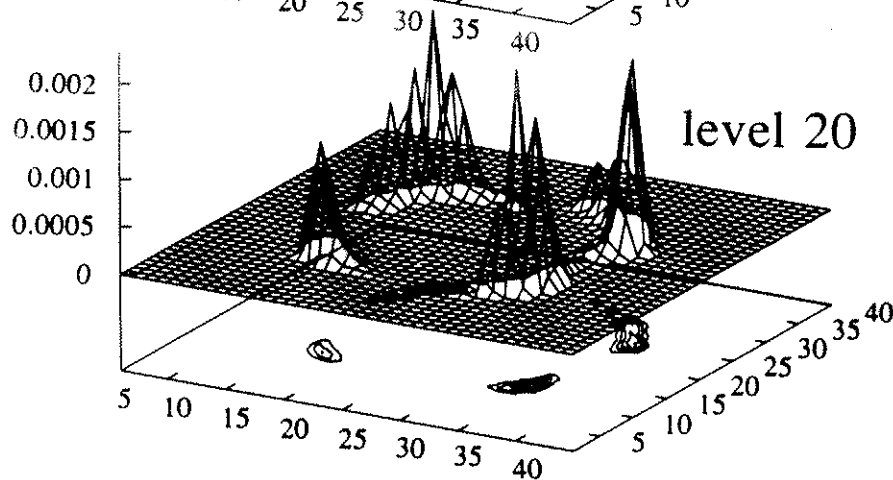
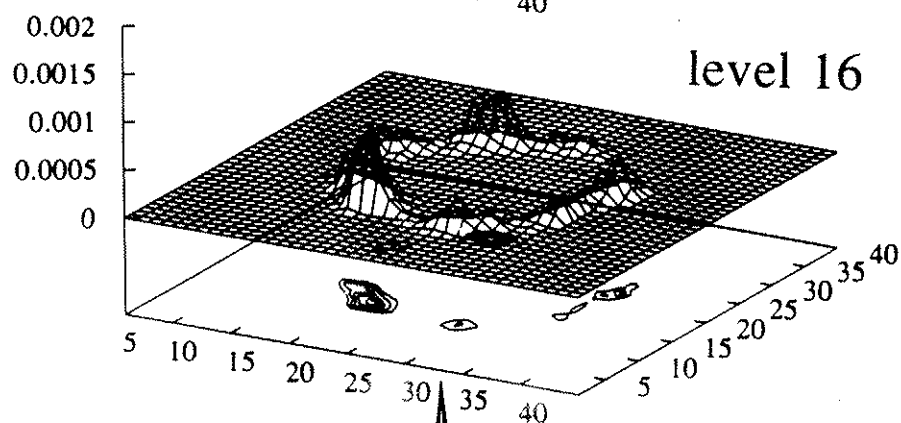
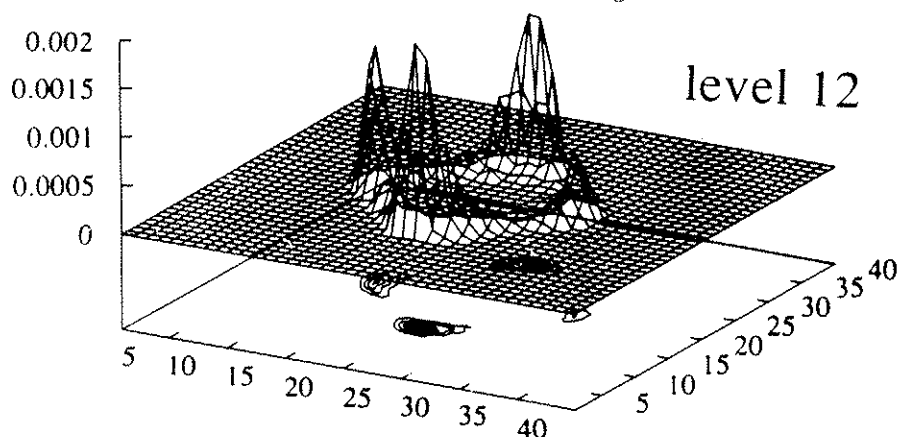
$$P^{(1)}(\vec{r}_1) = N P^{(1)}(\vec{r}_1) = \frac{N}{V} \text{ for an isotropic fluid}$$

This is the probability on making an observation of the configuration of the system, that a particle will be found at precisely \vec{r}_1 .

This is also called a one-body distribution function.

- Within a cavity, where do the molecules spend most of their time: like a snowball in the middle of the cavity? or like a thin film along the inside walls?

Cluster of Xe_8



Can generalize to the probability of finding a second particle at \vec{r}_2 when there is a particle at \vec{r}_1 (or any number of particles at that number of locations)

pair distribution function $g(r_{12})$ or radial distribution function or pair correlation function

$$P^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{N(N-1)}{V^2} \underbrace{P^{(2)}(\vec{r}_1, \vec{r}_2)}_{\int \dots \int_{r_3} \dots \int_{r_N} e^{-U(\vec{r}_1, \dots, \vec{r}_N)/kT} d^3\vec{r}_3 \dots d^3\vec{r}_N} = \frac{1}{V^2} g(\vec{r}_1, \vec{r}_2) = \frac{1}{V^2} g(r_{12})$$

$Z(T, V)$

if interaction is dependent only on distance rather than "radial" orientation

$P^{(2)}(\vec{r}_1, \vec{r}_2) = P^{(2)}(r_{12}) = \frac{N(N-1)}{V^2} g(r_{12}) \approx \left(\frac{N}{V}\right)^2 g(r_{12}) = \rho^2 g(r_{12})$

This is the probability (when multiplied by $d^3\vec{r}_1 d^3\vec{r}_2$) of finding one particle in the volume element $d^3\vec{r}_1$ at \vec{r}_1 and another particle simultaneously in $d^3\vec{r}_2$ at \vec{r}_2

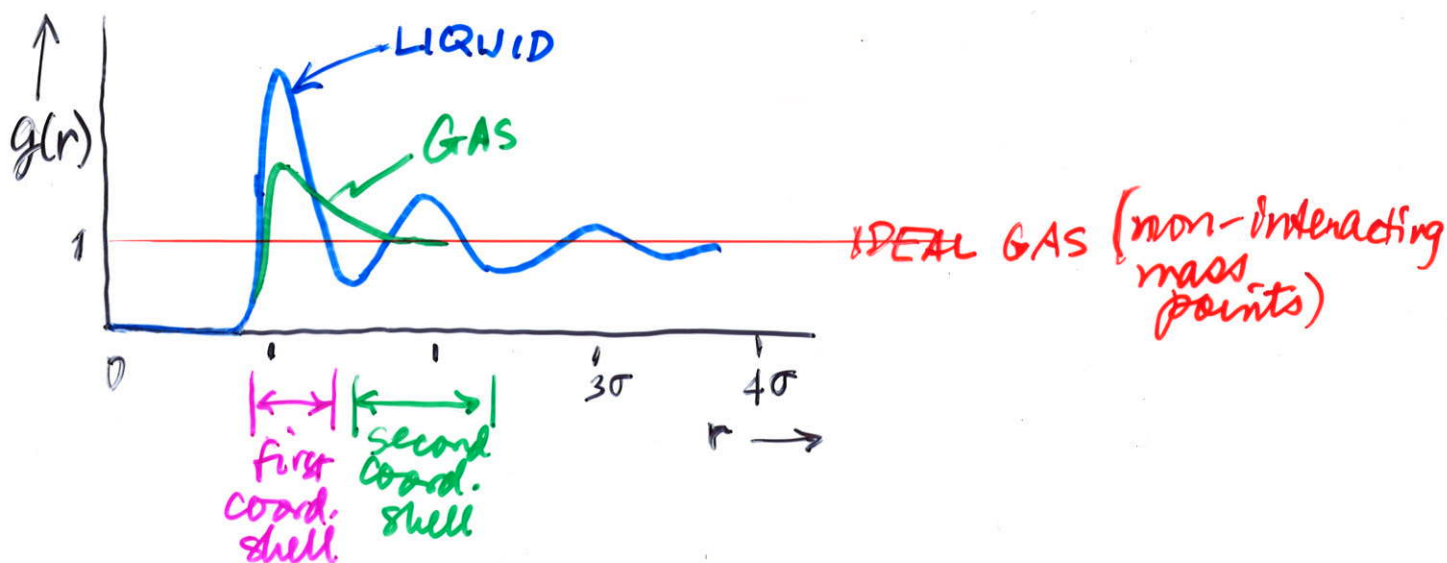
What is the shape of $g(r_{12})$?

