

Imperfect gases

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H} dp_1 \dots dp_N dr_1 \dots dr_N$$

Integration over momenta

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi m k T}{h^2} \right)^{3N/2} Z_N$$

$$Z_N = \int \dots \int e^{-U_N/kT} dr_1 dr_2 \dots dr_N$$

Non-ideal behavior

$$\frac{p}{kT} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \dots$$

$$B_2(T) = -b_2 = -\frac{Z_2 - Z_1^2}{2!V}$$

$$B_3(T) = 4b_2^2 - 2b_3 = -\frac{1}{3V^2} \left[V Z_3 - 3Z_2 Z_1 + 2Z_1^3 - 3 Z_2 - Z_z^2 \right]$$

...

Higher coefficients— too complicated
It is not suitable for condense phase,
high orders would be required

Liquids

Completely different than gases → different approach required

Example – argon in gas and liquid phase

$r_{vdW} = 188 \text{ pm}$
 $m = 39,95 \text{ g/mol}$
 $\rho_l = 1430 \text{ g/L}$
 $\rho_g = 1,784 \text{ g/L}$

	Density g/L	mol/L	Molecules /L	V(Ar) %
Gas	1,784	0,045	$2,69 \cdot 10^{22}$	0,075
Liquid	1430	35,795	$2,16 \cdot 10^{25}$	60,00

Gas

Virial expansion

Liquid

Pair distribution function

Introducing correlation function $g^{(2)}$

- $g^{(2)}$ can be obtained from diffractonal analysis
- TD variable can be expressed as a function of $g^{(2)}$

Distribution function

$$Z_N = \int \dots \int e^{-U_N/kT} dr_1 dr_2 \dots dr_N$$

(N, V, T)

Probability that molecule 1 is in $v dr_1$ around r_1 ... $N v dr_N$ around r_N

$$P^{(N)}(r_1, \dots, r_N) dr_1 \dots dr_N = \frac{e^{-\beta U_N} dr_1 \dots dr_N}{Z_N}$$

Probability that molecule 1 is in dr_1 around r_1 , ..., n in dr_n around r_n and other molecules are anywhere:

$$P^{(n)}(r_1, \dots, r_n) dr_1 \dots dr_n = \frac{\int \dots \int e^{-\beta U_N} dr_{n+1} \dots dr_N}{Z_N}$$

Probability that any molecule is in dr_1 around r_1 , ..., n in dr_n around r_n and other molecules are anywhere:

$$\rho^{(n)}(r_1, \dots, r_n) = \frac{N!}{(N-n)!} P^{(n)}(r_1, \dots, r_n)$$

$\rho^{(1)}$

The simplest distribution function
Crystal – periodic function
Liquid – a constant

$$\frac{\int \rho^{(1)}(r_1) dr_1}{V} = \rho^{(1)} = \frac{N}{V} = \rho$$

Molecules are totally independent:

$$\rho^{(n)}(r_1, \dots, r_n) = \rho^n$$

- Their motion is not correlated
- No interactions
- Non-zero probability to find two molecule at one point
- no phase transitions can occure

$$\rho^{(n)}(r_1, \dots, r_n) = \rho^n g^{(n)}(r_1, \dots, r_n)$$

↓
„Correlation function“

- It respects the interaction between molecules
- partial analogy to *ab initio*

Correlation function $g^{(n)}$ – represents non-dependence of molecules

$$\rho^{(n)}(r_1, \dots, r_n) = \rho^n g^{(n)}(r_1, \dots, r_n)$$

$$g^{(n)}(r_1, \dots, r_n) = \frac{V^n N!}{N^n (N-n)!} \frac{\int \dots \int e^{-\beta U_N} dr_{n+1} \dots dr_N}{Z_N}$$

$$= V^n (1 + O(N^{-1})) \frac{\int \dots \int e^{-\beta U_N} dr_{n+1} \dots dr_N}{Z_N}$$

$$g^{(2)}(r_1, r_2) = \frac{V^2 N!}{N^2 (N-2)!} \frac{\int \dots \int e^{-\beta U_N} dr_3 \dots dr_N}{Z_N}$$

Spherical molecules – $g^{(2)}$ depends only on the distance r_{12} : $g^{(2)}(r_{12}) = g^{(2)}(r)$

Probability of finding the second molecule in dr around r from the first molecule

