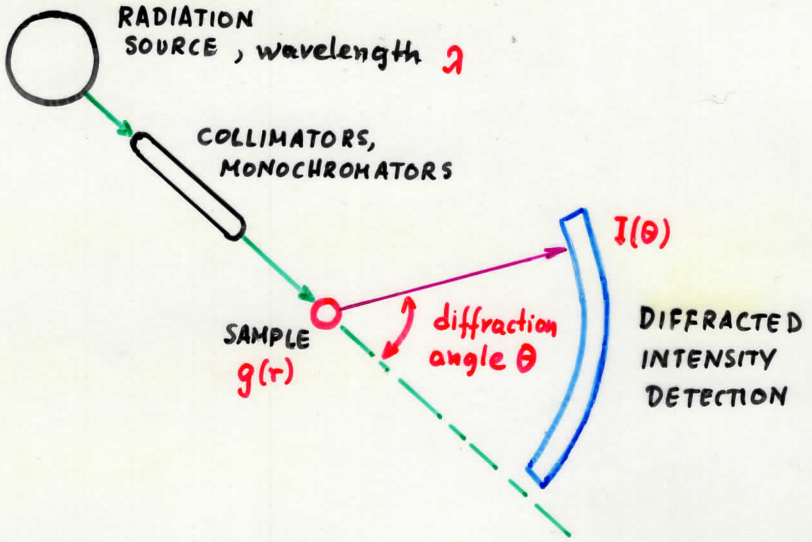
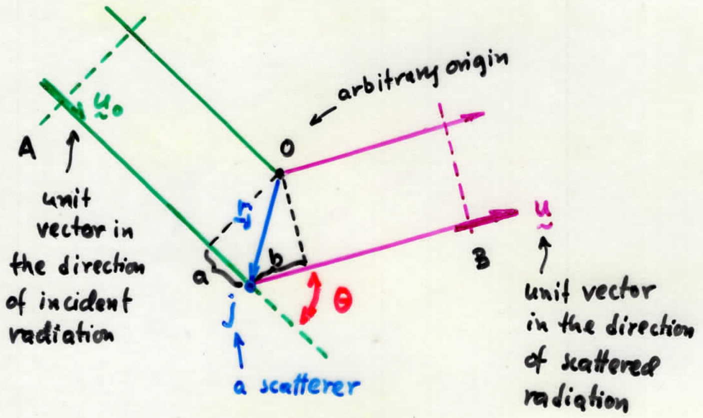
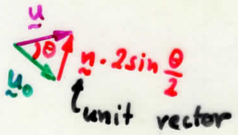
9.1.4. Experimental Measurement of g(r) : X-ray or neutron Diffraction.







Incident radiation has same phase over plane A. Scattered radiation of same wavelength λ as incident is considered. (elastic scattering).

Simple calculation of the diffracted intensity from a collection of N scatterers:

Incident wave (oscillating field) directed along unit vector $\utilde{u}_0$.

Diffracted wave studied at an angle θ; unit vector along diffracted wave is $\utilde{u}$.

$\utilde{r}_j$: position of one of the scatterers relative to the origin, O.

Radiation arriving at B is no longer in phase.

Path length difference betw. beam through j and beam through O:

$$a+b = \utilde{r}_j \cdot \utilde{u}_0 - \utilde{r}_j \cdot \utilde{u} = \utilde{r}_j \cdot (\utilde{u}_0 - \utilde{u}) = -\utilde{r}_j \cdot \utilde{n}\, 2\sin\frac{\theta}{2} = -2\, \utilde{r}_j \cdot \utilde{n} \sin\frac{\theta}{2} \qquad (9.18)$$

where $\utilde{n}$ = unit vector in the direction of $\utilde{u} - \utilde{u}_0$.

<u>Phase difference</u> betw. beam scattered by j and beam through origin at B:

$$\phi_j = 2\pi \frac{a+b}{\lambda} = -\underset{\sim}{r}_j \cdot \underset{\sim}{n}\, \frac{4\pi}{\lambda} \sin\frac{\theta}{2} = -\underset{\sim}{r}_j \cdot \underset{\sim}{k} \qquad (9.19)$$

where $\underset{\sim}{k} = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}\, \underset{\sim}{n} = \frac{4\pi}{\lambda} \sin\frac{\theta}{2} (\underset{\sim}{u} - \underset{\sim}{u}_0)$ = "Scattering vector". (9.20)

Electric field at B due to scattering by j: $\mathcal{E}_j = \underset{\text{amplitude}}{A} \cos\left[2\pi \underset{\text{radiation frequency.}}{\nu} t - \phi_j\right]$

Total electric field due to scatterers:

$$\mathcal{E} = \sum_{j=1}^{N} A \cos\left[2\pi\nu t - \phi_j\right] \qquad (9.21)$$

Intensity of scattered radiation is proportional to $\mathcal{E}^2$, averaged over one period:

$$I(\theta) = K \frac{\int_0^{1/\nu} dt\, \mathcal{E}^2}{\int_0^{1/\nu} dt} = K \nu A^2 \int_0^{1/\nu} \left(\sum_{j=1}^{N} \cos\left[2\pi\nu t - \phi_j\right]\right)^2 dt =$$

$$= K\nu A^2 \sum_{i=1}^{N} \sum_{j=1}^{N} \int_0^{1/\nu} \cos\left[2\pi\nu t - \phi_i\right] \cos\left[2\pi\nu t - \phi_j\right] dt =$$

$$= K\nu A^2 \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \int_0^{1/\nu} \left\{ \cos(4\pi\nu t - \phi_i - \phi_j) + \cos(\phi_i - \phi_j) \right\} dt =$$

$$= K\nu A^2 . \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \cos(\phi_i - \phi_j) . \frac{1}{\nu} = K . \frac{A^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \cos(\phi_i - \phi_j) =$$

$$= K . \frac{A^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \cos\left[\underset{\sim}{k} \cdot (\underset{\sim}{r}_i - \underset{\sim}{r}_j)\right]$$

Now, as $\theta \to 0$, $I(0) \to K \frac{A^2}{2} . N^2$ (scattered radiation at angle $\theta \to 0$).

The ratio of $I(\theta)$ to $I(0)$ becomes:

$$\frac{I(\theta)}{I(0)} = \frac{1}{N^2} \sum_{i=1}^{N} \sum_{j=1}^{N} \cos\left[\underset{\sim}{k} \cdot (\underset{\sim}{r}_i - \underset{\sim}{r}_j)\right] \qquad (9.22)$$

The above analysis was valid for a given configuration of the N scatterers. Averaging over all configurations, for a homogeneous and isotropic fluid,

$$\frac{I(\theta)}{I(0)} = \frac{1}{N^2}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \cos\left[\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)\right]\right\rangle = \frac{1}{N^2}\left\langle \sum_{i=1}^{N} 1 + \sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N} \cos\left[\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)\right]\right\rangle =$$

definition of $g_N^{(2)}$

$$= \frac{1}{N} + \frac{\rho^2}{N^2}\int g_N^{(2)}(\mathbf{r}_i,\mathbf{r}_j)\cos\left[\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)\right] d^3r_i\, d^3r_j =$$

$$= \frac{1}{N} + \frac{\rho^2 V}{N^2}\int g(\mathbf{r}_{ji})\cos\left[\mathbf{k}\cdot\mathbf{r}_{ji}\right] d^3\mathbf{r}_{ji} =$$

$$= \frac{1}{N} + \frac{\rho}{N}\int g(\mathbf{r})\cos(\mathbf{k}\cdot\mathbf{r})\, d^3r \qquad (9.23)$$

Given the spherical symmetry of $g(\mathbf{r})$, the integral of (9.23) can be written:

(polar coordinates used in the evaluation of the integral in 9.23)

$$\int g(\mathbf{r})\cos(\mathbf{k}\cdot\mathbf{r})\,d\mathbf{r} = \int_0^\infty r^2 dr \int_0^{2\pi} d\beta \int_0^\pi \sin\alpha\, d\alpha\; g(r)\cos(kr\cos\alpha) =$$

$$= -\int_0^\infty 2\pi r^2 g(r)\,dr\,\frac{1}{kr}\int_0^\pi d(kr\cos\alpha)\cos(kr\cos\alpha) = \int_0^\infty \frac{2\pi r^2}{kr} g(r)\,dr \int_{-kr}^{kr}\cos y\, dy =$$

$$= \int_0^\infty 2\pi r^2 g(r).\frac{1}{kr}\,dr.\left[\sin y\right]_{-kr}^{kr} = \int_0^\infty 4\pi r^2 \frac{\sin(kr)}{kr} g(r)\,dr$$

Therefore,

"Scattering Function" $$\frac{I(\theta)}{I(0)} = \frac{1}{N}\left[1 + \rho\int_0^\infty 4\pi r^2 \frac{\sin(kr)}{kr} g(r)\,dr\right] \qquad (9.24)$$

Moreover, if one considers the integral

$$\int g(\mathbf{r})\sin(\mathbf{k}\cdot\mathbf{r})\,d\mathbf{r} = \int_0^\infty r^2 dr \int_0^{2\pi} d\beta \int_0^\pi \sin\alpha\, d\alpha\; g(r)\sin(kr\cos\alpha) = \int_0^\infty \frac{2\pi r^2}{kr} g(r)\,dr \int_{-kr}^{kr}\sin y\, dy$$

$$= 0$$

Hence, we can write (9.23) as

$$\frac{I(\theta)}{I(0)} = \frac{1}{N}\left[1+\rho\int g(\underset{\sim}{r})\left[\cos(\underset{\sim}{k}\cdot\underset{\sim}{r}) - i\sin(\underset{\sim}{k}\cdot\underset{\sim}{r})\right] d^3\underset{\sim}{r}\,\right] =$$

$$= \frac{1}{N}\left[1+\rho\int g(\underset{\sim}{r})\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d^3 r\right] \qquad (9.25)$$