$g(0) = 0$ Two particles cannot occupy same space

$g(r_{12}) \rightarrow 1$ as $r_{12} \rightarrow \infty$

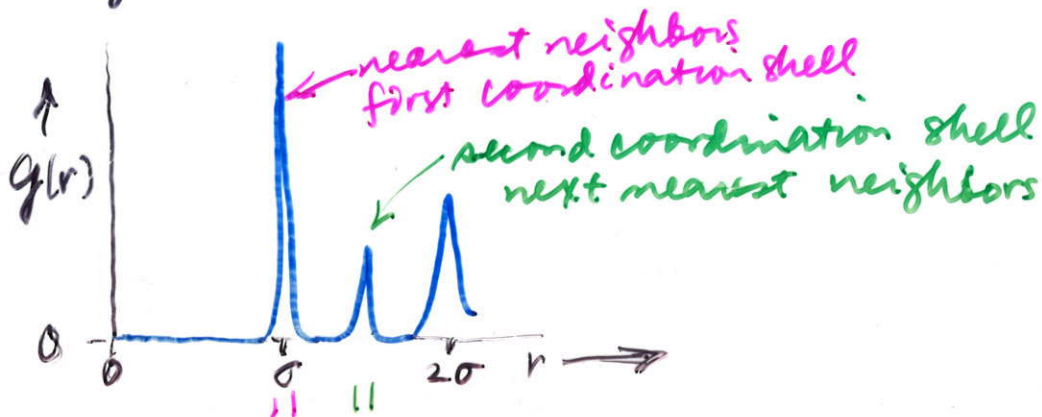
$g(r_{\min}) =$ local maximum where r_{\min} is near the bottom of the well (lowest energy for 2 particles)

There is a strong likelihood that a first neighbor shell will be found around $r = \sigma$ where σ is the van der Waals diameter. The nearest neighbors, which comprise the first coordination shell, tend to exclude the next nearest neighbors from an intermediate region around $r \approx 1.5\sigma$. Thus $g(r)$ will be less than 1 in that region and it will peak above the uncorrelated result near $r = 2\sigma$.

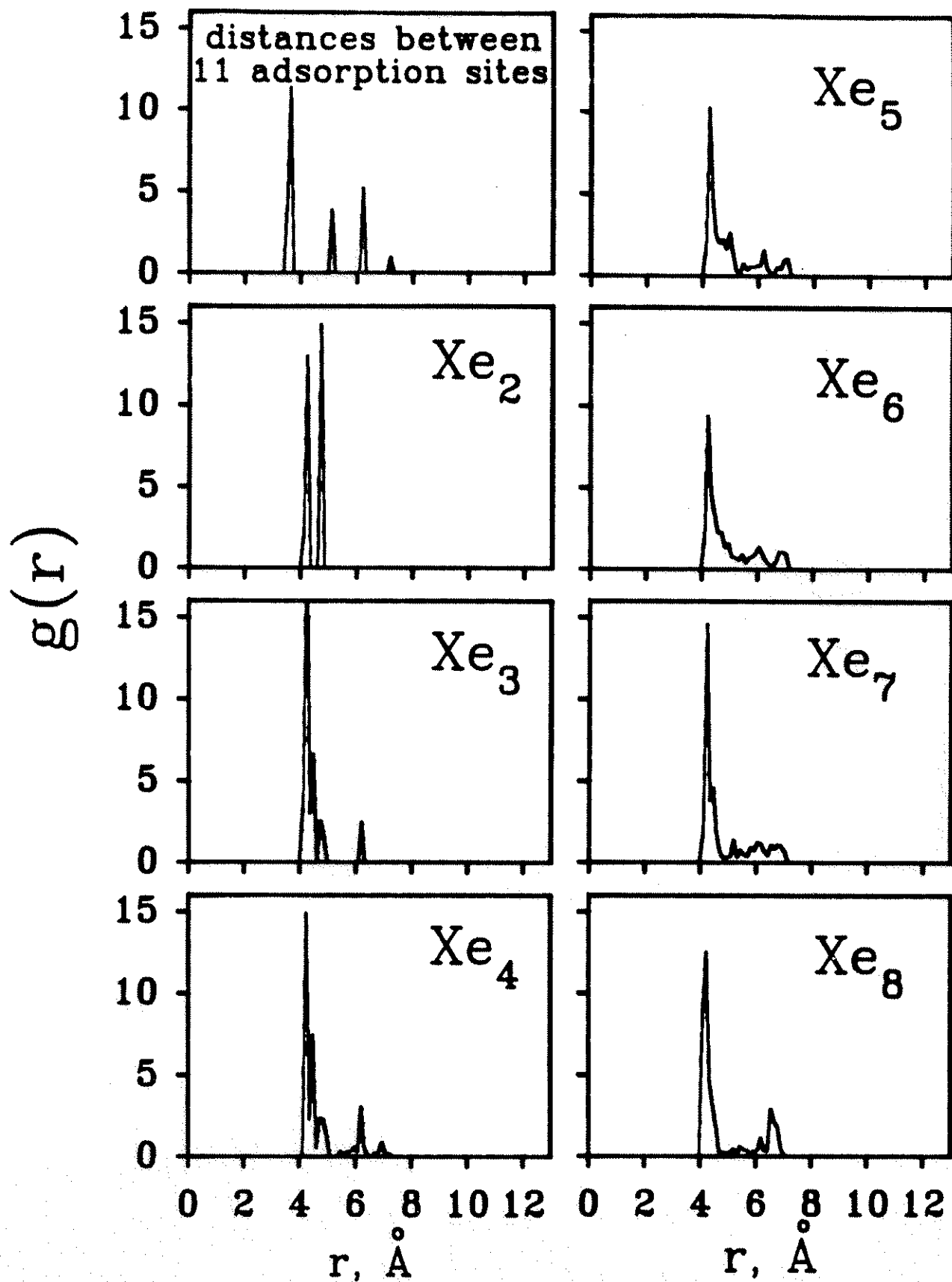


The second peak corresponds to the most probable location for the next nearest neighbors. These neighbors comprise the second coordination shell.

Compare with solid crystal ^{eg. bcc} 2 second nearest neighbors are at distance $\sqrt{2}\sigma$



Xe-Xe distances in the minimum energy configurations of Xe_n



Minimum energy site separations less than 13 Å.