$$\int_0^{\infty} \rho g(r) 4\pi r^2 dr = N - 1 \approx N$$

Radial distribution function

$g(r)$... Factor that gives local density from density

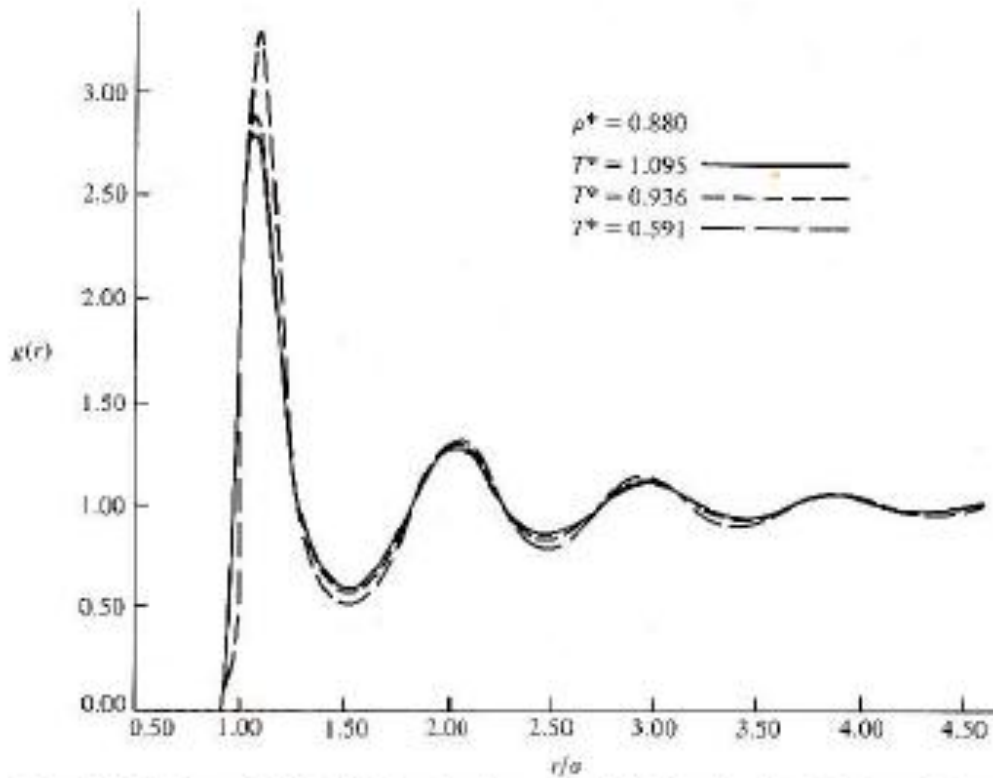


Figure 13-3. The radial distribution function of a fluid of molecules obeying a Lennard-Jones 6-12 potential from molecular dynamics calculations. $T^* = kT/\epsilon$ and $\rho^* = \sigma^3\rho$.

$r \rightarrow 0 \dots g(r) \rightarrow 0$

$r \rightarrow \infty \dots g(r) \rightarrow 1$

$$\int_0^{\infty} \rho g(r) 4\pi r^2 dr = N - 1 \approx N$$

Radial distribution function

$g(r)$... Factor that gives local density from density

Assuming pair-representability in potential energy

$$U_N(r_1, \dots, r_N) = \sum_{i < j} u(r_{ij})$$

All TD functions can be expressed as a function of $g(r)$

Radial distribution function can be obtained from diffraction experiments for liquids kapalin:

Scattering through
an angle θ

$$P(\theta) \propto \sum_i \sum_j \frac{\sin(sr_{ij})}{sr_{ij}} = \int_0^\infty 4\pi r^2 g(r) \frac{\sin(sr)}{sr} dr$$

Inter-atomic distances
 r_{ij} changes continuously

$$s = (4\pi / \lambda) \sin(\theta / 2)$$

$$P(\theta) \propto \int_0^\infty 4\pi r^2 (g(r) - 1) \frac{\sin(sr)}{sr} dr + \int_0^\infty 4\pi r^2 \frac{\sin(sr)}{sr} dr$$

=0

Fourier
transformation

$$P(\theta) \propto \int [g(r) - 1] e^{isr} dr$$

$$P(\theta) \propto \int [g(r) - 1] e^{isr} dr$$

$\times \rho$

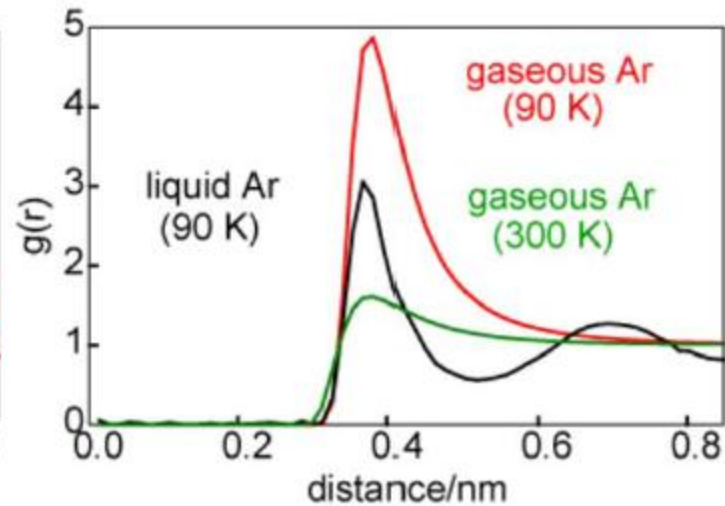
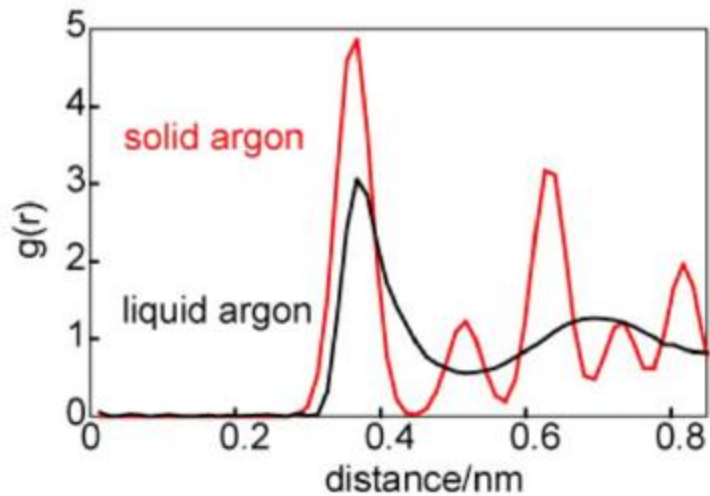
$$h(s) = \rho \int h(r) e^{isr} dr$$