We define the static structure factor $S(\underset{\sim}{k})$ by

$$S(\underset{\sim}{k}) = 1+\rho\int g(\underset{\sim}{r})\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r} \underset{\substack{\uparrow \\ \text{isotropic fluid: } S(\underset{\sim}{k})\equiv S(k)}}{=} 1+\rho\int_0^\infty 4\pi r^2\,\frac{\sin(kr)}{kr}\, g(r)\, dr \qquad (9.26)$$

In view of the above discussion, we realize the following:

- The structure factor is directly measurable experimentally by diffraction:

$$S(\underset{\sim}{k}) = \frac{\text{Diffracted intensity in direction } \underset{\sim}{k}}{\substack{\text{Diffracted intensity in same direction,} \\ \text{if scatterers formed an ideal gas.}}} \qquad (9.27)$$

- The quantity $S(\underset{\sim}{k})-1$ is the Fourier transform of $g(\underset{\sim}{r})$.
  As a consequence, $g(\underset{\sim}{r})$ can be obtained from the experimental observable $S(\underset{\sim}{k})$ by an inverse Fourier transform:

$$\rho\, g(\underset{\sim}{r}) = \frac{1}{(2\pi)^3}\int \exp(i\underset{\sim}{k}\cdot\underset{\sim}{r})\left[S(\underset{\sim}{k})-1\right] d\underset{\sim}{k} \underset{\substack{\uparrow \\ \text{isotropic} \\ \text{fluid: } g(\underset{\sim}{r}) = g(r)}}{=} \frac{1}{(2\pi)^3}\int_0^\infty 4\pi k^2\,\frac{\sin(kr)}{kr}\left[S(k)-1\right] dk \qquad (9.28)$$

Given that $\int e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d^3 r = \delta(\underset{\sim}{k})$, eq (9.26) is often written as:

$$S(\underset{\sim}{k}) - 1 = \rho\int\left[g(\underset{\sim}{r})-1\right] e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d\underset{\sim}{r} \qquad (\underset{\sim}{k}\neq\underset{\sim}{0}) \qquad (9.29)$$

If the $\delta(\underset{\sim}{k})$ ("forward scattering") term is ignored, eq (9.29) can be taken as valid for all $\underset{\sim}{k}$.

General features of the Structure Factor

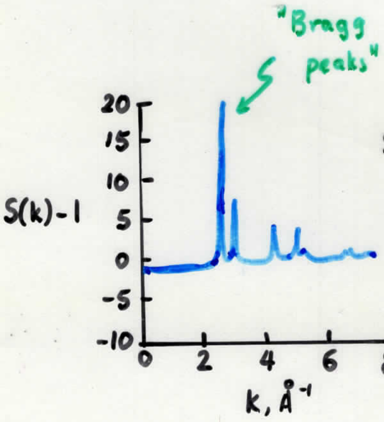
$$k = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \quad , \quad S(k) \propto I(\theta)$$

$$S(k)-1 = \rho\int_0^\infty 4\pi r^2 \underset{(k\neq 0)}{\frac{\sin(kr)}{kr}}\,[g(r)-1]\,dr \quad (9.29') \quad ; \quad g(r)-1 = \frac{1}{2\pi^2\rho r}\int_0^\infty k\sin(kr)\overset{\text{does not contain forw. scattering}}{[S(k)-1]} \quad (9.28')$$

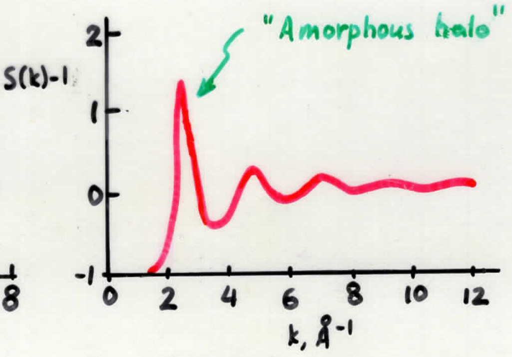
$S(k)$ will exhibit a peak at $k \approx \frac{2\pi}{\Delta r}$, where Δr the separation between successive peaks in $g(r)$.

The small-k ("small angle") region of $S(k)$ contains information about structural features with large characteristic lengths; The large-k ("wide angle") region of $S(k)$ contains information about short-range structure. "Wide-angle" X-ray, neutron, or electron diffraction experiments are needed to get $g(r)$ in liquids.

Examples.