Separation/Å	No. of sites at this distance	same/different cavity
6.4	4	same
6.6	4	different
9.1	1	same
9.2	2	different
10.7	4	different
11.1	4	different
12.5	8	different
12.8	4	different

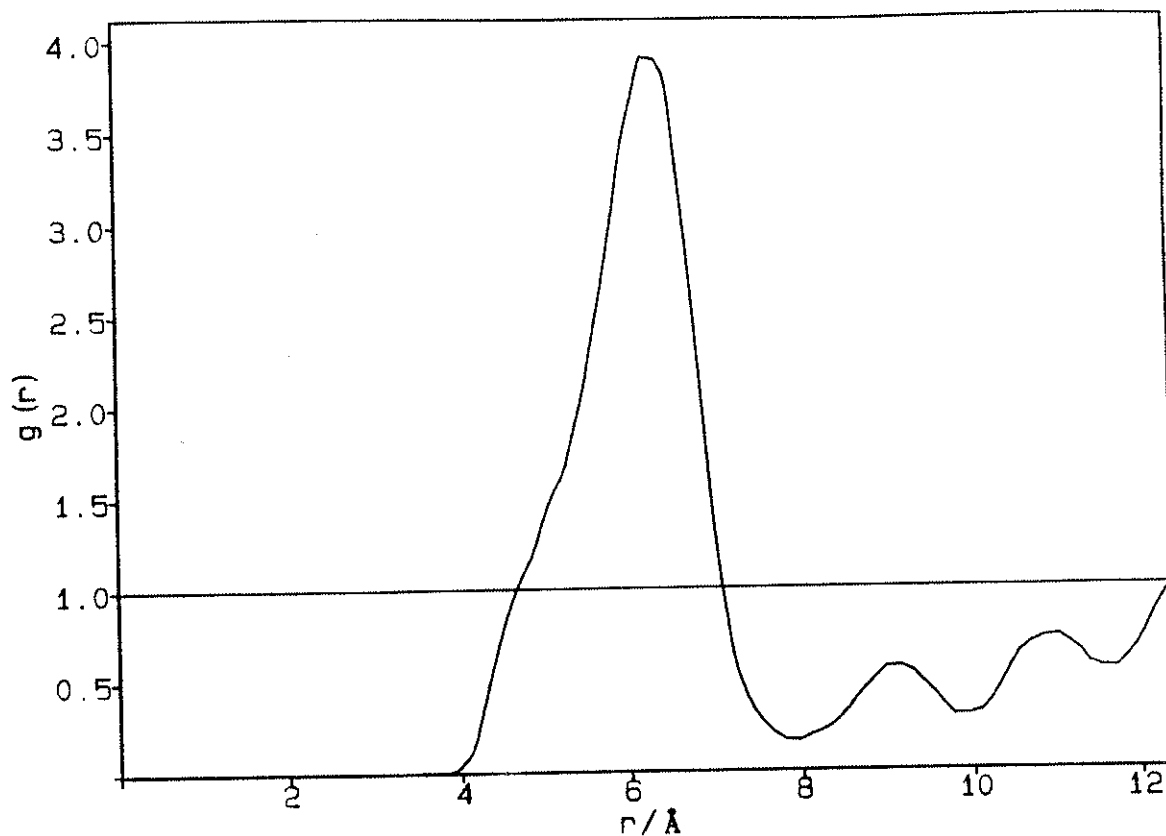


Figure 4.19 The pair distribution function, $g(r)$, for xenon at 144 K and an average occupancy of $\bar{N} = 1$ (27 atoms in 27 unit cells).

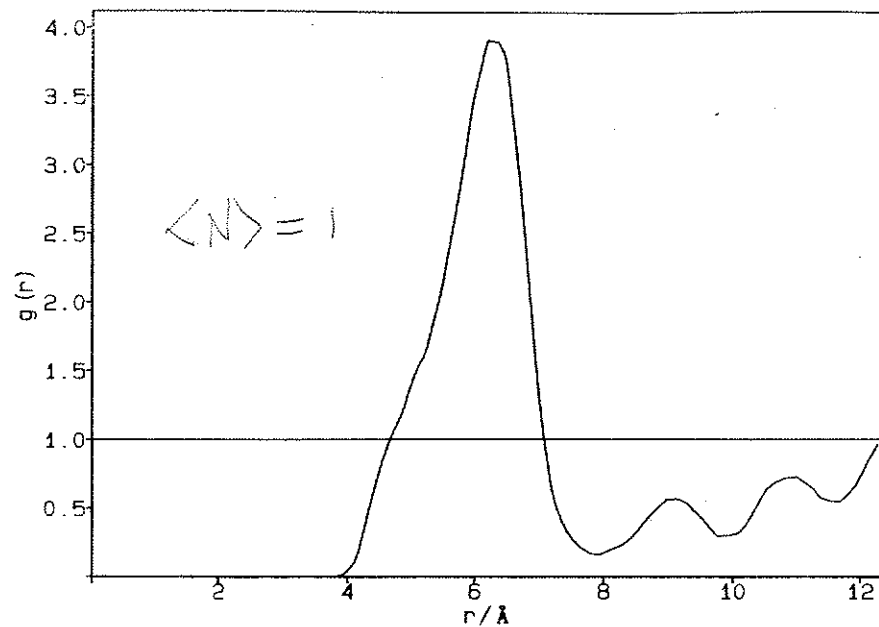


Figure 4.19 The pair distribution function, $g(r)$, for xenon at 144 K and an average occupancy of $\bar{N} = 1$ (27 atoms in 27 unit cells).

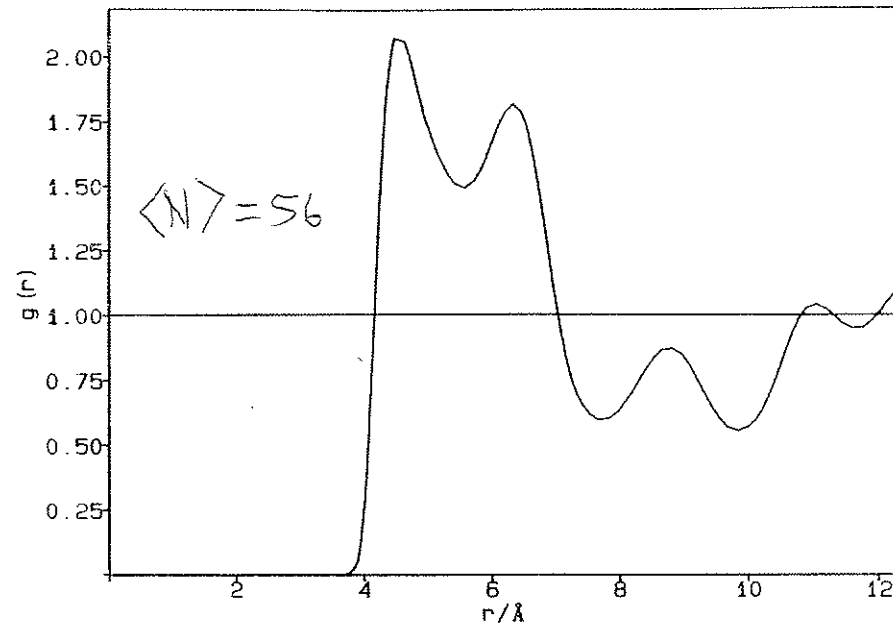


Figure 4.21 The pair distribution function, $g(r)$, for xenon at 144 K and an occupancy of $N = 56$.