$$h(r) = (g(r) - 1)$$

... Goes to 0 for large r

„Structure factor“

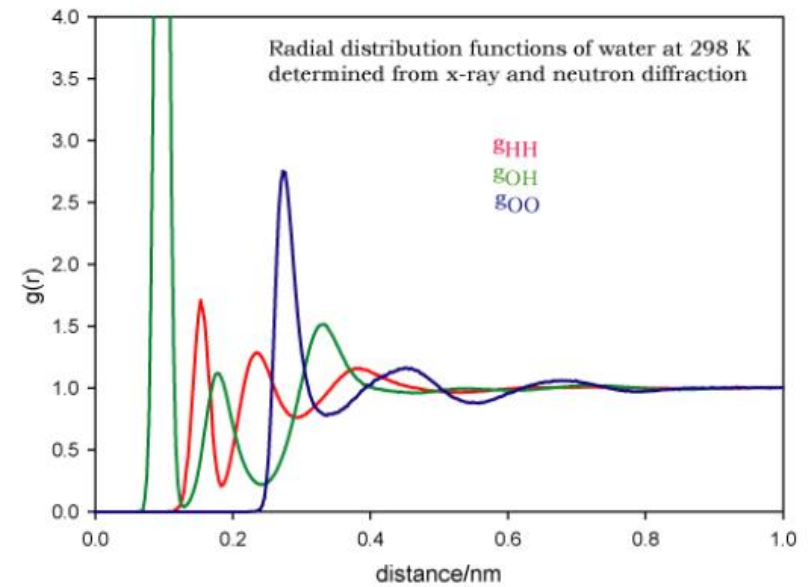
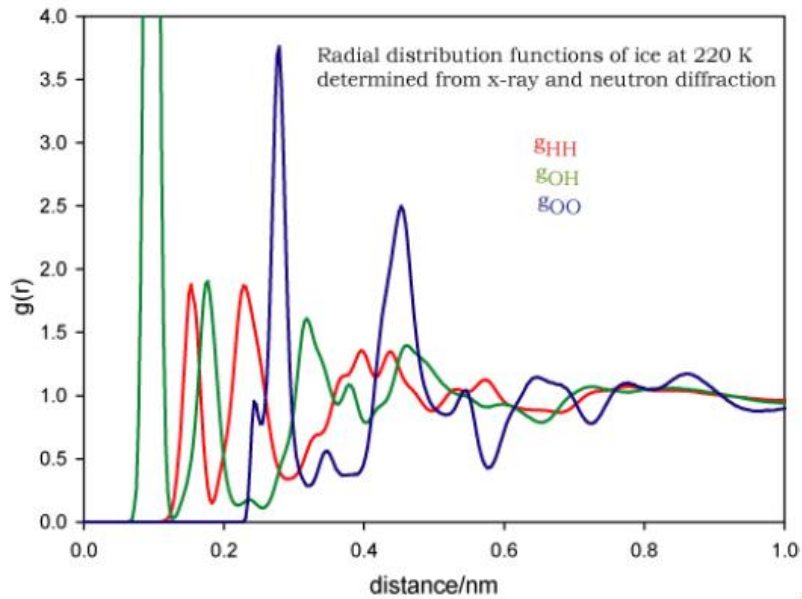
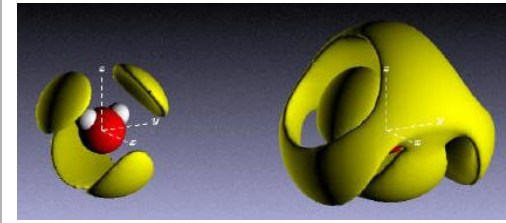
TD functions of liquids from diffraction analysis !!!