Al, powdered solid
923K

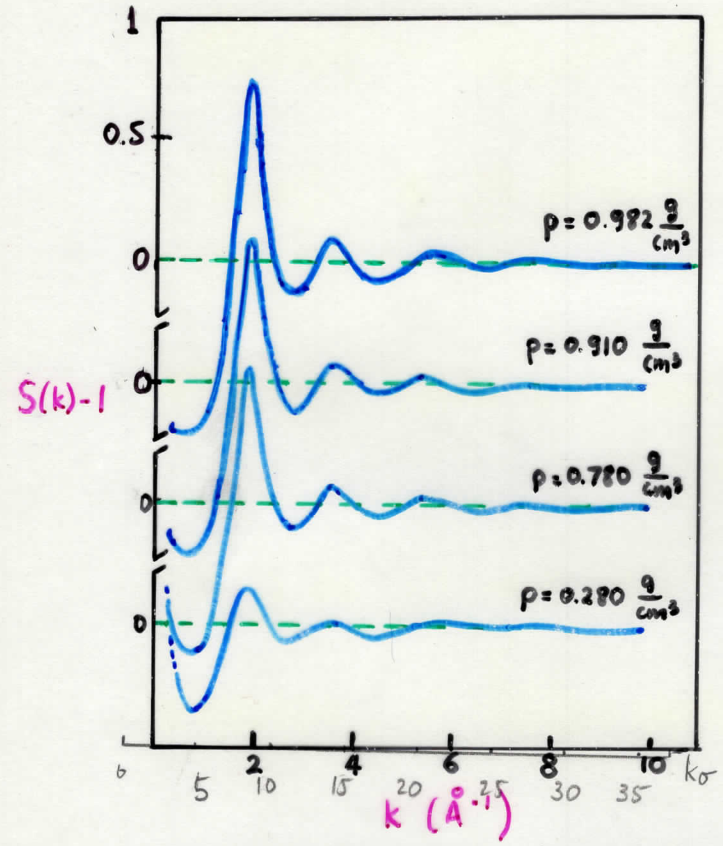


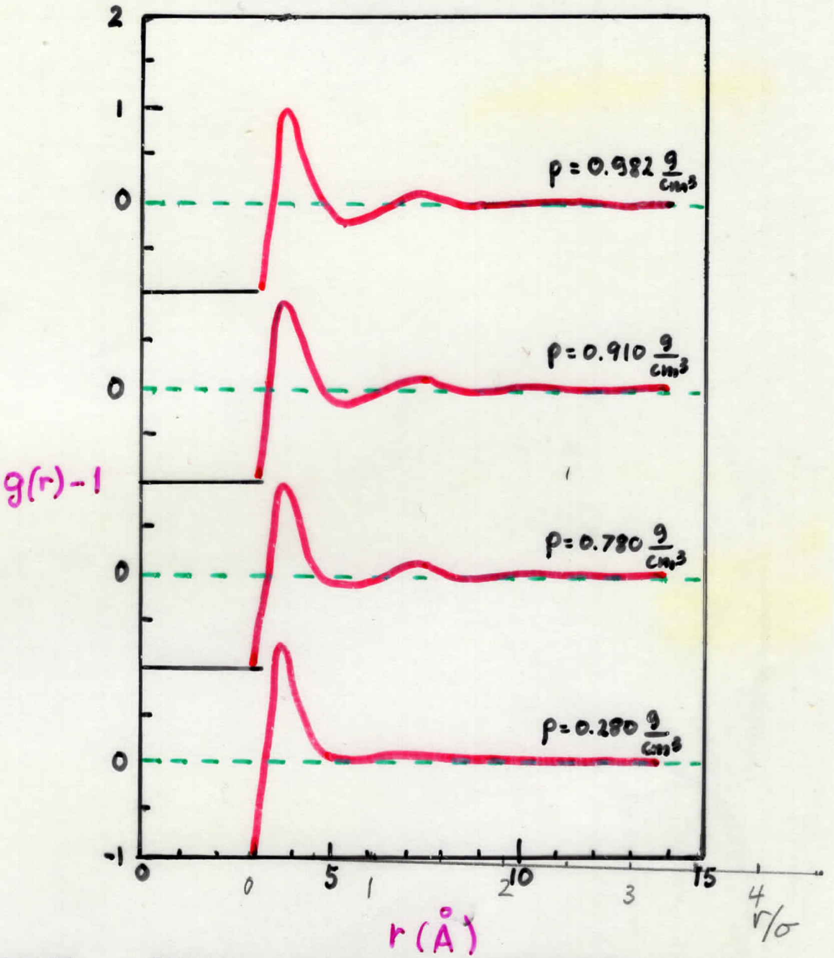
Al, liquid
923K

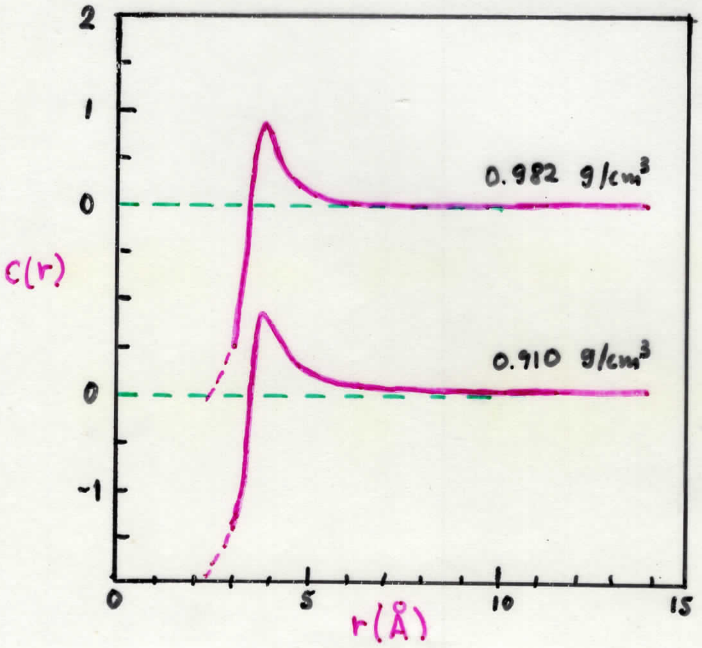
Argon , -125°C

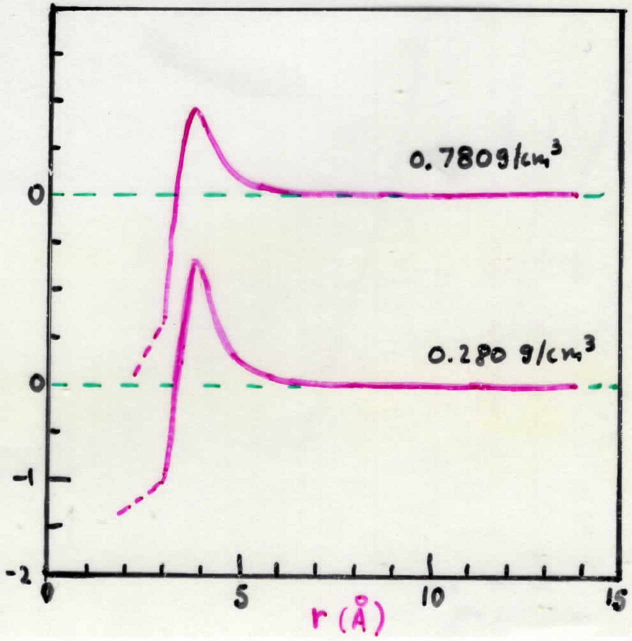
(Pings, C. J. Chemical Engineering Education , Winter 1970, p.18)

LJ parameters
$\sigma = 3.38 \pm 0.06$
$\epsilon/k_B = 134 \pm 10$









9.1.5. Thermodynamic properties from the pair distribution function.

Internal energy

We focus on the <u>excess internal energy</u>,

configurational average

$$U^{ex}(N,V,T) = U(N,V,T) - U^{ig}(N,V,T). \equiv \langle \mathcal{V}(\underline{r}_1,\dots,\underline{r}_N)\rangle \qquad (9.30)$$

Assuming pairwise additivity of interactions, with a pair potential $\mathcal{V}_{pair}(r)$, we have:

$$U^{ex}(N,V,T) = (\text{Number of molecules}) \cdot \sum_{\substack{\text{all distances } r\\ \text{from a given molecule}}} \left(\underset{\text{of radius } r \text{ to } r+dr}{\text{expected number of molecules within shell}}\right) \mathcal{V}_{pair}(r) \cdot \frac{1}{2}$$

avoid doublecounting interactions

or, in view of eq (9.16),

$$U^{ex}(N,V,T) = N \int_0^\infty \rho\, g(r)\, 4\pi r^2 dr\, \mathcal{V}_{pair}(r) \cdot \frac{1}{2} \quad \text{, or}$$

$$U^{ex}(N,V,T) \equiv U(N,V,T) - U^{ig}(N,V,T) = \frac{N}{2}\rho \int_0^\infty 4\pi r^2\, g(r)\, \mathcal{V}_{pair}(r)\, dr \qquad (9.31)$$

"energy equation"

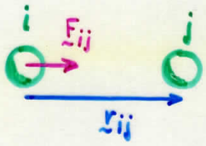
Pressure

We have seen (virial theorem for pairwise additive potential):

$$P = \rho k_B T + \frac{1}{3V} \left\langle \sum_{i=1}^{N} \sum_{j=i+1}^{N} (\underline{r}_i - \underline{r}_j) \cdot \underline{F}_{ij} \right\rangle = \rho k_B T + \frac{1}{3V} \left\langle \sum\sum_{\text{all pairs}} (\underline{r}_i - \underline{r}_j) \cdot \underline{F}_{ij} \right\rangle$$

(9.32)

Now, for a pairwise additive potential giving rise to central forces,



$\left.\frac{\partial \mathcal{V}_{pair}}{\partial r}\right|_{r=r_{ij}} >$

means attracti

$$\mathbf{F}_{ij} = -\nabla_{\mathbf{r}_{ji}} \mathcal{V}_{pair}(r_{ij}) = \left.\frac{\partial \mathcal{V}_{pair}}{\partial r}\right|_{r=r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}}$$

$(\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i)$

and

$$(\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} = -\mathbf{r}_{ij} \cdot \mathbf{F}_{ij} = -\left.\frac{\partial \mathcal{V}_{pair}}{\partial r}\right|_{r=r_{ij}} \frac{\mathbf{r}_{ij}^2}{r_{ij}} = -r_{ij} \left.\frac{\partial \mathcal{V}_{pair}}{\partial r}\right|_{r=r_{ij}} \qquad (9.33)$$

In view of eq (9.17), eq (9.32) and (9.33) give:

$$P = \rho k_B T + \frac{1}{3V} \int_0^\infty \underset{\substack{\uparrow \\ \text{total number of} \\ \text{pairs in system}}}{\frac{N(N-1)}{2}} \cdot \underbrace{\frac{N}{N-1} \cdot \frac{1}{V}\, 4\pi r^2\, g(r)\, dr}_{\substack{\text{fraction of pairs} \\ \text{at distance } r \text{ to } r+dr}} \underbrace{\left[-r \frac{\partial \mathcal{V}_{pair}}{\partial r}\right]}_{\substack{\text{contribution to virial} \\ \text{from given pair.}}}$$

or

$$P = \rho k_B T - \frac{\rho^2}{6} \int_0^\infty r \frac{\partial \mathcal{V}_{pair}}{\partial r}\, 4\pi r^2\, g(r)\, dr \qquad (9.34)$$

"pressure equation"

Isothermal Compressibility

An interesting connection between the isothermal compressibility and the pair distribution function can be arrived at, starting from the normalization condition (9.11) in the Grand Canonical ensemble:

$$\rho^2 \int g^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 \overset{\substack{(\text{homg. syst., } 9.14) \\ \downarrow}}{=} \rho^2 V \int g^{(2)}(\mathbf{r}_{12})\, d\mathbf{r}_{12} = \langle N^2 \rangle - \langle N \rangle \qquad (9.11)$$

On the other hand, an analysis of fluctuations in the Grand Canonical ensemble has given (see equation 6.20):

isothermal compressibility

$$\langle (\delta N)^2 \rangle = \langle (N - \langle N \rangle)^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2 = k_B T \frac{\langle N \rangle^2}{V} \kappa_T \qquad (6.20)$$

Then, combining (9.11) and (6.20),

$$\rho^2 V \int g^{(2)}(\underset{\sim}{r}_{12})\, d\underset{\sim}{r}_{12} = k_B T \frac{\langle N \rangle^2}{V} \kappa_T + \langle N^2 \rangle - \langle N \rangle = k_B T \rho^2 V \kappa_T + \rho^2 V^2 - \rho V$$

or

$$\rho k_B T \kappa_T = \rho \int g^{(2)}(\underset{\sim}{r})\, d\underset{\sim}{r} - \rho V + 1 = 1 + \rho \int g^{(2)}(\underset{\sim}{r})\, d\underset{\sim}{r} - \rho \int d\underset{\sim}{r}$$

or

$$\underline{\rho k_B T \kappa_T = 1 + \rho \int \left[g^{(2)}(\underset{\sim}{r}) - 1 \right] d^3 r = 1 + \rho \int_0^\infty 4\pi r^2 \left[g^{(2)}(r) - 1 \right] dr} \qquad (9.35)$$

"compressibility equation"

It is remarkable that the compressibility equation does not presuppose pairwise additivity.

In view of eq (9.29), a straightforward relationship can be established between the isothermal compressibility and the zero-wavevector value of the static structure factor (ignoring the forward-scattering contribution):

$$\underline{S(\underset{\sim}{0}) = \lim_{\underset{\sim}{k} \to \underset{\sim}{0}} S(\underset{\sim}{k}) = \rho k_B T \kappa_T = \frac{\kappa_T}{\kappa_T^{ig}}} \qquad (9.36)$$

9.1.6. Potential of Mean Force and Pair Distribution Function.

Define a pair energy quantity $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ by:

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \exp\left[-\beta\, w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)\right] \qquad (9.37)$$

By definition, (9.8)

$$g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{N(N-1)}{\rho^2}\, \frac{\int \exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]\, d^3r_3 \cdots d^3r_N}{Z(N,V,T)}$$

$$w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\frac{1}{\beta} \ln\left[\frac{N(N-1)}{N^2}\, \frac{V^2}{Z(N,V,T)}\right] - \frac{1}{\beta} \ln \int \exp[-\beta \mathcal{V}(\mathbf{r}_1, \cdots, \mathbf{r}_N)]\, d^3r_3 \cdots d^3r_N$$

In a homogeneous system we can use position $\mathbf{r}_1$ as an origin for measuring coordinates, in which case we obtain:

$$w_N^{(2)}(\mathbf{r}_{12}) = -\frac{1}{\beta} \ln\left[\frac{N(N-1)}{N^2}\, \frac{V^2}{Z(N,V,T)}\right] - \frac{1}{\beta} \ln \int \exp[-\beta \mathcal{V}(\mathbf{r}_{12}, \mathbf{r}_{13}, \cdots \mathbf{r}_{1N})\, d^3r_{13} \cdots d^3r_{1}$$

Taking the gradient with respect to $\mathbf{r}_1$:

$$\nabla_{\mathbf{r}_1} w_N^{(2)}(\mathbf{r}_{12}) = -\frac{1}{\beta}(-\beta)\, \frac{\int \{\nabla_{\mathbf{r}_1} \mathcal{V}(\mathbf{r}_{12}, \cdots \mathbf{r}_{1N})\} \exp[-\beta \mathcal{V}(\mathbf{r}_{12}, \cdots, \mathbf{r}_{1N})]\, d^3r_{13} \cdots d^3r_{1N}}{\int \exp[-\beta \mathcal{V}(\mathbf{r}_{12}, \cdots, \mathbf{r}_{1N})]\, d^3r_{13} \cdots d^3r_{1N}}$$

$$-\nabla_{\mathbf{r}_1} \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N) = \mathbf{F}_1(\mathbf{r}_1, \mathbf{r}_2, \cdots, \mathbf{r}_N)$$

total force experienced by 1 in given system configuration ($\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N$)