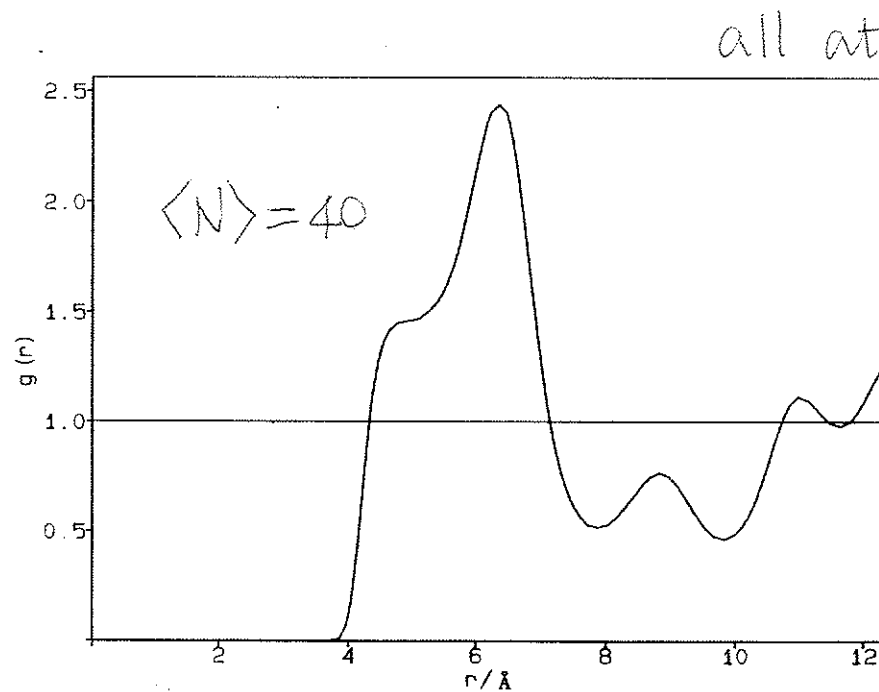


Figure 4.20 The pair distribution function, $g(r)$, for xenon at 144 K and an occupancy of $N = 40$.

