Chapter 32 - **STRUCTURE FACTORS FOR PARTICULATE SYSTEMS**

Scattering factors from nanostructures consisting primarily of particles (think spheres) in a background medium (think solvent) are described here in the case of non-dilute systems. The Ornstein-Zernike approach is a suitable way to describe inter-particle contributions.

1. THE ORNSTEIN-ZERNIKE EQUATION

The radial distribution function for a pair of scattering particles with no internal structure separated by a distance r is called g(r). It is the probability of finding a scatterer at radial distance r provided that there is a scatterer at the origin. g(r) is related to the inter-particle interaction potential U(r) as follows:

$$g(r) = \exp[-U(r)/k_B T] \,. \qquad (1)$$

Since the potential of mean-force U(r) contains contributions from many-body interactions, it is expanded in terms of binary (w_{ij}), ternary (w_{ijk}), and higher order interactions:

$$U(r) = \sum_{i,j} w_{ij}(r) + \sum_{i,j,k} w_{ijk}(r) + \ldots \qquad (2)$$

Note that g(r) is zero for very short distances since two particles cannot occupy the same space and is equal to one for large distances since at far enough distance, a particle can be located for sure.

Direct interactions between the pair of interacting particles are represented by the direct correlation function c(r) whereas interactions through other particles are represented by the total correlation function h(r) = g(r) -1.

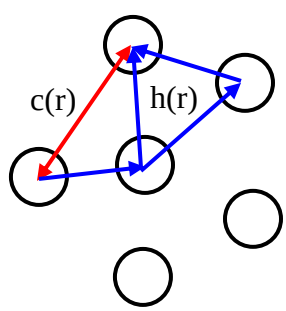

Figure 1: Direct and indirect inter-particle interactions.

The Ornstein-Zernike integral equation (Ornstein-Zernike, 1918; Hansen-McDonald, 1986) is a relation between the direct correlation function c(r) and the total correlation function h(r).

$$h(\vec{r}) = c(\vec{r}) + \overline{N}\int d\vec{r}'\, c(\vec{r} - \vec{r}')h(\vec{r}') . \qquad (3)$$

$\overline{N} = N/V$ is the particle number density.

In the Fourier variable space, this equation reads:

$$H(Q) = C(Q) + \overline{N}\, C(Q)\, H(Q) . \qquad (4)$$

The inter-particle structure factor is defined as:

$$S_I(Q) = 1 + \overline{N}\, H(Q) = \frac{1}{1 - \overline{N}C(Q)} . \qquad (5)$$

Note that the Ornstein-Zernike equation contains two unknowns (h(r) and c(r)). It can be solved only if another (so called "closure") relation is added. Many of these closure relations have been introduced (hypernetted chains, Born-Green, Percus-Yevick, Mean Spherical Approximation, etc). Using one such closure relation, numerical solutions of the Ornstein-Zernike equation yield realistic inter-particle structure factors. The last two closure relations (Percus-Yevick and Mean Spherical Approximation) are discussed here because they permit simple analytical solutions to the integral equation.

Three inter-particle interaction potentials can be considered: hard sphere, screened Coulomb and square well. The hard sphere potential is used with the Percus-Yevick closure relation and the screened Coulomb potential is used with the Mean Spherical Approximation.

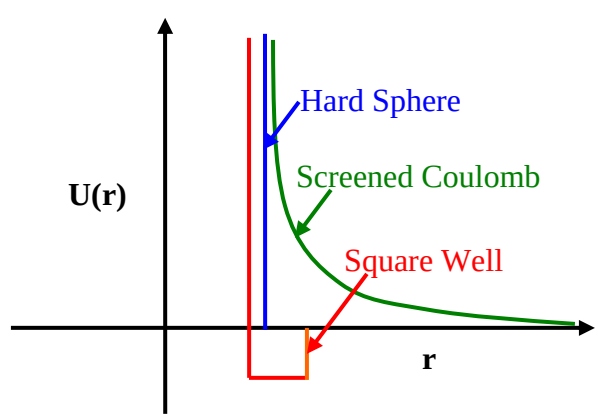

Figure 2: Representation of the various inter-particle interaction potentials.

2. THE PERCUS-YEVICK APPROXIMATION

The Percus-Yevick approximation (Percus-Yevick, 1958) uses the following closure relation in order to solve the Ornstein-Zernike integral equation:

$$c(r) = g(r)\left[1 - \exp\left(-\frac{w(r)}{k_B T}\right)\right]. \qquad (6)$$

Assume the following hard sphere interaction potential between particles:

$$\begin{aligned} w(r) &= 0 \qquad \text{for } r > D \\ w(r) &= \infty \qquad \text{for } r < D\,. \end{aligned} \qquad (7)$$

Here D is the sphere diameter. Solution to the Ornstein-Zernike equation is analytical:

$$\begin{aligned} c(r) &= 0 \qquad \text{for } r > D \\ c(r) &= -\lambda_1 - 6\phi\lambda_2 \frac{r}{D} - \frac{\phi}{2}\lambda_1 \frac{r^3}{D^3} \qquad \text{for } r < D\,. \end{aligned} \qquad (8)$$

The following parameters have been defined:

$$\begin{aligned} \lambda_1 &= \frac{(1+2\phi)^2}{(1-\phi)^4} \\ \lambda_2 &= \frac{-(1+\phi/2)^2}{(1-\phi)^4}\,. \end{aligned} \qquad (9)$$

ϕ is the particle volume fraction ($\phi = \pi\overline{N}D^3/6$), $\overline{N}$ is the density of scattering particles and D is the "effective" particle diameter.