Three different pair-distribution functions – X-ray gives only their superposition and it cannot be simply decomposed

Combination of X-ray and neutron diffraction for H₂O and D₂O gives enough data for decomposition

<http://www.isis.stfc.ac.uk/groups/disordered-materials/database/>



TD functions in terms of $g(r)$

$$Q_N(V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N = \frac{Z_N}{N! \Lambda^{3N}}$$

$$Q_N = \frac{1}{N!} \left(\frac{Q_1}{V} \right)^N Z_N$$

Expression for E, p, μ must be found
(Others can be obtained from these)

Holds in classical limit
(for monoatomic gas)

Imperfect gases

Accounting for inter-molecular interactions – consider monoatomic gas for simplicity

$$Q(N, V, T) = \frac{1}{N! h^{3N}} \int \dots \int e^{-\beta H} dp_1 \dots dp_N dr_1 \dots dr_N$$

Integration over momenta

$$Q(N, V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N$$

$$Z_N = \int \dots \int e^{-U_N/kT} dr_1 dr_2 \dots dr_N$$

$$H = \frac{1}{2m} \sum_{n=1}^N p_{xn}^2 + p_{yn}^2 + p_{zn}^2 + U(x_1, y_1, \dots, z_N)$$

TD functions in terms of $g(r)$

Expression for E, p, μ must be found
(Others can be obtained from these)

$$Q_N \text{ } V, T = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N = \frac{Z_N}{N! \Lambda^{3N}}$$

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

$$\bar{E} = \frac{3}{2} NkT + kT^2 \left(\frac{\partial \ln Z_N}{\partial T} \right)_{N,V} = \frac{3}{2} NkT + \bar{U}$$

kinetic potential

$$\bar{U} = \frac{\int \dots \int U e^{-\beta U} dr_1 dr_N}{Z_N}$$

Pair representation – all contributions are equivalent:

$$\bar{U} = \frac{N(N-1)}{2} \frac{\int \dots \int u(r_{12}) e^{-\beta U} dr_1 dr_N}{Z_N} = \frac{N(N-1)}{2} \int \int u(r_{12}) \left\{ \frac{\int \dots \int e^{-\beta U} dr_3 dr_N}{Z_N} \right\} dr_1 dr_2$$

$$\bar{U} = \frac{N(N-1)}{2} \frac{\int \cdots \int u(r_{12}) e^{-\beta U} dr_1 dr_N}{Z_N} = \frac{N(N-1)}{2} \int \int u(r_{12}) \left\{ \frac{\int \cdots \int e^{-\beta U} dr_3 dr_N}{Z_N} \right\} dr_1 dr_2$$

$$\rho^{(2)}(r_1, r_2) = N(N-1) \frac{\int \cdots \int e^{-\beta U} dr_3 \cdots dr_N}{Z_N}$$

$$\bar{U} = \frac{1}{2} \int \int u(r_{12}) \rho^{(2)}(r_1, r_2) dr_1 dr_2$$

$$\rho^{(n)}(r_1, \dots, r_n) = \rho^n g^{(n)}(r_1, \dots, r_n)$$

$$\bar{U} = \frac{N^2}{2V} \int_0^\infty u(r) g(r) 4\pi r^2 dr$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT} \int_0^\infty u(r) g(r, \rho, T) 4\pi r^2 dr$$

$$\bar{p} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T}$$

$$Q_N(V, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} Z_N = \frac{Z_N}{N! \Lambda^{3N}}$$

Only Z_N depends on V

$$\bar{p} = kT \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = kT \left(\frac{\partial \ln Z_N}{\partial V} \right)_{N,T}$$

Assuming that for large V the pressure does not depend on the container shape – use a cube of volume V .

$$Z_N = \int \dots \int e^{-U_N/kT} dr_1 dr_2 \dots dr_N = \int_0^{V^{1/3}} \dots \int_0^{V^{1/3}} e^{-\beta U} dx_1 dy_1 dz_1 \dots dx_N dy_N dz_N$$

$$x_A = V^{1/3} x'_A$$

Substitution – introduction of fractional coordinates

$$Z_N = V^N \int_0^1 \int_0^1 e^{-U_N/kT} dx'_1 \dots dz'_N$$

Z_N is a function of volume, and even U_N depends on volume :

Assuming that interaction energy can be express as a sum of pair interactions:

$$U_N = \sum_{i=1}^N \sum_{j>i}^N u(r_{ij})$$

$$r_{ij} = [(x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2]^{1/2} = V^{1/3} [(x'_i - x'_j)^2 + (y'_i - y'_j)^2 + (z'_i - z'_j)^2]^{1/2}$$

$$Z_N = V^N \int_0^1 \int_0^1 e^{-U_N/kT} dx'_1 \dots dz'_N$$

→
$$Z_N = V^N \int_0^1 \int_0^1 \exp\left(-\beta \sum_{i=1}^N \sum_{j>i}^N u(V^{1/3}, x'_i, \dots, z'_N)\right) dx'_1 \dots dz'_N$$

$$\left(\frac{\partial Z_N}{\partial V}\right)_{N,T} = \frac{N}{V} Z_N - \frac{V^N}{kT} \int_0^1 \int_0^1 \left(\frac{\partial U}{\partial V}\right) \exp\left(-\beta \sum_{i=1}^N \sum_{j>i}^N u(V^{1/3}, x'_i, \dots, z'_N)\right) dx'_1 \dots dz'_N$$

$$\left(\frac{\partial U}{\partial V}\right)_{N,T} = \sum_{i=1}^N \sum_{j>i}^N \frac{du(r_{ij})}{dr_{ij}} \frac{dr_{ij}}{dV} = \frac{1}{3V} \sum_{i=1}^N \sum_{j>i}^N r_{ij} \frac{du(r_{ij})}{dr_{ij}}$$