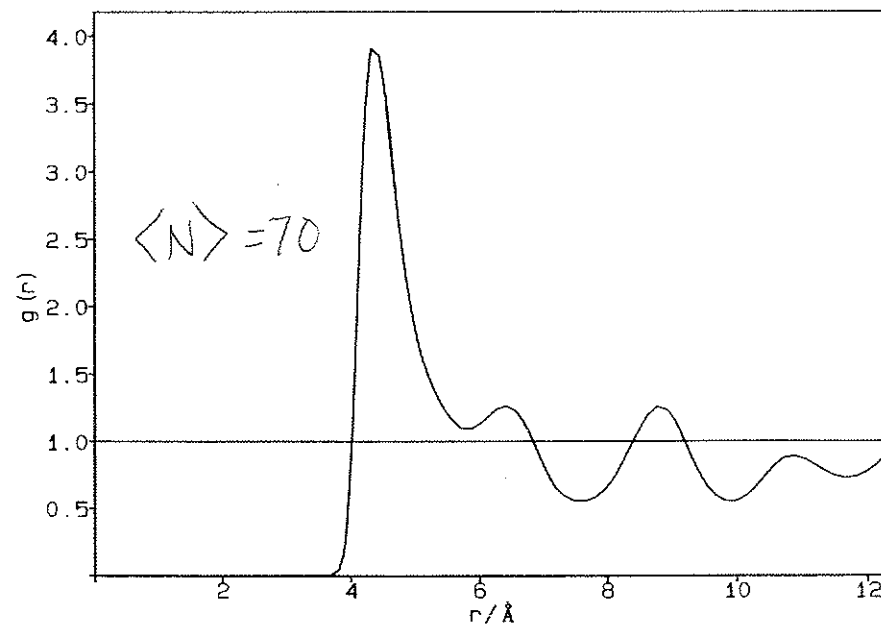
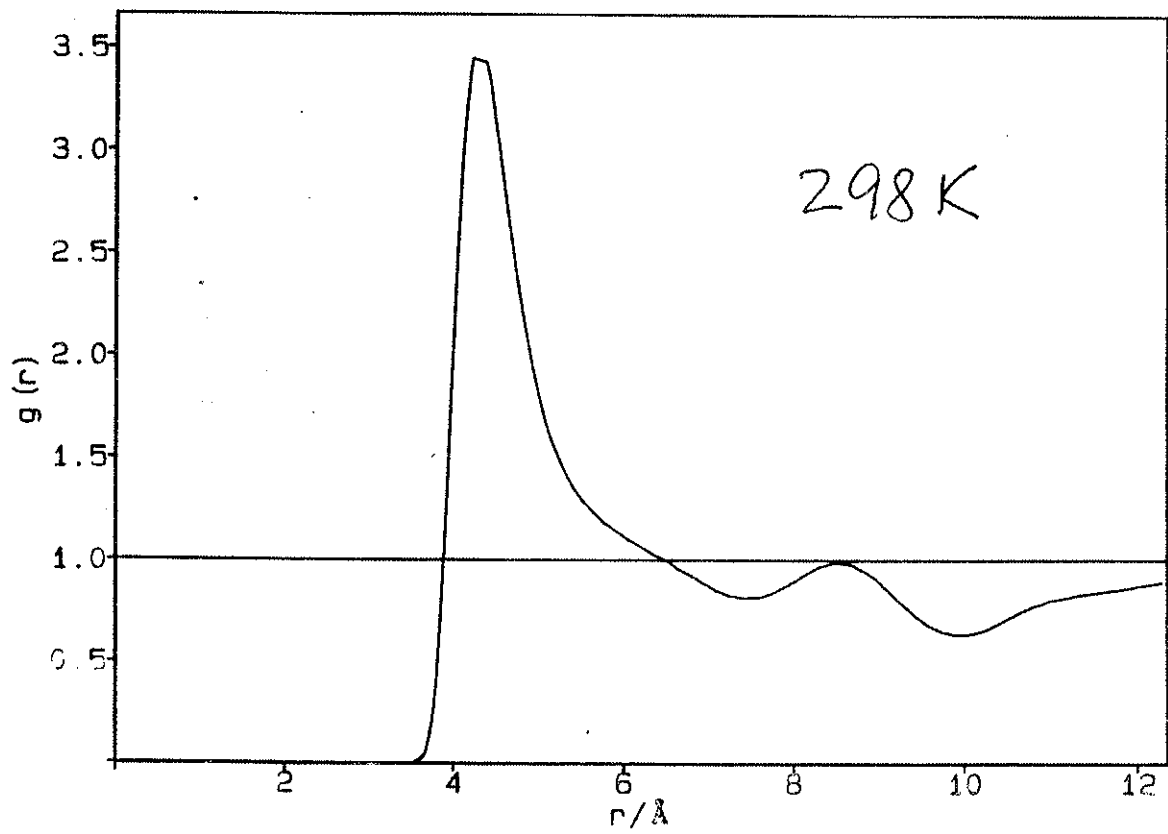
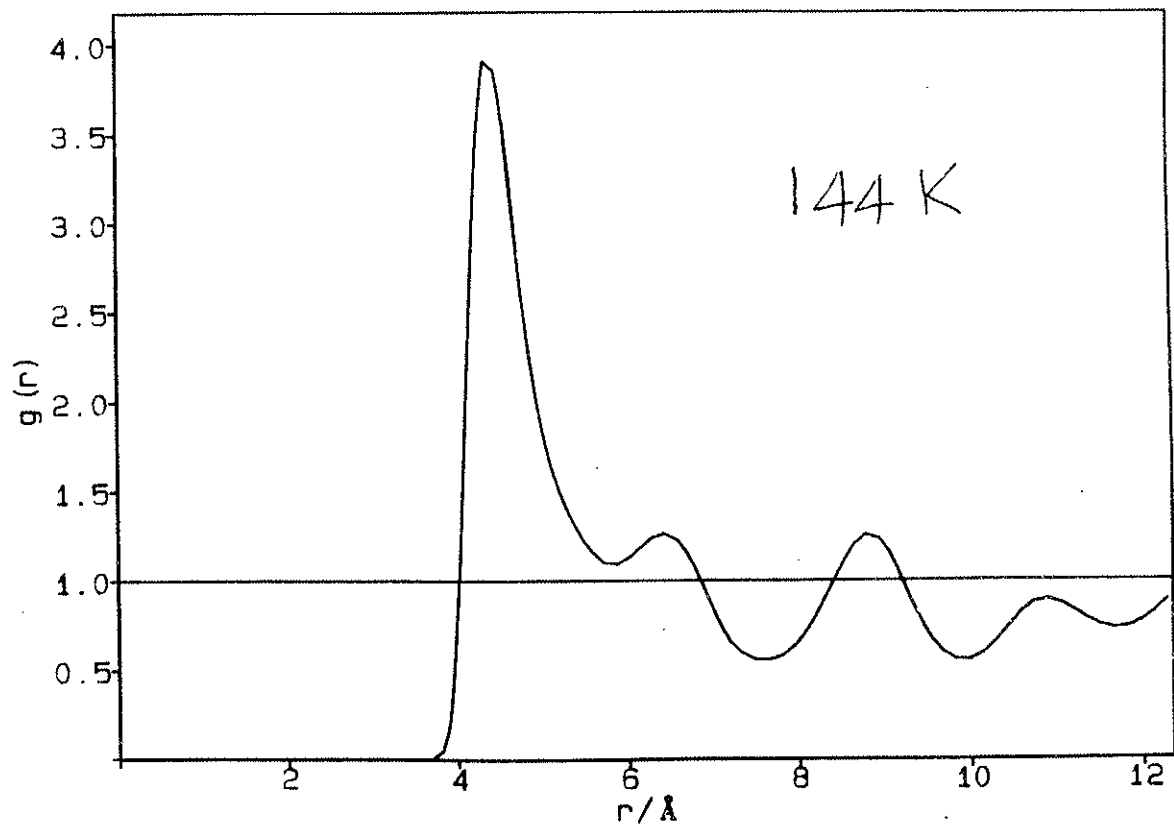
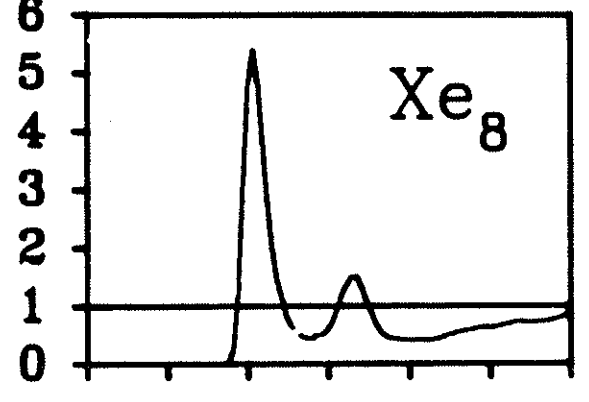
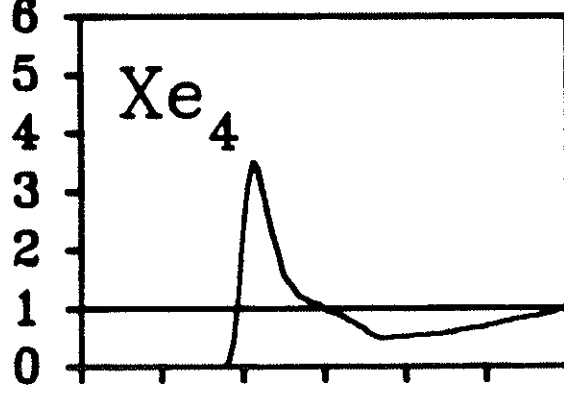
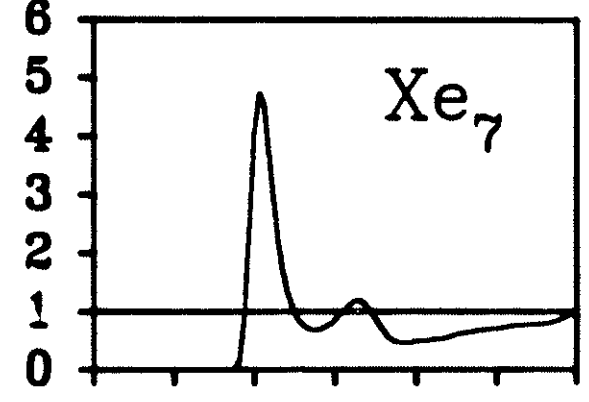
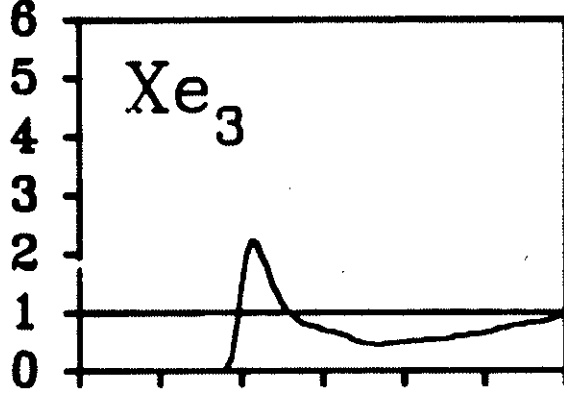
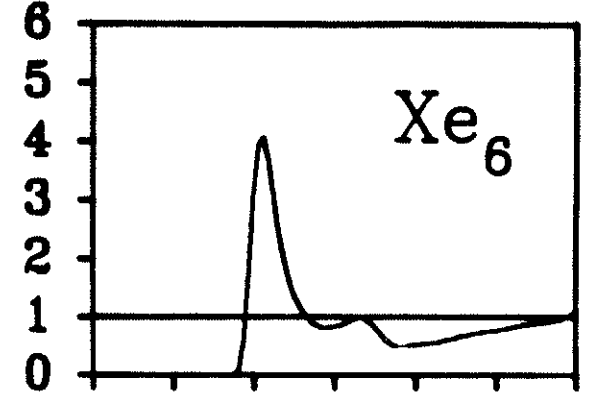
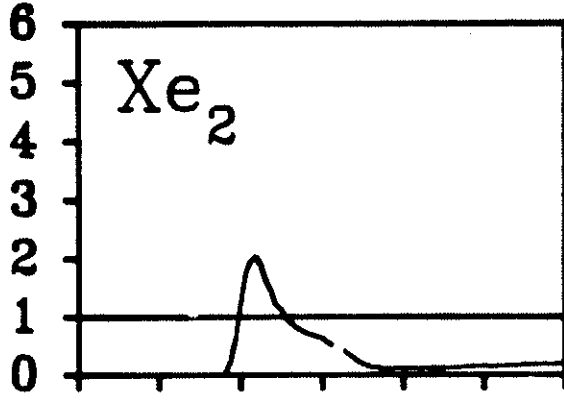
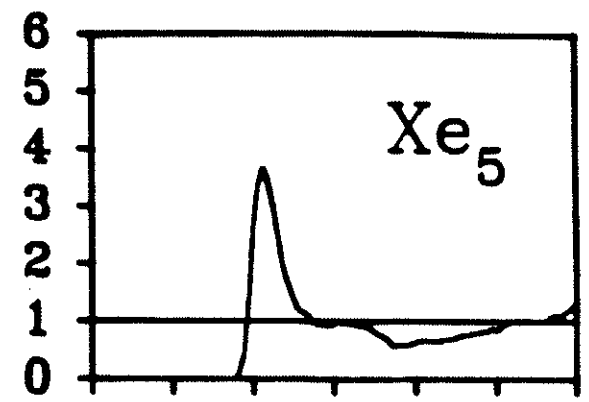
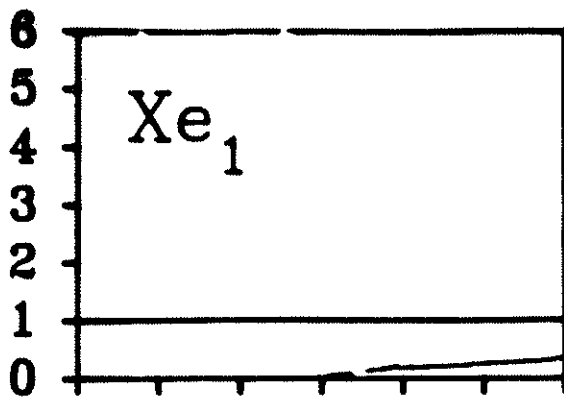