In a homogeneous system, $w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ will depend only on the relative position vector $\mathbf{r}_{12}$

and $\nabla_{\mathbf{r}_1} w_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = -\nabla_{\mathbf{r}_{12}} w_N^{(2)}(\mathbf{r}_{12})$

$\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$

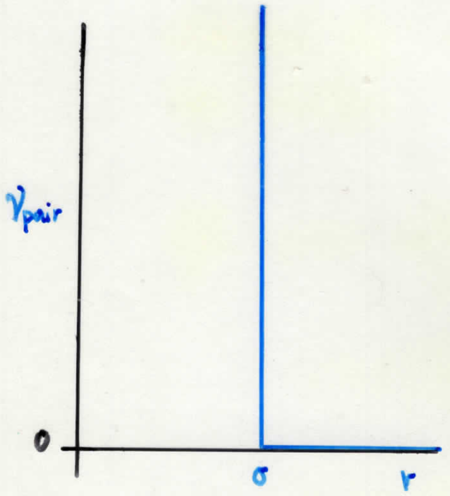
Then,

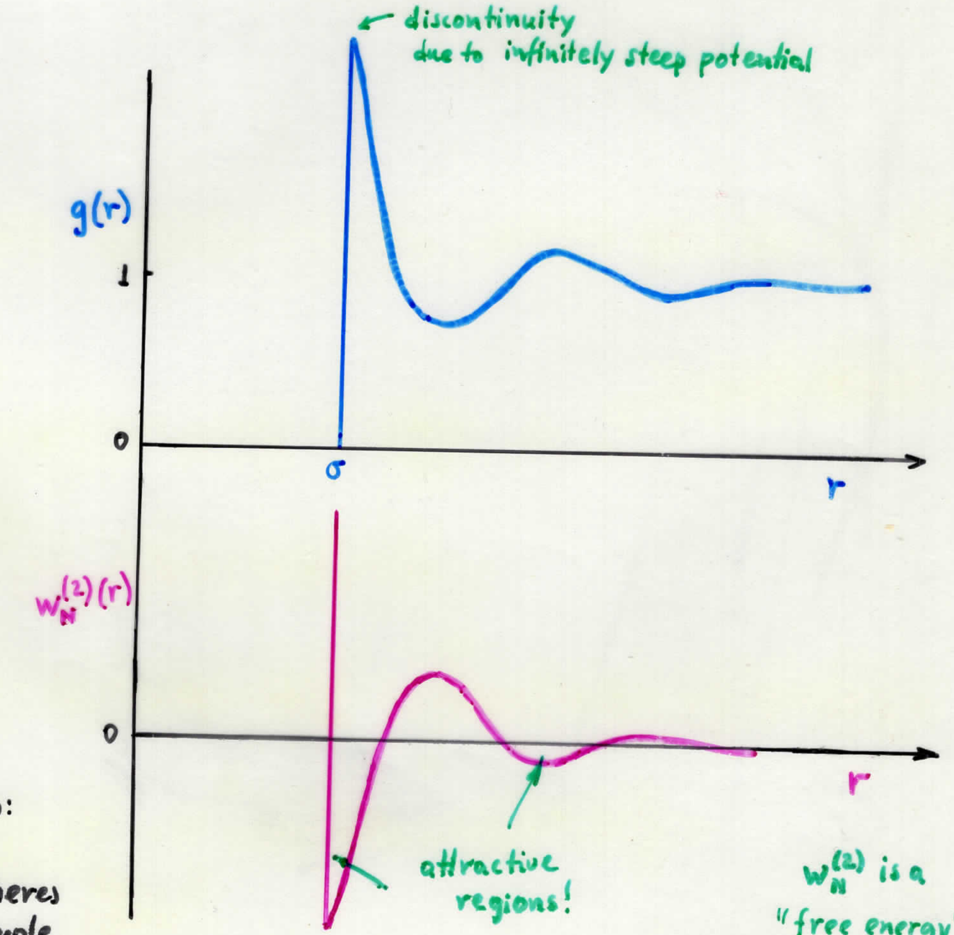
$$\nabla_{\mathbf{r}_{12}} w_N^{(2)}(\mathbf{r}_{12}) = \frac{\int \mathbf{F}_1 \exp[-\beta V(\mathbf{r}_{12}, \dots, \mathbf{r}_{1N})]\, d\mathbf{r}_{13} \cdots d\mathbf{r}_{1N}}{\int \exp[-\beta V(\mathbf{r}_{12}, \dots, \mathbf{r}_{1N})]\, d\mathbf{r}_{13} \cdots d\mathbf{r}_{1N}} \qquad (9.39)$$

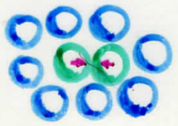
From eq (1.6.38) it is obvious that $w_N^{(2)}(\mathbf{r}_{12}) \equiv -k_B T \ln g_N^{(2)}(\mathbf{r}_{12})$ can be viewed as a potential that generates the force of interaction on a molecule 1 at fixed relative position $\mathbf{r}_{12}$ with respect to another molecule 2 in the fluid, averaged over all configurations of the remaining (N-2) molecules. Hence the name potential of mean force for $w_N^{(2)}(\mathbf{r}_{12})$.

It is remarkable that $w_N^{(2)}(\mathbf{r}_{12})$ can be attractive over some separation ranges even in cases where the pair potential is purely repulsive.

Example: Hard Spheres.







Interpretation:
Pounding by rest of the spheres around the couple creates effective attraction.

$w_N^{(2)}$ is a "free energy", as opposed to an energy.

9.7. Low-density limit of the pair distribution function.
Application: Second virial coefficient in terms of pair potential.

When the density ρ becomes very small, the interaction between two molecules fixed at a distance r apart is not affected by the remaining $(N-2)$ molecules.

Thus, the potential of mean force $W_N^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) \rightarrow \mathcal{V}_{\text{pair}}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$ and

$$\text{As } \rho \rightarrow 0, \qquad g(r) \rightarrow \exp\left[-\beta\, \mathcal{V}_{\text{pair}}(r)\right] \qquad (9.42)$$

LOW-DENSITY LIMIT of $g(r)$.

Application

Inserting the low-density expression into the pressure equation (9.34), one obtains:

$$\frac{\beta P}{\rho} \simeq 1 - \frac{2\pi\beta}{3}\rho \int_0^\infty \exp\left[-\beta \mathcal{V}_{\text{pair}}(r)\right] r^3 \frac{d\mathcal{V}_{\text{pair}}}{dr}\, dr \overset{\text{integration by parts}}{=}$$

$$= 1 + \frac{2\pi}{3}\rho \int_0^\infty r^3\, d\left[\exp\{-\beta \mathcal{V}_{\text{pair}}(r)\}\right] =$$

$$= 1 + \frac{2\pi}{3}\rho \left\{ \left[r^3 \exp\{-\beta \mathcal{V}_{\text{pair}}(r)\}\right]_0^\infty - \int_0^{\infty} \exp\left[-\beta \mathcal{V}_{\text{pair}}(r)\right] . 3r^2 dr \right\} =$$

$$= 1 + \frac{2\pi}{3}\rho \lim_{R\rightarrow\infty} \left\{ \underset{\substack{\downarrow \\ 3\int_0^R r^2 dr}}{R^3} - 3\int_0^R \exp\left[-\beta \mathcal{V}_{\text{pair}}(r)\right] r^2 dr \right\} =$$

$$= 1 + \frac{2\pi}{3}\rho\, 3 \lim_{R\rightarrow\infty} \int_0^R \left[1 - \exp\{-\beta \mathcal{V}_{\text{pair}}(r)\}\right] r^2 dr \quad , \text{or}$$

$$\frac{\beta P}{\rho} = 1 - 2\pi\rho \int_0^\infty \left[\exp\{-\beta \mathcal{V}_{pair}(r)\} - 1\right] r^2 dr$$

or $\frac{\beta P}{\rho} = 1 + B_2(T)\rho$ Virial expansion, truncated at second term.

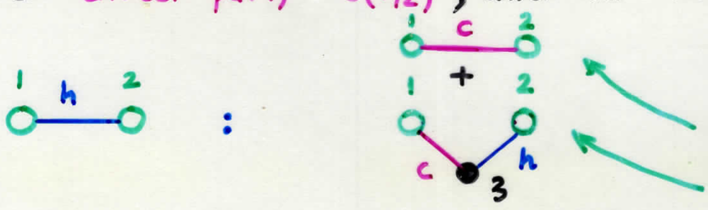
where $B_2(T) = -2\pi \int_0^\infty \left[\exp\{-\beta \mathcal{V}_{pair}(r)\} - 1\right] r^2 dr$ SECOND VIRIAL COEFFICIENT (9.44)

9.1.8. Pair Correlation function h(r) and Direct Correlation function c(r). Ornstein-Zernike equation.

DEFINITION: Pair Correlation function $h(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - 1$ (9.45)

For a homogeneous, isotropic fluid, $h(r_{12}) = g(r_{12}) - 1$
$h(r_{12})$ is a measure of the total influence of molecule 1 on molecule 2 at a distance r_{12}. ("total correlation" betw. 1, 2).

Ornstein and Zernike (1914): Division of $h(r_{12})$ into two parts: a direct part, $c(r_{12})$, and an indirect part.



1 is correlated with 2 because
1 is directly correlated with 2, and
1 is directly correlated to a third molecule 3, which is correlated to 2 directly or indirectly through other particles.

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, h(r_{32})\, d^3 r_3 \qquad (9.46)$$

ORNSTEIN-ZERNIKE EQUATION.