$$\frac{dr_{ij}}{dV} = \frac{1}{3V^{2/3}} [(x'_i - x'_j)^2 + (y'_i - y'_j)^2 + (z'_i - z'_j)^2] = \frac{1}{3V} r_{ij}$$

$$x'_i \rightarrow x_i$$

$u(r_{12})$ is the same as any other term $\rightarrow \frac{1}{2}N(N-1)$ terms

Integration splitted into integration over coordinates of 1 and 2 and on other coordinates

$$\frac{p}{kT} = \left(\frac{\partial \ln Z_N}{\partial V} \right)_{N,T} = \frac{N}{V} - \frac{N(N-1)}{Z_N kT 6V} \int_0^\infty \int_0^\infty dr_1 dr_2 r_{12} \frac{du(r_{12})}{dr_{12}} \int_0^\infty \dots \int_0^\infty \exp -\beta u dr_3 \dots dr_N$$

$$\rho^{(2)} = \rho^2 g^{(2)} = \rho^2 \frac{V^2 N!}{N^2 (N-2)! Z_N} \frac{1}{3} \int_N \dots \int_N \exp -\beta u dr_3 \dots dr_N$$

$$\rho^2 \frac{V^2 N!}{N^2 (N-2)!} \sim \frac{N^2}{V^2} V^2 = N^2$$

$$\left(\frac{\partial \ln Z_N}{\partial V} \right)_{N,T} = \frac{N}{V} - \frac{1}{6VkT} \int_V \int_V r_{12} \frac{du(r_{12})}{dr_{12}} \rho^{(2)} r_1, r_2 dr_1 dr_2$$

$$\frac{p}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^\infty ru'(r)g(r)4\pi r^2 dr$$

„Pressure equation“

Holds for both liquids and gases

Expanding $g(r, \rho, T)$ over the density – virial coefficients can be obtained

Expression for E, p, μ must be found
(Others can be obtained from these)

$$\left(\frac{\partial A/T}{\partial 1/T} \right)_{N,V} = E$$

$$\xi \in \langle 0,1 \rangle$$

„coupling parameter“ Switching on/off the interaction

$$\xi u(r_{1,j})$$

Switching the interaction between molecules 1 and j

$$U_{r_1, \dots, r_N, \xi} = \sum_{j=2}^N \xi u_{r_{1j}} + \sum_{2 \leq i < j \leq N} u_{r_{ij}}$$

Addition/deletion of molecules from the system
molecule „1“ is in the system just partially (ξ)

$$g(r, \rho, T; \xi)$$

Radial distribution function depends on ξ .

$$\mu = \left(\frac{\partial \ln A}{\partial N} \right)_{V,T}$$

For large N

$$\mu = A(N, V, T) - A(N-1, V, T)$$

$$A(N, V, T) = -kT \ln Q$$

$$Q_N(V, T) = \frac{Z_N}{N! \Lambda^{3N}}$$

$$-\frac{\mu}{kT} = \ln \frac{Z_N}{Z_{N-1}} - \ln N - \ln \Lambda^3$$

$$-\frac{A}{kT} = \ln Z_N - \ln N! - 3N \ln \Lambda$$

$$-\frac{\mu}{kT} = \ln \frac{Z_N}{Z_{N-1}} - \ln N - \ln \Lambda^3$$

Express as a function of ξ

$$\begin{aligned} Z_N \xi = 1 &= Z_N \\ Z_N \xi = 0 &= V Z_{N-1} \end{aligned}$$

Integration over dr_1

$$\ln \frac{Z_N}{Z_{N-1}} = \ln \frac{Z_N \xi = 1}{Z_N \xi = 0} + \ln V$$

$$\ln \frac{Z_N}{Z_{N-1}} = \ln V + \int_0^1 \left(\frac{\partial \ln Z_N}{\partial \xi} \right) d\xi$$

$$Z_N \xi = \int \dots \int e^{-\beta U_N \xi} dr_1 dr_2 \dots dr_N$$

$$U_{r_1, \dots, r_N, \xi} = \sum_{j=2}^N \xi u_{r_{1j}} + \sum_{2 \leq i < j \leq N} u_{r_{ij}}$$

$$\frac{\partial Z_N}{\partial \xi} = -\frac{1}{kT} \int \dots \int e^{-\beta U_N \xi} \left[\sum_{j=2}^N u(r_{1j}) \right] dr_1 \dots dr_N$$

$$\frac{\partial \ln Z_N}{\partial \xi} = -\frac{1}{NkT} \int \int_V u(r_{12}) \rho^{(2)}(r_1, r_2) dr_1 dr_2 = -\frac{\rho}{kT} \int_0^\infty u(r) g(r; \xi) 4\pi r^2 dr$$

$$\frac{\mu}{kT} = \ln \rho \Lambda^3 + \frac{\rho}{kT} \int_0^1 \int_0^\infty u(r) g(r; \xi) 4\pi r^2 dr d\xi$$

$$\frac{E}{NkT} = \frac{3}{2} + \frac{\rho}{2kT} \int_0^{\infty} u(r)g(r, \rho, T)4\pi r^2 dr$$