Figure 4.22 The pair distribution function, $g(r)$, for xenon at 144 K and an occupancy of $N = 70$.

$$\langle N \rangle = 70$$



$g(r)$



0 2 4 6 8 10 12

r , angstroms

0 2 4 6 8 10 12

r , angstroms

For an ideal gas, $g(r_{12}) = 1$

$$[P^{(2)}(\vec{r}_1, \vec{r}_2)] = \frac{N(N-1)}{V^2} = \rho^2 \left(1 - \frac{1}{N}\right) \approx \rho^2$$

Put particle 1 at origin:

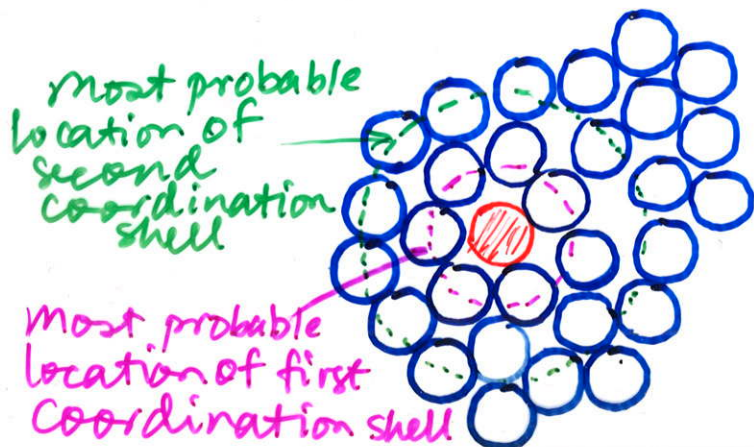
$$P^{(2)}(0, \vec{r}) = \rho^2 g(r)$$

$$\frac{P^{(2)}(0, \vec{r})}{\rho} = \rho g(r) = \text{Conditional probability that a particle will be found at } \vec{r} \text{ given that another is at the origin.}$$

= average density of particles at \vec{r} given that a tagged particle is at the origin

When the terminology "LIQUID STRUCTURE" is used, one is referring to quantities like $g(r)$. Unlike a crystal, the single particle (or one-body) distribution for a fluid is trivial. It is simply a bulk property, the DENSITY.

Once the isotropic symmetry is broken (e.g. by stating that a particle is known to be at a particular location) there is interesting microscopic structure.



simple liquid structure

origin at

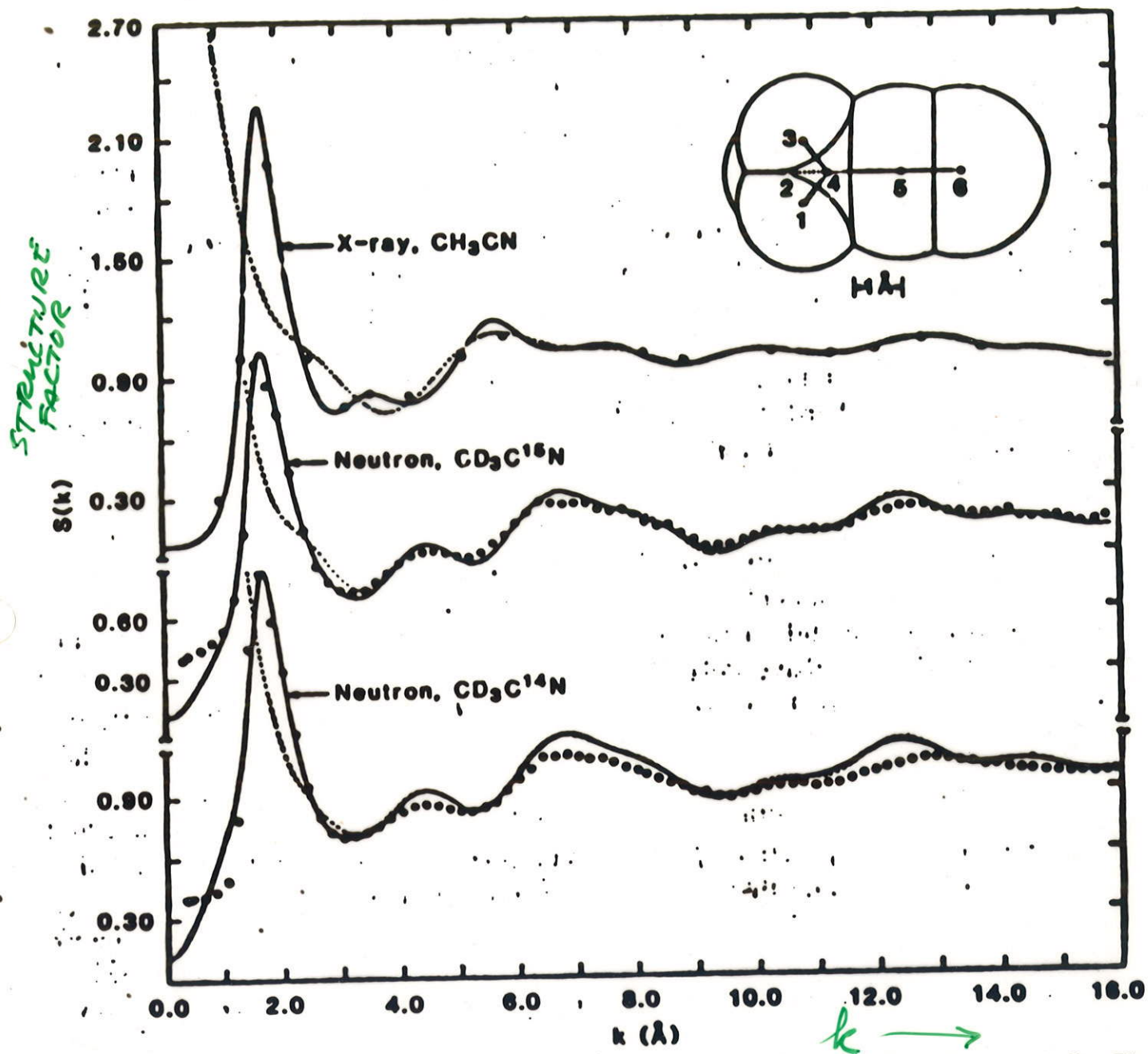


Fig. 5. Structure factors, $S(k)$, for scattering neutrons and x-rays from liquid acetonitrile. The circles represent experimental points. The solid lines are the predictions of the RISM theory, using the hard core model drawn at the upper right (atoms 1, 2, and 3 are hydrogens; atoms 4 and 5 are carbons; and atom 6 is nitrogen). The dashed line shows the scattering cross section associated with only single independent molecules as opposed to the full liquid intermolecular correlations. [After Hsu and Chandler (39)]

$$S(k) = 1 + \left(\frac{N}{V} \right) \int d\vec{r} g(r) e^{i\vec{k} \cdot \vec{r}}$$

Fourier transform

$$\approx S(k) = 1 + \frac{4\pi\rho}{k} \int_0^\infty r dr \sin(kr) g(r)$$

The $g(r)$ gives information about the average relative arrangements of pairs of atoms. $g(r)$ is measured by diffraction experiments since the scattering of neutrons or X-ray radiation from a liquid is dominated by the interference from the distributed pairs of scattering centers.