In essence, a definition of the direct correlation function $c(\underset{\sim}{r})$
($h(\underset{\sim}{r})$ is a <u>total</u> correlation function)

Note that recursive use of the Ornstein - Zernike equation leads to:

$$h(r_{12}) = c(r_{12}) + \rho \int c(r_{13})\, c(r_{32})\, d^3r_3 + \rho^2 \iint c(r_{13})\, c(r_{34})\, c(r_{42})\, d^3r_3\, d^3r_4 + \cdots$$

(sum chains of direct correlations going through fluid particles and terminating at 1 and 2)

The Ornstein - Zernike equation becomes particularly simple in Fourier- transformed space, by use of the convolution theorem.

Let $\hat{h}(k) = \int h(r)\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d^3r$, $\hat{c}(k) = \int c(r)\, e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, d^3r$.

Then, (9.46) gives $\hat{h}(k) = \hat{c}(k) + \rho\, \hat{c}(k)\, \hat{h}(k)$

(9.47)

or $\hat{h}(k) = \dfrac{\hat{c}(k)}{1 - \rho\, \hat{c}(k)}$

Note that, from (9.29'),

Structure factor $S(k) = 1 + \rho\, \hat{h}(k)$

hence there is a simple relation between structure factor and $\hat{c}(k)$

$$S(k) = \frac{1}{1 - \rho \hat{c}(k)} \qquad (9.48)$$

In particular, the compressibility equation (9.36) gives

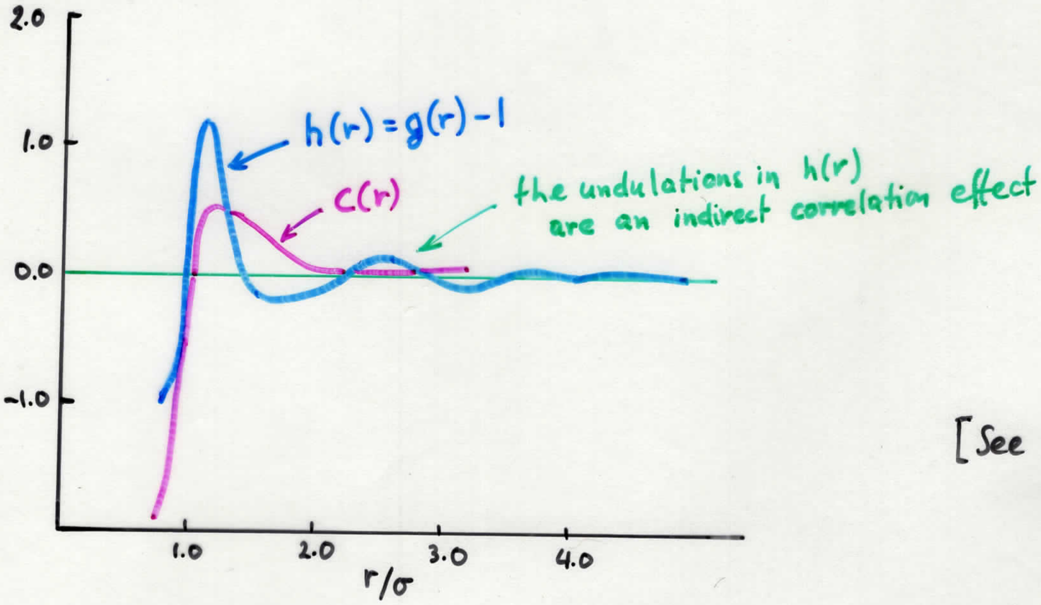
$$\rho \int c(r)\, d^3r = \rho\, \hat{c}(0) = 1 - \frac{1}{\rho k_B T \kappa_T} = 1 - \frac{\kappa_T^{ig}}{\kappa_T} \qquad (9.49)$$

Why introduce the direct correlation function $c(r)$?

General observation: $c(r)$ has the range of the pair potential v_{pair}.
(i.e. is significantly different from zero over distances commensurate with potential range).

This means that, in non-ionic fluids, $c(r)$ will be significantly shorter-ranged than $h(r)$.

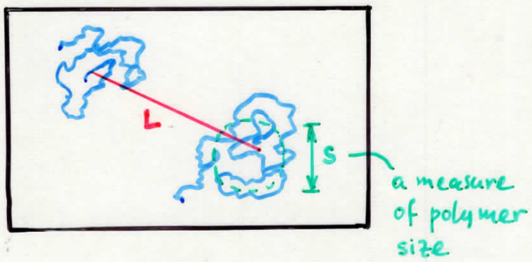
Example: LJ fluid.



[See also plots for liq. Ar from diffraction]

In molecular liquids, both intramolecular and intermolecular correlations between atoms (sites) must be considered. An extension of the Ornstein-Zernike equation to molecular fluids forms the basis of the Reference Interaction Site Model (RISM) of Chandler and Andersen (1972).

An Aside: Determination of chain radius of gyration through SANS



e.g. polyethylene chains in matrix of perdeuterated polyethylene melt.

Envision a system of chains infinitely dilute in a matrix ($s \ll L$). Chains don't "see" each other. Chains are labelled so that there is contrast between them and the matrix with respect to diffraction.

Small angle (low $\underset{\sim}{k}$-) diffraction experiment at $ks \leq 2\pi$ will reveal intramolecular correlations at the length scale of the entire chain.

In this case, $\rho g_{tot}(r) = \omega(r) + \rho g(r) \simeq \omega(r) + \rho$

ideal gas contribution (no intermolecular structure)

and (9.29') gives:

$$S(k) - 1 = \int_0^\infty 4\pi r^2 \frac{\sin(kr)}{kr}\,\omega(r)\,dr = \hat{\omega}(k) = \frac{1}{n}\left\langle \sum_{i=1}^{n} \sum_{\substack{j=1 \\ i \neq j}}^{n} \frac{\sin(kr_{ij})}{kr_{ij}} \right\rangle$$

$\omega(r)$: intramolecular pair density function

n: number of mers per chain

r_{ij}: separation between two chain segments

For $ks \ll 1$, we can introduce the approximation

$$\frac{\sin(kr_{ij})}{kr_{ij}} = \frac{1}{kr_{ij}}\left[kr_{ij} - \frac{(kr_{ij})^3}{3!} + \frac{(kr_{ij})^5}{5!} \cdots\right] =$$

$$= 1 - \frac{(kr_{ij})^2}{6} + \frac{(kr_{ij})^4}{120} + \cdots$$

Keeping terms up to second order in kr_{ij},

$$S(k)-1 \simeq \frac{1}{n}\left\langle \sum_{\substack{i=1\\ i\neq j}}^{n}\sum_{j=1}^{n}\left\{1-\frac{(kr_{ij})^2}{6}\right\}\right\rangle = \frac{1}{n}\sum_{\substack{i=1\\ i\neq j}}^{n}\sum_{j=1}^{n} 1 - \frac{1}{3n}\left\langle \sum_{\substack{i=1\\ i<j}}^{n}\sum_{j=1}^{n} (kr_{ij}$$

$$= \frac{n(n-1)}{n} - \frac{1}{3n}\left\langle \sum_{\substack{i=1\\ i<j}}^{n}\sum_{j=1}^{n} (kr_{ij})^2 \right\rangle = n-1-\frac{k^2}{3n}\left\langle \sum\sum_{1\leq i<j\leq n} r_{ij}^2 \right\rangle$$

or

"Debye scattering function" $(ks \ll 1)$

$$P(k) = \frac{\overset{\text{scattered intensity}}{I(k)}}{\underset{\text{(incl. forward scattering)}}{I(0)}} = \frac{S(k)}{n} = 1-\frac{k^2}{3}\cdot\frac{1}{n^2}\left\langle \sum\sum_{1\leq i<j\leq n} r_{ij}^2 \right\rangle$$

(The above development is not specific to a chain; it is valid for <u>any</u> finite body consisting of point scatterers in the range of k much smaller than the overall dimensions of the body.)

What is the quantity $\frac{1}{n^2}\left\langle \sum\sum_{1\leq i<j\leq n} r_{ij}^2 \right\rangle$?

Lagrange's theorem (1783)

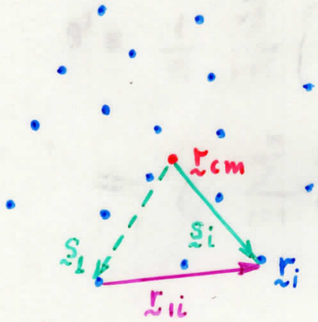
Given a collection of n points of equal mass, located at positions $\underset{\sim}{r}_i$ $(1 \leq i \leq n$ the quantity $\frac{1}{n^2}\sum\sum_{1\leq i<j\leq n} r_{ij}^2$, with $r_{ij} = |\underset{\sim}{r}_j - \underset{\sim}{r}_i|$, equals the

squared radius of gyration s^2 of the collection of points.