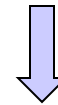
$$\frac{P}{kT} = \rho - \frac{\rho^2}{6kT} \int_0^{\infty} ru'(r)g(r)4\pi r^2 dr$$

$$\frac{\mu}{kT} = \ln \rho \Lambda^3 + \frac{\rho}{kT} \int_1^0 \int_0^{\infty} u(r)g(r; \xi)4\pi r^2 dr d\xi$$

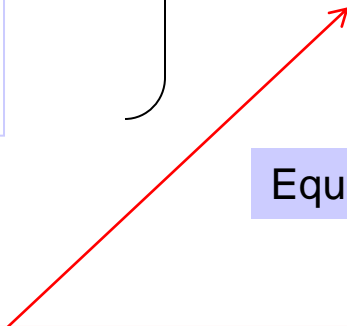


Other TD functions

$$+ g(r)$$



Equations for liquids



We need an expression for $g(r)$

One has to use some approximative expression – still difficult

Different levels of approximations/complications

Distribution function in a system of N-1 molecules

Kirkwood integral equation(1930)

$$kT \ln \rho^{(n)}(1, \dots, n, \xi) = kT \ln \rho + kT \ln \rho_{N-1}^{(n-1)}(2, \dots, n - \xi \sum_{j=2}^n u(r_{1j}) + \frac{1}{N} \int_0^\xi \int_V \int u(r_{12}) \rho^{(2)}(r_1, r_2, \xi) dr_1 dr_2 d\xi - \int_0^\xi \int u(r_{1,n+1}) \frac{\rho^{(n+1)}(1, \dots, n, n+1, \xi)}{\rho^{(n)}(1, \dots, n, \xi)} dr_{n+1} d\xi$$

n=2

$$-kT \ln g^{(2)}(1, 2, \xi) = \xi u(r_{12}) + \rho \int_0^\xi \int_V u(r_{13}) \left[\frac{g^{(3)}(1, 2, 3, \xi)}{g^{(2)}(1, 2, \xi)} - g^{(2)}(1, 3, \xi) \right] dr_3 d\xi$$

Cannot be solved without approximations

Coupled equations – hierarchy

To find a solution – they must be uncoupled – approximations.

$$g^{(n)}(r_1, \dots, r_n) = e^{-\beta w^{(n)}(r_1, \dots, r_n)} \quad \text{Definition of function } w$$

$$-\nabla_j$$

Gradient of $w^{(n)}$ with respect to the position of molecule j

$$-\nabla_j U$$

Force acting on molecule j for any fixed configuration of molecules 1...N

$$g^{(2)}(r_1, r_2) = \frac{V^2 N!}{N^2 (N-2)!} \frac{\int \dots \int e^{-\beta U_N} dr_3 \dots dr_N}{Z_N}$$

$$-\nabla_j w^{(n)} = \frac{\int \dots \int e^{-\beta U} -\nabla_j U dr_{n+1} \dots dr_N}{\int \dots \int e^{-\beta U} dr_{n+1} \dots dr_N}, \quad j = 1, 2, \dots, n$$

$$f_j^{(n)} = -\nabla_j w^{(n)}$$

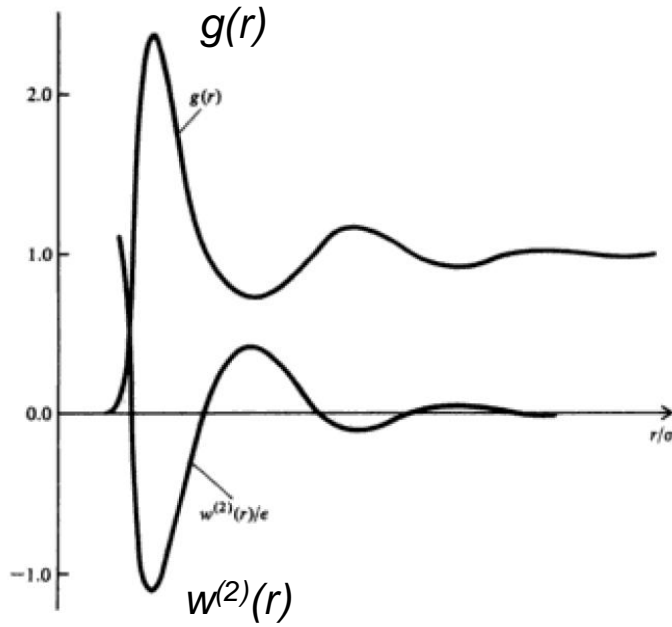
Mean force acting on molecule j averaged over all configurations of other (n+1, N) molecules

$$w^{(n)}$$

Potential that gives the mean force acting on particle j

$$w^{(2)}(r_{ij})$$

„Effective“ potential between 2 molecules separated by r_{ij} averaged over the positions of all other molecules



g and w – like a mirror image

For low density

$$w^{(2)}(r) \rightarrow u(r)$$

Hard spheres: $w^{(2)}$ is attractive even if u isn't
Other molecules provides attraction