(see figure for example of structure factors from neutron and X-ray scattering)

Note that if we integrate over \vec{r}_1 and \vec{r}_2 we get

$$\int_{\vec{r}_1} \int_{\vec{r}_2} P^{(2)} d^3r_1 d^3r_2 = \frac{\int \dots \int e^{-U(\vec{r}_1, \dots)/k_B T} d^3r_1 d^3r_2 \dots d^3r_N}{Z(T, V)} = 1$$

Therefore, since

$$P^{(2)} = \frac{1}{V^2} g(r_{12})$$

then integrating this over \vec{r}_1 and \vec{r}_2 should

$$\text{give } 1 = \frac{1}{V^2} \int_{\vec{r}_1} \int_{\vec{r}_2} g(r_{12}) d^3r_1 d^3r_2$$

$$\text{So that } \int_{\vec{r}_1} \int_{\vec{r}_2} g(r_{12}) d^3r_1 d^3r_2 = V^2$$

Note that the value of $g(r_{12})$ is independent of the position of the first particle, if the coordinates of particle 2 are measured with respect to the coordinates of particle 1

$$\therefore \int_{\vec{r}_1} g(r_{12}) d^3r_1 d^3r_2 = V g(r_{12}) d^3r_{12}$$

integrating again should give us V^2

$$\text{and so } \int g(r_{12}) d^3r_{12} = V \leftarrow \text{Provides a test}$$

The probability of finding a molecule in the volume element d^3r_{12} at a distance r_{12} from another molecule is $\frac{N}{V} g(r_{12}) d^3r_{12}$

Probability per unit volume of finding a second particle at a distance r from a given particle.

$\frac{N}{V} g(r) 4\pi r^2 dr$ is the probability of finding a second particle in the spherical shell at a distance r from a given particle (taken as the origin).

How to implement the calculation of $g(r_{12})$?

Average number of atoms whose distance from a given atom in the fluid lies in the interval $(r, r+dr)$ assigned bin no. j

$$(a) = \frac{N P A R C C (j)}{N P A R T O T \cdot N}$$

counter: how many times information was collected

no. of atoms in the system

The average number of atoms in the same interval in an ideal gas at the same density is

$$(b) = \frac{4\pi P}{3} [(r+dr)^3 - r^3]$$

The normalized $g(r + \frac{1}{2}dr)$ is $\frac{(a)}{(b)}$

C Pair distribution function bin width δr
PBWIDTH = SIZE/2.0D0/DFLOAT(N1D)

C *****

C Make a 1d histogram of the pair distribution functions

IF (MOD(NSUM,NPAIRSUB).EQ.0) THEN

NPAIRTOT = NPAIRTOT + 1

DO 70 I=1,NMOLE-1

DO 71 J=I+1,NMOLE — number of atoms at this time

RX(J) = X(I) - X(J)

RY(J) = Y(I) - Y(J)

RZ(J) = Z(I) - Z(J)

RX(J) = RX(J) - SIZE*ANINT(RX(J)/SIZE)

RY(J) = RY(J) - SIZE*ANINT(RY(J)/SIZE)

RZ(J) = RZ(J) - SIZE*ANINT(RZ(J)/SIZE)

RR(J) = RX(J)**2 + RY(J)**2 + RZ(J)**2

R(J) = SQRT(RR(J))

} Minimum image convention

71 CONTINUE

DO 72 J = I+1, NMOLE

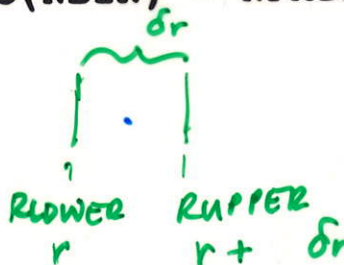
NBIN = INT(R(J)/PBWIDTH) + 1

IF (NBIN.LE.N1D) NPAIRCC(NBIN) = NPAIRCC(NBIN) + 2

72 CONTINUE

70 CONTINUE

END IF



* WRITE(13,'(//1X,A)') 'PAIR DISTRIBUTION FUNCTION'
* WRITE(13,'(1X,A)') ' R G(R)'

PI = 3.1415926D0

RHO = DENSUM/DFLOAT(NSUM)

CONST = 4.0D0*PI*RHO/3.0D0

XPAIRTOT = FLOAT(NPAIRTOT)

YMAX = 0.0

DO 111 I=1,N1D

RLOWER = DFLOAT(I-1)*PBWIDTH

RUPPER = RLOWER + PBWIDTH

XNIDEAL = CONST*(RUPPER**3 - RLOWER**3)

R(I) = RLOWER + PBWIDTH/2.0

G(I) = FLOAT(NPAIRCC(I))/XPAIRTOT/RUNOCC/XNIDEAL

IF (G(I).GT.YMAX) YMAX = G(I)

111 CONTINUE

XMAX = SIZE/2.0

YMAX = YMAX + YMAX/20.0

WRITE (12,*) XMAX, YMAX

WRITE (12,*)N1D

DO 52 I=1,N1D

WRITE (12,*) R(I),G(I)

52 CONTINUE

← volume of spherical shell

<N>

average number of atoms

per simulation box

r_{12} $g(r_{12})$

Property Averages in presence of Interactions

THERMODYNAMIC FUNCTIONS OF A FLUID:
(Canonical ensemble)

$$\bar{E} = kT^2 \left[\frac{\partial (\ln Q)}{\partial T} \right]_{N, V}$$

$$= \frac{3}{2} NkT + kT^2 \left(\frac{\partial \ln Z(T, V)}{\partial T} \right)_V \quad \text{not including internal energy}$$

$$\text{where } Z(T, V) = \int_{\vec{r}_1} \dots \int_{\vec{r}_N} e^{-U(\vec{r}_1, \dots, \vec{r}_N)/kT} d^3r_1 d^3r_2 \dots d^3r_N$$

Note that

$$\frac{\partial Z}{\partial T} = \frac{1}{kT^2} \int \dots \int U(\vec{r}_1, \dots) e^{-U(\vec{r}_1, \dots)/kT} d^3r_1 d^3r_2 \dots d^3r_N$$

$$kT^2 \frac{\partial \ln Z}{\partial T} = \frac{\int \dots \int U(\vec{r}_1, \dots) e^{-U(\vec{r}_1, \dots)/kT} d^3r_1 \dots d^3r_N}{Z(T, V)}$$

$$= \bar{U}(T, V, N) \quad \approx \quad \langle U \rangle_{T, V, N}$$

$$\bar{E} = \underbrace{\frac{3}{2} NkT}_{\text{K.E.}} + \underbrace{\bar{U}(T, V, N)}_{\text{P.E.}} + \text{internal energy}$$

Average of any property

$$\bar{\sigma}(T, p) = \frac{\int_{\vec{r}_1} \dots \int_{\vec{r}_N} \sigma(\vec{r}_1, \dots, \vec{r}_N) e^{-U(\vec{r}_1, \dots, \vec{r}_N)/kT} d^3r_1 d^3r_2 \dots d^3r_N}{\int_{\vec{r}_1} \dots \int_{\vec{r}_N} e^{-U(\vec{r}_1, \dots, \vec{r}_N)/kT} d^3r_1 \dots d^3r_N}$$