DEFINITION: Radius of gyration for a collection of material points of equal mass

$$s^2 \equiv \frac{1}{n}\sum_{i=1}^{n}\underbrace{\left(\underset{\sim}{r}_i - \frac{1}{n}\sum_{j=1}^{n}\underset{\sim}{r}_j\right)}_{\text{distance of } i \text{ from center of mass}}{}^2$$

PROOF



We introduce the notation:

$$\underset{\sim}{r}_{cm} = \frac{1}{n}\sum_{i=1}^{n} \underset{\sim}{r}_i \quad \text{(center of mass position)}$$

$$\underset{\sim}{s}_i = \underset{\sim}{r}_i - \underset{\sim}{r}_{cm} \quad \text{(distance vector of } i \text{ from center of mass)}$$

In this notation,

$$s^2 = \frac{1}{n}\sum_{i=1}^{n} \underset{\sim}{s}_i^{\,2}$$

Furthermore, we choose to express all $\underset{\sim}{s}_i$ relative to $\underset{\sim}{s}_1$:

$$\underset{\sim}{s}_i = \underset{\sim}{s}_1 + \underset{\sim}{r}_i - \underset{\sim}{r}_1 = \underset{\sim}{s}_1 + \underset{\sim}{r}_{1i}$$

Now,

$$s^2 = \frac{1}{n}\sum_{i=1}^{n}(\underset{\sim}{s}_1 + \underset{\sim}{r}_{1i})^2 = \frac{1}{n}\sum_{i=1}^{n}\underset{\sim}{s}_1^{\,2} + \frac{2}{n}\sum_{i=2}^{n}\underset{\sim}{s}_1\cdot\underset{\sim}{r}_{1i} + \frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2}$$

From the fact that

$$\sum_{j=1}^{n}\underset{\sim}{s}_j = \sum_{j=1}^{n}\underset{\sim}{r}_j - n\underset{\sim}{r}_{cm} = \underset{\sim}{0}\text{ , we have: } \sum_{j=1}^{n}(\underset{\sim}{s}_1 + \underset{\sim}{r}_{1j}) = \underset{\sim}{0} \Rightarrow$$

$$\Rightarrow n\underset{\sim}{s}_1 + \sum_{j=2}^{n}\underset{\sim}{r}_{1j} = \underset{\sim}{0} \quad \Rightarrow \quad \underset{\sim}{s}_1 = -\frac{1}{n}\sum_{j=2}^{n}\underset{\sim}{r}_{1j}$$

Then,

$$\underset{\sim}{s}_1^{\,2} = \frac{1}{n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}\underset{\sim}{r}_{1i}\cdot\underset{\sim}{r}_{1j}$$

and $$\frac{2}{n}\sum_{i=2}^{n}\underset{\sim}{s}_1\cdot\underset{\sim}{r}_{1i} = -\frac{2}{n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}\underset{\sim}{r}_{1i}\cdot\underset{\sim}{r}_{1j}$$

Hence, $$s^2 = -\frac{1}{n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}\underset{\sim}{r}_{1i}\cdot\underset{\sim}{r}_{1j} + \frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2}$$

Now, by the law of cosines: $\underset{\sim}{r}_{1i}\cdot\underset{\sim}{r}_{1j} = \dfrac{\underset{\sim}{r}_{1i}^{\,2} + \underset{\sim}{r}_{1j}^{\,2} - \underset{\sim}{r}_{ij}^{\,2}}{2}$

and so,

$$s^2 = -\frac{1}{2n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}(\underset{\sim}{r}_{1i}^{\,2} + \underset{\sim}{r}_{1j}^{\,2} - \underset{\sim}{r}_{ij}^{\,2}) + \frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2} = -\frac{1}{2n^2}(n-1)\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2} - \frac{1}{2n^2}(n-1)\sum_{j=2}^{n}\underset{\sim}{r}_{1j}^{\,2} +$$

$$+\frac{1}{2n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}\underset{\sim}{r}_{ij}^{\,2} + \frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2} = -\frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2} + \frac{1}{n^2}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2} + \frac{1}{2n^2}\sum_{i=2}^{n}\sum_{j=2}^{n}\underset{\sim}{r}_{ij}^{\,2} +$$

$$+\frac{1}{n}\sum_{i=2}^{n}\underset{\sim}{r}_{1i}^{\,2}$$

$$s^2 = \frac{1}{n^2}\left[\sum_{i=2}^{n} \underset{\sim}{r}_{1j}^{\,2} + \frac{1}{2}\sum_{i=2}^{n}\sum_{j=2}^{n} \underset{\sim}{r}_{ij}^{\,2}\right] = \frac{1}{2n^2}\sum_{i=1}^{n}\sum_{j=1}^{n} r_{ij}^2$$

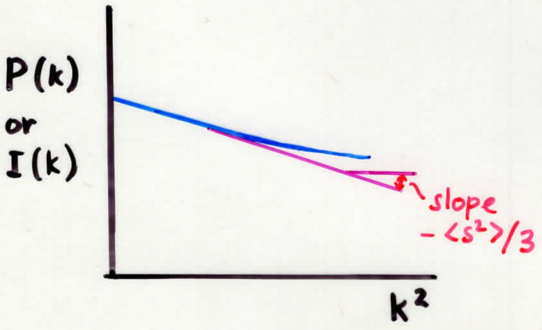
or $$s^2 = \frac{1}{n^2}\sum\sum_{1\le i<j\le n} r_{ij}^2 \quad , \text{QED}$$

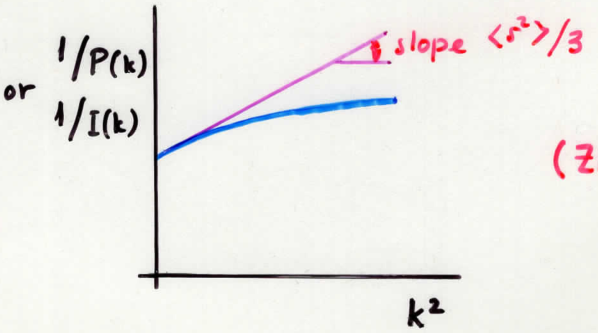
We have proved, therefore, that, for scattering from isolated polymer chains,

$$k\langle s^2\rangle^{1/2} \ll 1 \quad \rightarrow \quad P(k) = \frac{S(k)}{n} = 1 - \frac{k^2}{3}\langle s^2\rangle \qquad \text{GUINIER LAW}$$

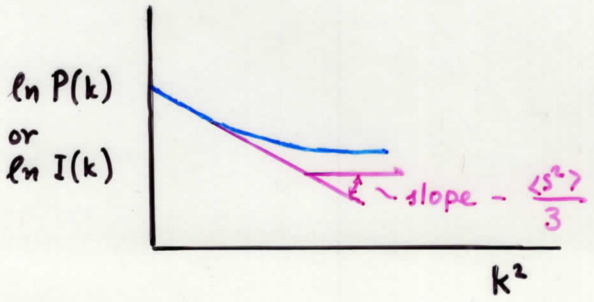
This relationship forms the basis for determining the mean squared radius of gyration of chains through small angle neutron scattering, using isotopically labelled chains in melts or glasses. It is also a basis for determining the radius of gyration through light scattering in solution.

Common ways of plotting experimental data:





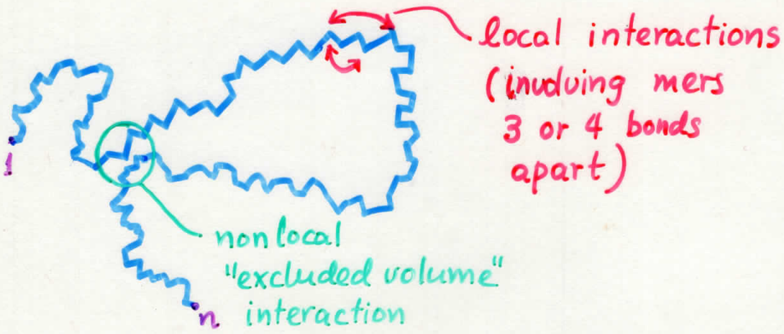
(Zimm Plot)



(Guinier Plot)

Benoit et al. (1970s, Institut Charles Sadron, Strasbourg)

Experimental confirmation of Flory's random coil hypothesis for chain conformations in the amorphous polymer bulk through SANS measurements of $\langle s^2 \rangle$ as a function of n.



Flory, 1943

RANDOM COIL HYPOTHESIS

In the amorphous bulk, chains remain unperturbed by nonlocal interactions between distant segments. Their conformation is dictated only by local interactions along backbone.

Consequence ($n>>1$): $$\underbrace{\langle r_{1n}^2 \rangle}_{\text{mean squared end-to-end distance}} \simeq 6 \underbrace{\langle s^2 \rangle}_{\text{mean squared radius of gyration}} = \underbrace{C_\infty}_{\text{characteristic ratio. Describes equil. conformational "stiffness". Dictated by local interactio}} (\overset{\text{number of skel. bonds}}{n-1}) \underbrace{\ell^2}_{\text{bond length}}$$

UNPERTURBED = "random walk"- type behavior.

Important realization:

The validity of Flory's random coil hypothesis greatly simplifies the calculation of the intramolecular pair density function $\omega(r)$ given the chemical constitution of a chain: Single unperturbed chains, subject only to local interactions need be considered.

show Dodd plot of $\omega(r)$, $P(q)$

9.2.4. A note on the numerical solution of integral equation theories

It is the exception, rather than the rule, that an analytic solution to an integral equation theory can be found. Iterative schemes for determining the solution to an integral equation theory analytically are thus necessary.

In a numerical solution to an integral equation, range of r is usually divided into equal intervals by defining N points on the r-axis. [usual value: N = 1024 - facilitates FFT].

Functions h, c can be regarded as vectors

$$\underset{\sim}{h} = (h(r_1), \ldots, h(r_i), \ldots, h(r_N)) \qquad (r_i = r_{i-1} + \delta r)$$

$$\underset{\sim}{c} = (c(r_1), \ldots, c(r_i), \ldots, c(r_N))$$

$\underset{\sim}{h}$ can be obtained from $\underset{\sim}{c}$ through the closure relations, and vice versa. Thus, either $\underset{\sim}{h}$ or $\underset{\sim}{c}$ can be considered as the vector of unknowns of the problem. In practice, $\underset{\sim}{\gamma} = \underset{\sim}{h} - \underset{\sim}{c}$ is a better choice as the vector of unknowns, as it is smoother as a function of r.