Pair additivity is assumed

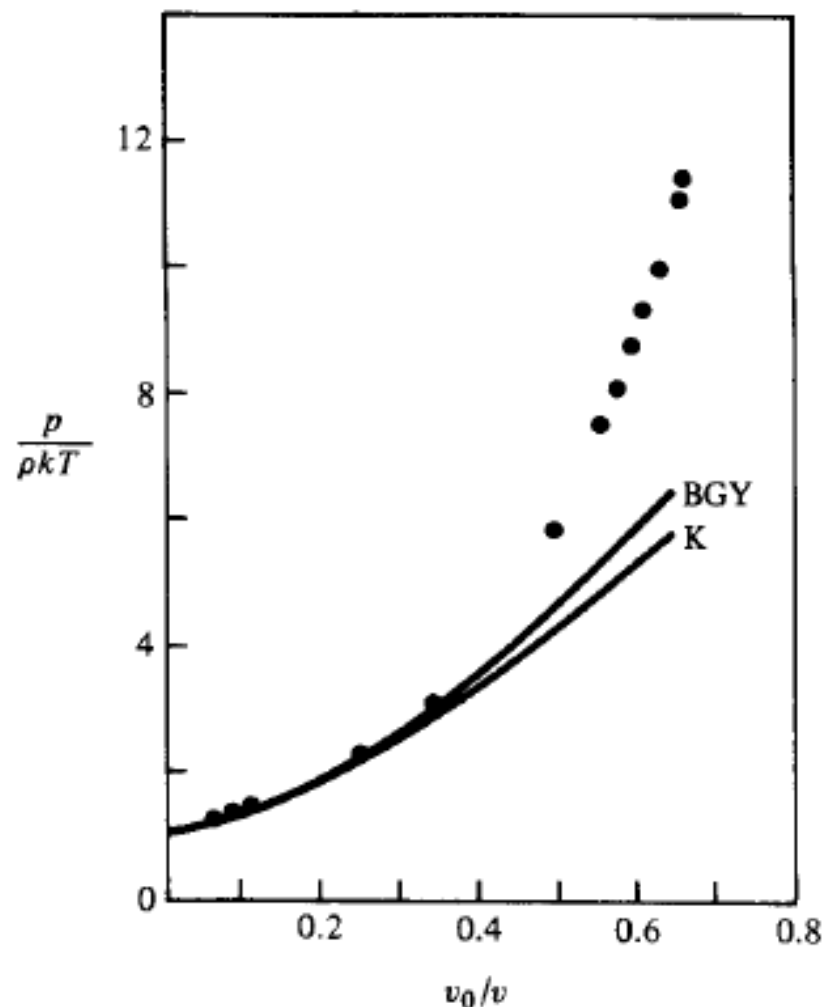
$$w^{(3)}(1, 2, 3) \approx w^{(2)}(1, 2) + w^{(2)}(2, 3) + w^{(2)}(1, 3)$$

$$g^{(3)}(1, 2, 3) \approx g^{(2)}(1, 2)g^{(2)}(2, 3)g^{(2)}(1, 3)$$

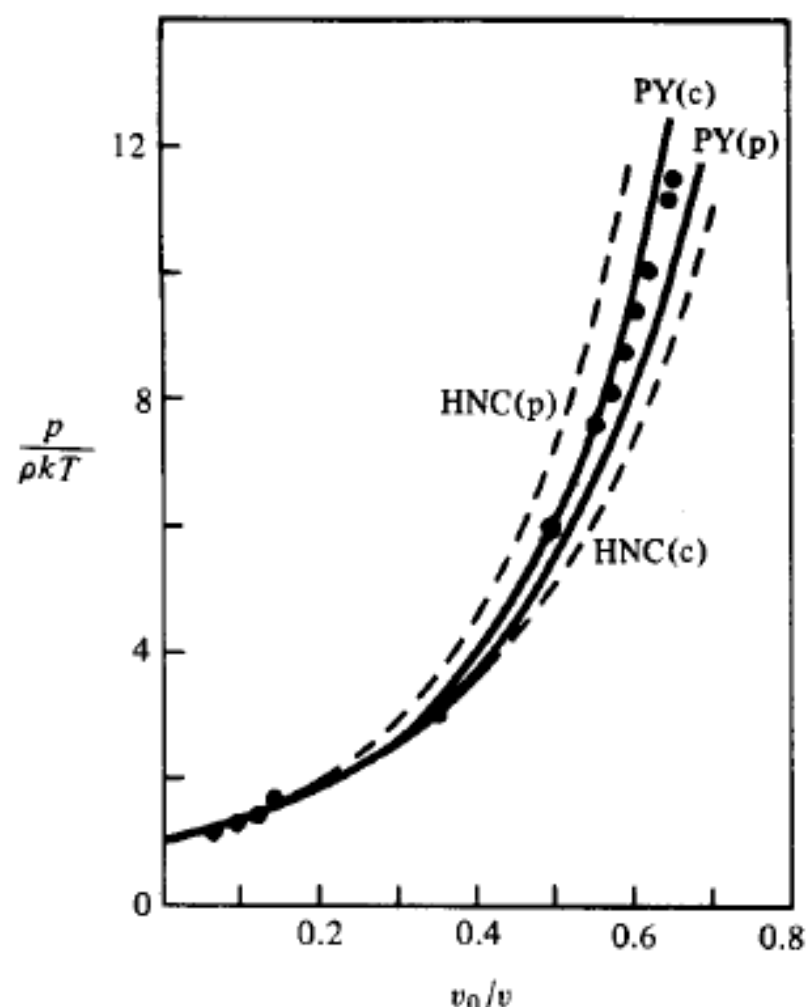
$$-kT \ln g(r_{12}, \xi) = \xi u(r_{12}) + \rho \int_0^\xi \int_V u(r_{13}) g(r_{13}, \xi') [g(r_{23}) - 1] dr_3 d\xi'$$