The ASSUMPTION of PAIR POTENTIALS

$$\text{Let } U(\vec{r}_1, \dots, \vec{r}_N) = \sum_{1 \leq i} \sum_{i < j \leq N} u(r_{ij}) = \underbrace{u(r_{12}) + u(r_{13}) + \dots}_{\frac{N(N-1)}{2} \text{ terms}}$$

$$\bar{U} = \frac{N(N-1)}{2} \int_{\vec{r}_1} \int_{\vec{r}_2} u(r_{12}) d^3 r_1 d^3 r_2 \quad [\quad]$$

$$P^{(2)}(\vec{r}_1, \vec{r}_2) = \frac{\int_{\vec{r}_3} \dots \int_{\vec{r}_N} e^{-U(\dots)/kT} d^3 r_3 \dots d^3 r_N}{Z} = \frac{1}{V^2} g(\vec{r}_1, \vec{r}_2)$$

$$\bar{U} = \frac{N(N-1)}{2} \int_{\vec{r}_1} \int_{\vec{r}_2} u(r_{12}) P^{(2)}(r_1, r_2) d^3 r_1 d^3 r_2$$

$$= \frac{1}{2} \int_{\vec{r}_1} \int_{\vec{r}_2} u(r_{12}) \rho^{(2)}(r_1, r_2) d^3 r_1 d^3 r_2$$

$$= \frac{1}{2} \frac{N(N-1)}{V^2} \int_{\vec{r}_1} \int_{\vec{r}_2} g(r_{12}) u(r_{12}) d^3 r_1 d^3 r_2$$

Integrate over \vec{r}_1 to get V

$$\bar{U} = \frac{1}{2} \frac{N^2}{V} \int_{\vec{r}_2} u(r_{12}) g(r_{12}) d^3 r_{12}$$

$$\text{or } \frac{1}{2} \frac{N^2}{V} \int_{r=0}^{\infty} u(r) g(r) 4\pi r^2 dr$$

$$E = \frac{3}{2} NkT + \frac{1}{2} N \cdot \left(\frac{N}{V} \right) \int_{r=0}^{\infty} u(r) g(r) 4\pi r^2 dr$$

particle density

if $u(\vec{r}_{12})$ depends only on r_{12}
 spherical molecules or spherical potential

EQUATION OF STATE IN A FLUID WITH PAIR POTENTIAL

Pressure:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T = kT \left(\frac{\partial \ln \Omega}{\partial V} \right)_T = kT \frac{\partial \ln Z(T, V)}{\partial V}$$

$$= kT \left\{ \frac{N}{V} - \frac{N(N-1)}{6VkT} \int_{r_1}^{r_{12}} \int_{r_{12}}^{\infty} r_{12} \frac{dU(r_{12})}{dr_{12}} \underbrace{P^{(2)}(r_{12})}_{\substack{\uparrow \text{spherical molecules} \\ P^{(2)}(r_{12}) = \frac{g(r_{12})}{V^2}}} d^3r_1 d^3r_2 \right\}$$

↑
integrate over r_1 to get V

$$= \frac{NkT}{V} \left\{ 1 - \frac{(N-1)}{6VkT} \int_{r_{12}=0}^{\infty} r_{12} \frac{dU(r_{12})}{dr_{12}} g(r_{12}) 4\pi r_{12}^2 dr_{12} \right\}$$

$$\frac{PV}{NkT} = 1 + \underbrace{\left(\frac{N}{N_{\text{Avog}} V} \right)}_{\rho \text{ moles/liter}} \underbrace{\left[- \frac{N_{\text{Avog}}}{6kT} \int_{r=0}^{\infty} g(r) \frac{dU(r)}{dr} 4\pi r^3 dr \right]}_{B(T)}$$

Generalize to a fluid with POTENTIAL allowing 3-particle, etc. interactions:

$$\frac{PV}{NkT} = 1 + B(T)\rho + C(T)\rho^2 + \dots$$

The VIRIAL EXPANSION $B(T)$ is called the second virial coefficient

ideal gas $\frac{dU}{dr} = 0 \Rightarrow B(T) = 0, \frac{PV}{NkT} = 1$

For a dilute gas it can be shown independently that $B(T) = -\frac{N_{A00}}{6kT} \int_{r=0}^{\infty} e^{-U(r)/kT} \frac{dU(r)}{dr} 4\pi r^3 dr$

Therefore $g(r_{12}) = e^{-U(r_{12})/kT}$ only the first term for a dilute gas

GENERAL THEORY OF MACROSCOPIC PROPERTIES OF REAL DILUTE GASES —

For a macroscopic property S' which for a set of independent molecules is the sum of mean contributions of individual molecules, use a virial expansion of the property in a dilute gas:

$$S' = N\bar{s}_1 + \frac{B_S(T)}{V} + \frac{C_S(T)}{V^2} + \dots$$

If only interacting pairs need be considered

$$S' = N \left\{ \bar{s}_1 + \int_{\vec{r}_{12}} \left[\frac{1}{2} \Delta_{12}(\vec{r}_{12}) - \bar{s}_1 \right] \frac{N}{V} g(\vec{r}_{12}) d^3 r_{12} \right\}$$

↑
avoids counting twice

probability per unit volume of finding a molecule in the volume element $d^3 r_{12}$ at a distance r_{12} from another molecule.

$$S' = N\bar{a}_1 + \frac{N}{V} \int_{\vec{r}_{12}} N \left[\frac{1}{2} A_{12}(\vec{r}_{12}) - \bar{a}_1 \right] g(\vec{r}_{12}) d^3 r_{12} + \dots$$

$$\therefore B_S(T) = \frac{N^2}{V} \int_{\vec{r}_{12}} \left[\frac{1}{2} A_{12}(\vec{r}_{12}) - \bar{a}_1 \right] g(\vec{r}_{12}) d^3 r_{12}$$

For example

$$E = N \left(\frac{3}{2} kT + \bar{E}_{int} \right) + \frac{N^2}{V} \int_{r=0}^{\infty} \frac{1}{2} u(r) g(r) 4\pi r^2 dr$$

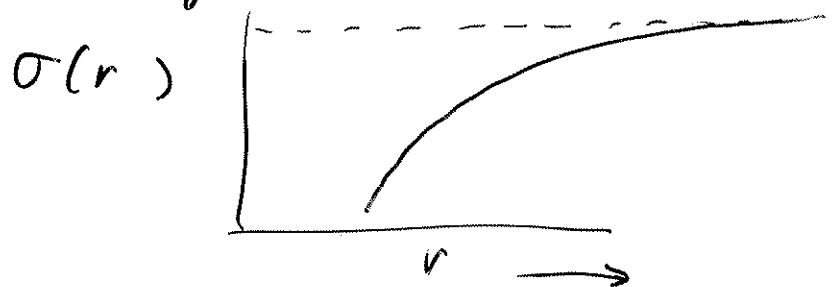
for spherical molecules

+ ...

For a macroscopic property which is not an additive property,

$$\sigma = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \dots$$

Let $\sigma(r)$ be a function of intermolecular separation, for example



$\sigma_0(T)$ = a single particle property

$$\sigma_1(T) = \int_{r=0}^{\infty} \sigma(r) g(r) 4\pi r^2 dr$$

for spherical particles

$$\sigma_1(T) = \int_{r=0}^{\infty} \sigma(r) e^{-u(r)/kT} 4\pi r^2 dr$$

having integrated over orientations
SECOND VIRIAL COEFFICIENT of property σ