The Ornstein-Zernike equation,

$$h(r) - c(r) = \rho \int d^3r' \, h(\underset{\sim}{r}') \, c(|\underset{\sim}{r} - \underset{\sim}{r}'|)$$

becomes a set of nonlinear algebraic equations in $\underset{\sim}{\gamma}$.
In practice, it is much more efficient to use the Fourier-transformed form of the Ornstein-Zernike equation: $\hat{h}(k) = \hat{c}(k) + \rho \hat{h}(k) \hat{c}(k)$ where $\underset{\sim}{\hat{h}}$, $\underset{\sim}{\hat{c}}$ are obtainable by Fast Fourier transform from $\underset{\sim}{h}, \underset{\sim}{c}$. ($\mathcal{O}(N \log_2 N)$ operations)

Simple numerical scheme: Successive substitution (Picard scheme)

- Guess γ_i
- Find c_i from γ_i from closure eq. e.g., PY: $c_i = (1+\gamma_i)\left[\exp(-\beta v_{pair,i})-1\right]$
- Find $\hat{c}_j$ through FFT: $\hat{c}_j \equiv \hat{c}(k_j) = \frac{4\pi\delta r}{k_j}\sum_{i=1}^{\frac{1}{2}N-1} r_i \sin(k_j r_i) c_i \ , \ k_j = \frac{2\pi j}{N\delta r}$
- Find $\hat{\gamma}_j$ from Ornstein-Zernike: $\hat{\gamma}_j = \rho\frac{\hat{c}_j^{\,2}}{1-\rho\hat{c}_j}$
- Find γ_i' through FFT^{-1}: $\gamma_i' = \frac{\delta k}{2\pi^2 r_i}\sum_{j=1}^{\frac{1}{2}N-1} k_j \sin(k_j r_i)\,\hat{\gamma}_j \ , \ r_i = i\,\delta r, \ \delta k = \frac{2\pi}{N\delta}$

Picard scheme is very inefficient. Converges only at low densities, high temperatures. "Mixing" of successive approximations to $\underset{\sim}{\gamma}$ may be used to prevent divergence. Even then, scheme inefficient (hundreds to thousands of iterations until convergence, even with good initial guess).

Better numerical approach: Solve system of nonlinear equations through Newton-Raphson iteration with respect to $\underset{\sim}{\gamma}$.

PROBLEM: N×N matrix has to be inverted at each iteration.

An efficient compromise: Gillan's method. (Mol. Phys. 1979, 38, 1781)

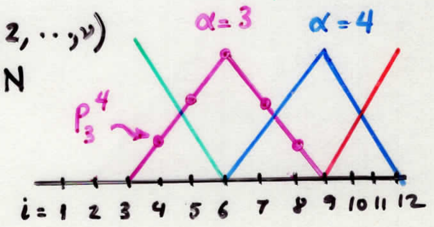
$\underset{\sim}{\gamma}$ decomposed into a fine and a coarse part.

$$\gamma_i = \underbrace{\sum_\alpha a_\alpha P_\alpha^i}_{\text{coarse}} + \underbrace{\Delta\gamma_i}_{\text{fine}}$$

$(\alpha = 1, 2, \ldots, \nu)$

$\nu < N$

Basis functions are much fewer than no points!



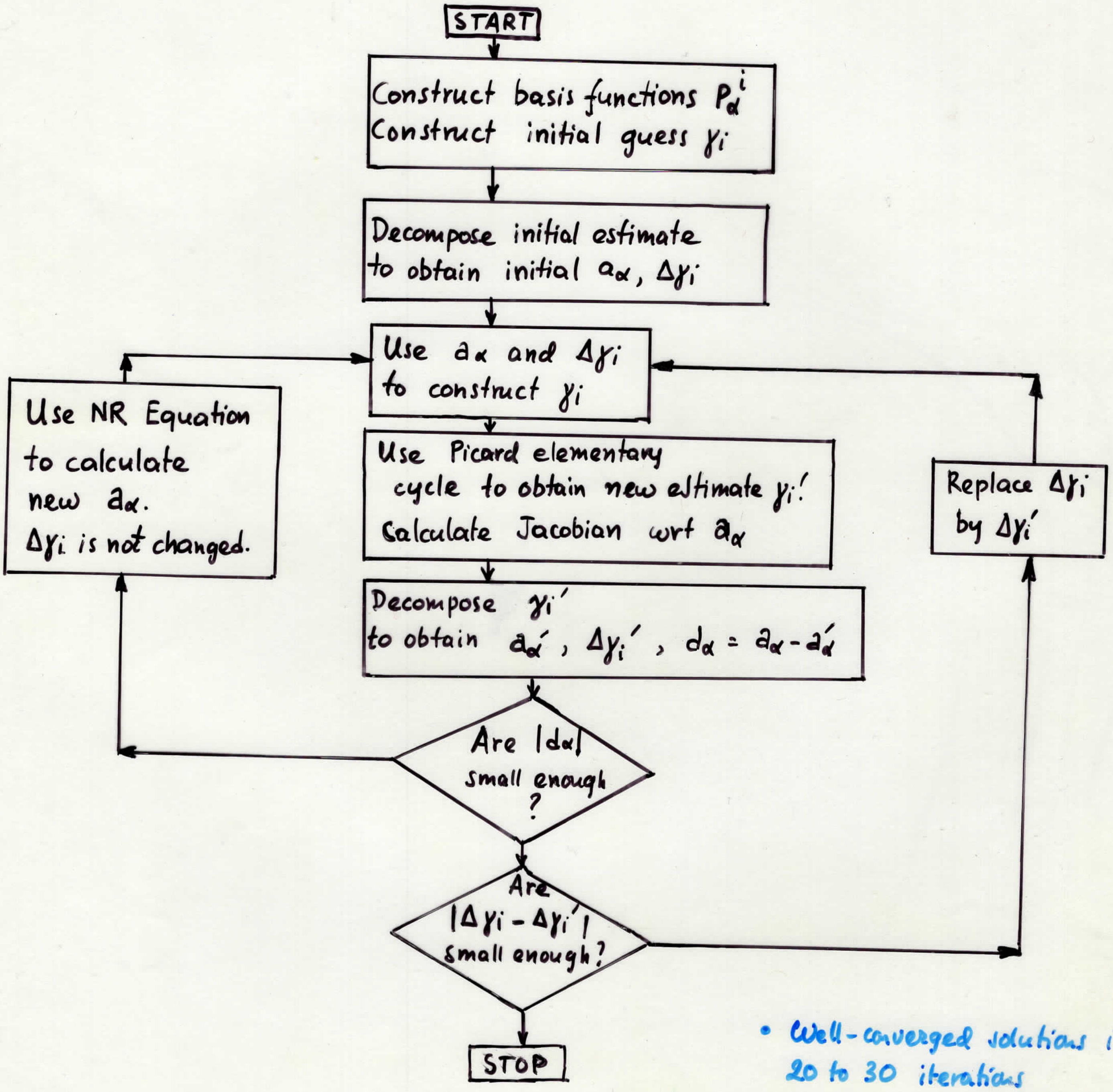
with P_α^i = basis functions (e.g., "roof functions")

satisfying $\sum_i P_\alpha^i \Delta\gamma_i = 0 \quad \forall\alpha$

Decomposition of a given $\underset{\sim}{\gamma}$ to determine $a_\alpha, \Delta\gamma_i$ is fast and unique.

- Iteration with Newton-Raphson under fixed $\Delta\gamma_i$ to determine a_α so that O-Z equations are satisfied.
  [only $\nu \times \nu$ matrix has to be inverted - Jacobian readily calculable.]

- Iteration with Picard method under fixed a_α to determine $\Delta\gamma_i$ so that O-Z equations are satisfied.



- Well-converged solutions in 20 to 30 iterations
- Robust wrt. initial guess.

9.4. A note on RISM: An integral equation theory for molecular fluids. Application to a polymer melt.

Molecular fluid consisting of one type of sites (e.g. polyethylene melt):

$$\underset{\substack{\uparrow\\ \text{density}\\ \text{of sites}\\ \text{(mers)}}}{\rho}\;\underset{\substack{\uparrow\\ \text{total pair}\\ \text{distribution}\\ \text{function}}}{g_{tot}}(r) = \underset{\substack{\uparrow\\ \text{intramolecular}\\ \text{pair density}\\ \text{function}}}{\omega(r)} + \rho\,\underset{\substack{\nwarrow\\ \text{intermolecular}\\ \text{pair distribution}\\ \text{function.}}}{g(r)}$$

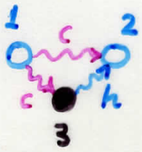
- For a fluid of rigid molecules (e.g. 3-site propane), $\omega(r)$ is known.
- For a long-chain polymer melt, $\omega(r)$ can be readily estimated from analysis or simulation of unperturbed chains (Flory random coil hypothesis).

Reference Interaction Site Model (RISM): Chandler, Andersen (1972)
An integral equation approach to molecular fluids.

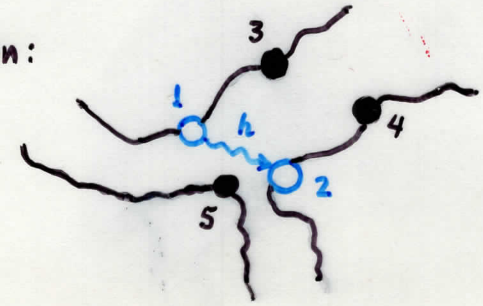
RISM starts from an Ornstein-Zernike type equation

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

Simple fluid OZ: $\hat{h}(k) = \hat{c}(k) + \rho\,\hat{c}(k)\,\hat{h}(k)$

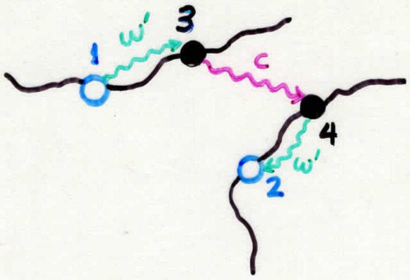


RISM equation:



Want to express total correlation between two segments 1, 2 on two different chains. Correlation may be mediated by segments on same or other chains (3,4,

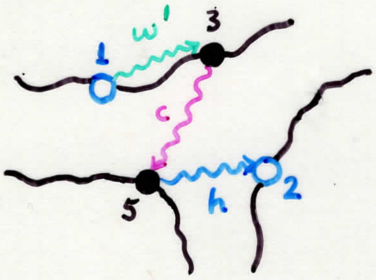
RISM Equation



Site 1 is correlated to site 2 because:

(a) It is intramolecularly correlated to itself and other sites on its chain (3), which are directly correlated to sites (4) on the chain of 2, which are intramolecularly correlated to 2 or coincide with 2

Contribution: $\hat{\omega}' \hat{c}\, \hat{\omega}'$



(b) It is intramolecularly correlated to itself and other sites on its chain (3), which are directly correlated to sites (5) on other chains than the ones to which 1 or 2 belong. These other sites (5), in turn, are correlated to 2 through total intermolecular correlations.