Kirkwood integral equation

Ornstein-Zernike equation - similar
Percus-Yevick
Hypernetted-chain } Different type of equations



(a)



(b)

Figure 13-6. (a) Equation of state of hard spheres calculated from the Born-Green-Yvon and Kirkwood integral equations compared with the results of molecular dynamics calculations. v_0 is the closest-packing volume, $N\sigma^3/\sqrt{2}$. (b) Equation of state of hard spheres calculated from the HNC and Percus-Yevick integral equations compared with the results of molecular dynamics calculations. (From D. Henderson, *Ann. Rev. Phys. Chem.*, **15**, p. 31, 1964.)

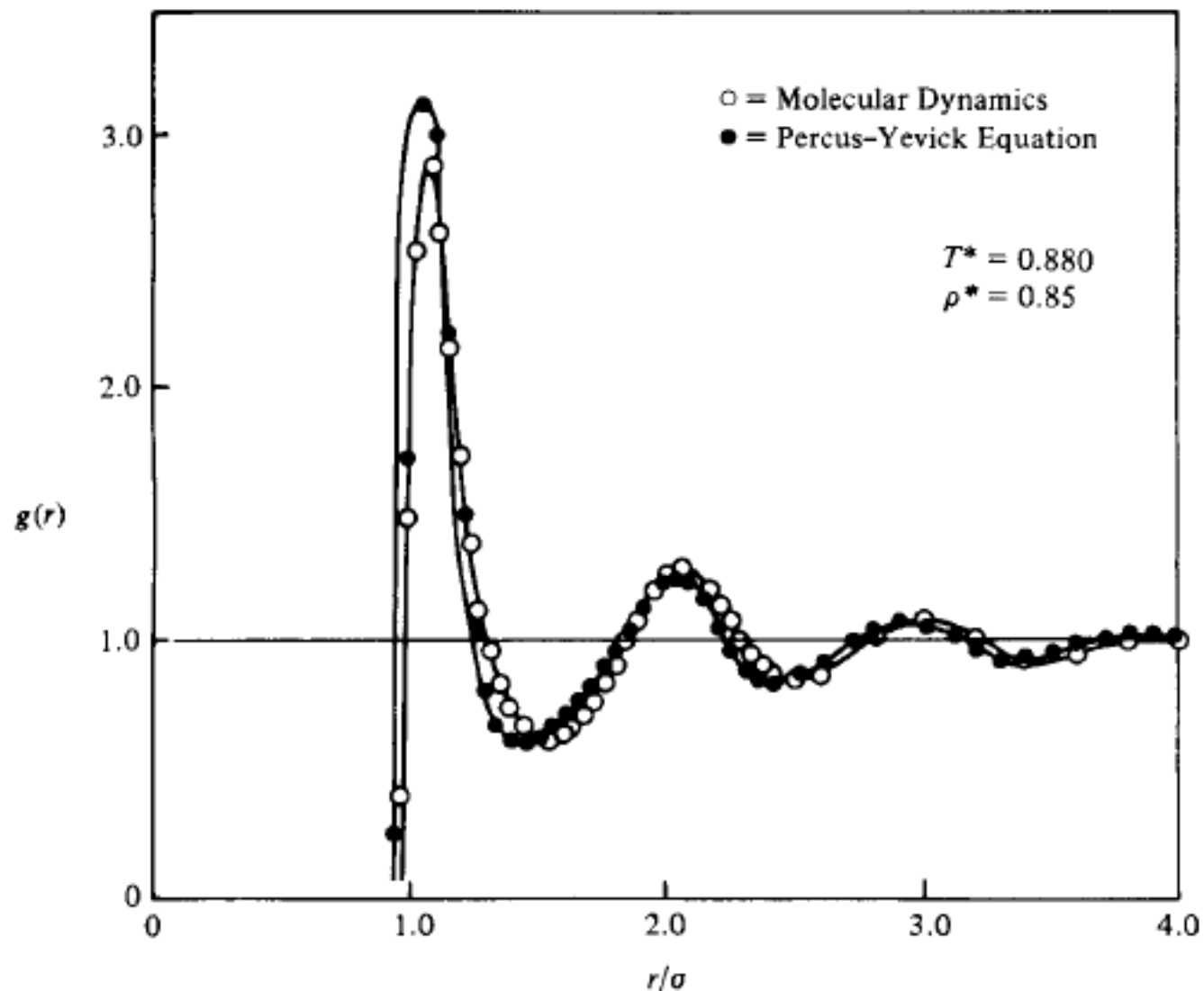


Figure 13-11. The radial distribution function from the Percus-Yevick equation for the Lennard-Jones 6-12 potential. (From F. Mandel, R. J. Bearman, and M. Y. Bearman, *J. Chem. Phys.*, **52**, p. 3315, 1970.)