Contribution: $\rho\hat{\omega}' \hat{c}\, \hat{h}$

RISM equation:

$$\hat{h}(k) = \hat{\omega}'(k)\, \hat{c}(k)\, \hat{\omega}'(k) + \rho\, \hat{\omega}'(k)\, \hat{c}(k)\, \hat{h}(k)$$

or $h(r_{12}) = \int \omega'(r_{13})\, c(r_{34})\, \omega'(r_{42})\, d^3r_3\, d^3r_4 + \rho \int \omega'(r_{13})\, c(r_{35})\, h(r_{52})\, d^3r_3\, d^3r_5$

where $\omega'(r) = \delta(\underset{\sim}{r}) + \omega(r)$ (includes self-correlation)

and $\hat{\omega}'(k) = 1 + \hat{\omega}(k)$ the Fourier transform of $\omega'(r)$.

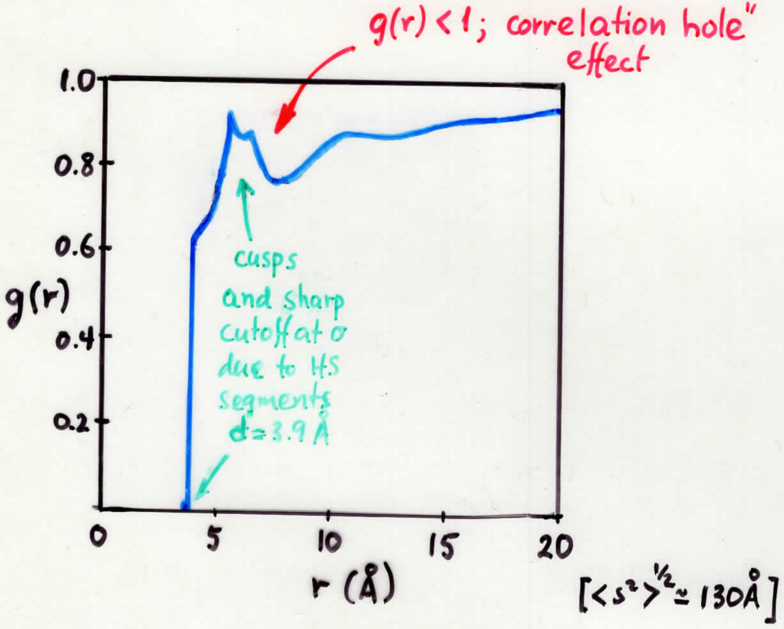
RISM equation can be supplemented with a closure relating h and c (e.g. Percus-Yevick), to form an integral equation theory for the molecular system.

An example: Determination of the structure of molten polyethylene.

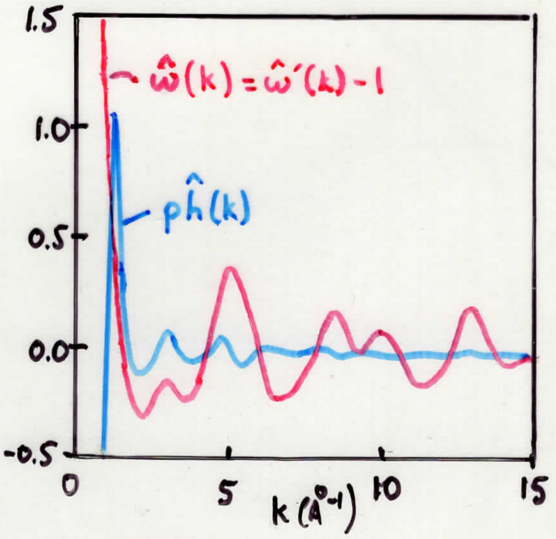
Honnell, K.G.; McCoy, J.D.; Curro, J.G.; Schweizer, K.S.; Narten, A.H.; Habenschuss, A. J. Chem. Phys. 1991, 94, 4659-4662.

- Polymer RISM equation
- PY closure
- Hard-sphere representation of mers (d adjustable); $n \doteq 6{,}429$ mers
- $\omega(r)$ obtained assuming unperturbed chains, based on correct bonded geometry and local conformational energetics (Rotational Isomeric State enumeration with 500 cal/mol trans-gauche difference and 2000 cal/mol for pentane effect)

Results:

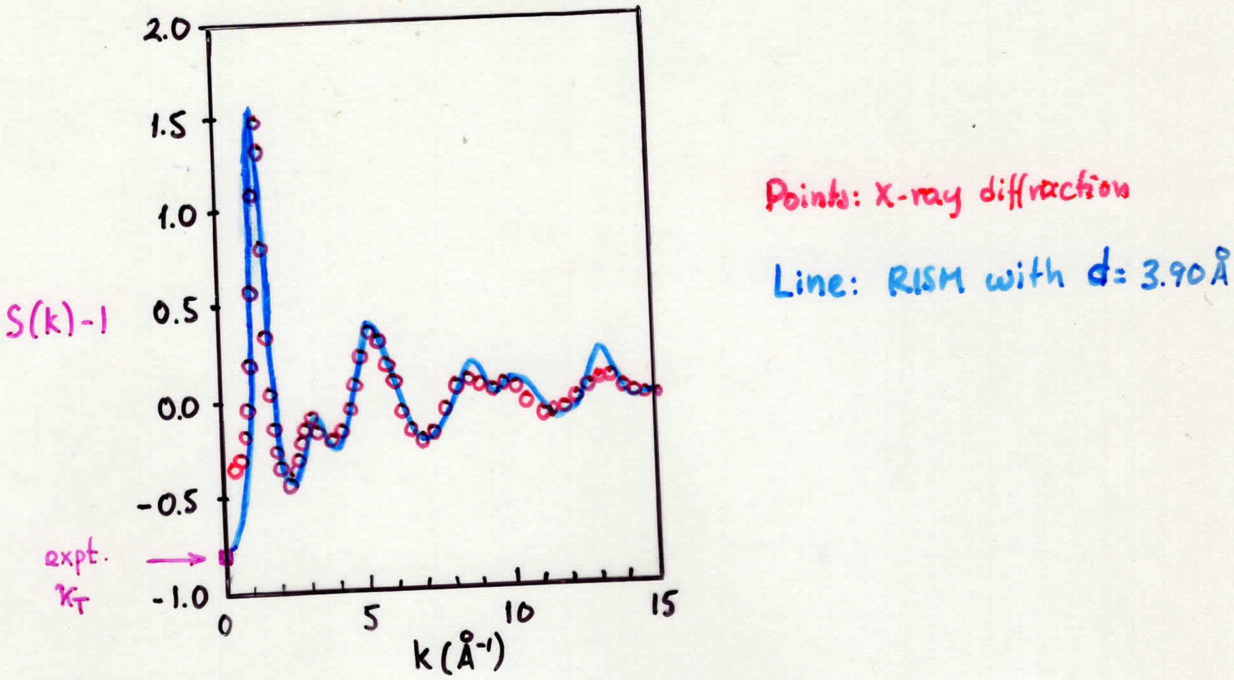


$[\langle s^2\rangle^{1/2} \simeq 130\text{Å}]$



$\hat{\omega}'(0) = n = 6429$

$\rho\,\hat{h}(0) = -6428.76$


2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
S(k)-1
expt.
κ_T
0
5
10
15
k(Å⁻¹)
Points: X-ray diffraction
Line: RISM with d= 3.90Å

Basis of all perturbation theories: Separation of the pair potential

$$\mathcal{V}_{\text{pair}}(r) = \underset{\text{reference system}}{v_0(r)} + \underset{\text{perturbation}}{w(r)} \qquad (1.6.60)$$

A systematic way of calculating the effect of the perturbation on the thermodynamic properties is provided by the "λ expansion".

The λ-expansion

Consider a pair potential $v_\lambda(r)$, of the form

$$v_\lambda(r) = v_{\lambda_0}(r) + w_\lambda(r) \qquad (1.6.61)$$

$\lambda_0 < \lambda < \lambda_1$

$\lambda = \lambda_0$ → $w_\lambda = 0$, and $v_{\lambda_0} \equiv v_0$ reduces to potential of reference system

$\lambda = \lambda_1$ → v_{λ_1} is the potential of the system of interest.

λ = "coupling parameter". Varying λ continuously from λ_0 to λ_1 amounts to gradually "switching on" the perturbation.

Let $\mathcal{V}(\lambda)$ stand for the total potential energy of the system, evaluated with the pair potential $v_\lambda(r)$:

$$\mathcal{V}(\lambda) = \sum_{i<j}^{N}\sum v_\lambda(i,j) \qquad (1.6.62)$$

dependence on coordinates omitted

Excess free energy $A(\lambda)$ is given by:

$$-\beta A(\lambda) = \ln\left[\underset{\text{depends on } N,V,T}{Z}(\lambda)/V^N\right] = \ln\left[\int \exp[-\beta\mathcal{V}(\lambda)]\, d\underset{\sim}{r}^N / V^N\right]$$

Approximation:

$$g_0(r) \simeq y_d(r)\ \exp[-\beta u_0(r)] \qquad (1.6.70)$$

insensitive to exact form of potential. A hard-sphere property; calculable, as soon as d is known.

soft repulsive core of reference fluid

What is the best way to choose the equivalent hard sphere diameter d for CWA?

Choice: Match the isothermal compressibilities of the reference system and the equivalent hard sphere system:

$$\kappa_{T,0} = \kappa_{T,d} \ \underset{\substack{(1.6.46)\\(1.6.70)}}{\overset{(1.6.35)}{\Longrightarrow}} \ \int d\underset{\sim}{r}\left[y_d \exp\{-\beta u_0\} - 1\right] = \int d\underset{\sim}{r}\left[y_d \exp(-\beta u_d) - 1\right] \qquad (1.6.71)$$

Eq (1.6.71) is an equation in d.
It gives the equivalent hard sphere diameter as a function of temperature and density.

$d\downarrow$ as $T\uparrow$

The theoretical justification for condition (1.6.71) actually lies in a functional Taylor expansion of the excess Helmholtz energy density in powers of $\exp[-\beta u_0(r)] - \exp[-\beta u_d(r)]$ (see Hansen + McDonald, p156)