The Fourier transform of the direct correlation function can be calculated as:

$$\overline{N}C(Q) = -24\phi\left\{\lambda_1\left[\frac{\sin(QD)-(QD)\cos(QD)}{(QD)^3}\right] - 6\phi\lambda_2\left[\frac{(QD)^2\cos(QD)-2(QD)\sin(QD)-2\cos(QD)+2}{(QD)^4}\right]\right.$$

$$\left. -\phi\frac{\lambda_1}{2}\left[\frac{(QD)^4\cos(QD)-4(QD)^3\sin(QD)-12(QD)^2\cos(QD)+24(QD)\sin(QD)+24\cos(QD)-24}{(QD)^6}\right]\right\} \qquad (10)$$

The structure factor for a liquid of structureless particles is given by:

$$S_I(Q) = \frac{1}{1 - \overline{N}C(Q)} \qquad (11)$$

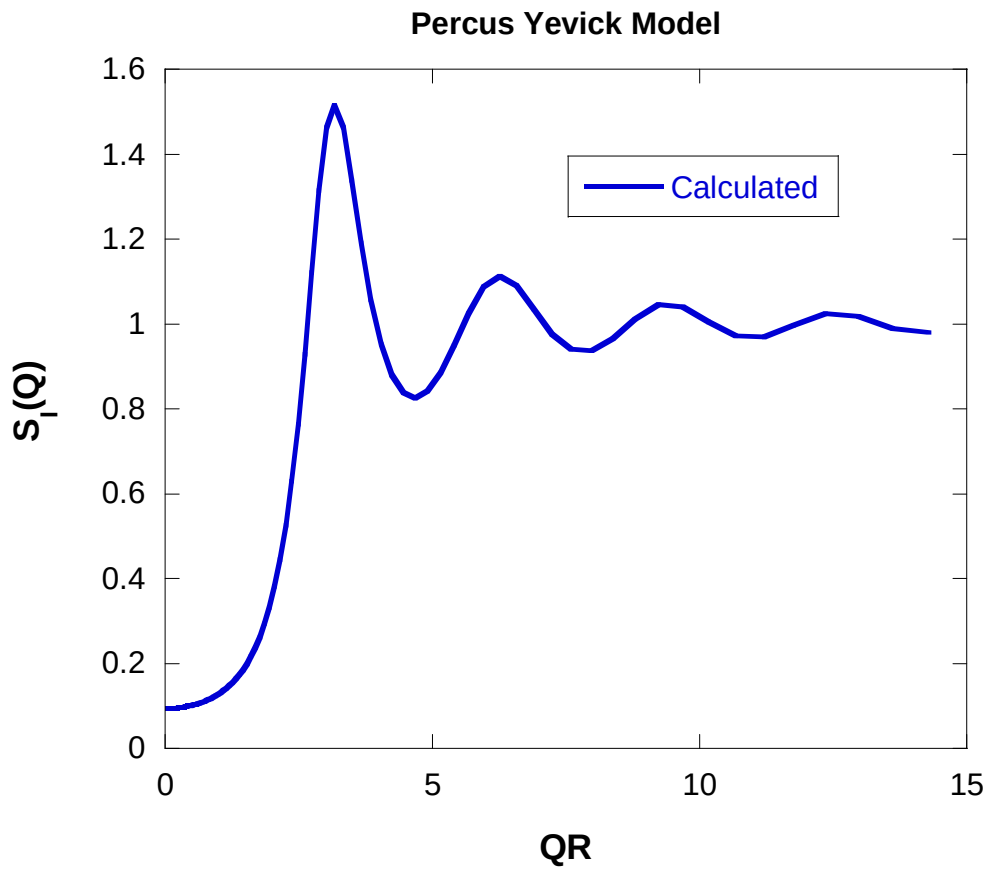

Figure 3: Inter-particle structure factor $S_I(QR)$ *vs* QR prediction from the Percus-Yevick model (with hard sphere potential) for $\phi = 0.30$. Note that the sphere radius is R = D/2.

The scattering cross section involves the product of the form factor and the structure factor:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 \phi V_P P(Q) S_I(Q). \qquad (12)$$

Here $\Delta\rho^2$ is the contrast factor, ϕ is the volume fraction and V_P is the particle volume ($V_P = 4\pi R^3/3$). Note that in this simple "hard sphere" interaction potential model, the sphere diameter that enters in the form factor is taken to be the same as the hard sphere radius used in the structure factor.

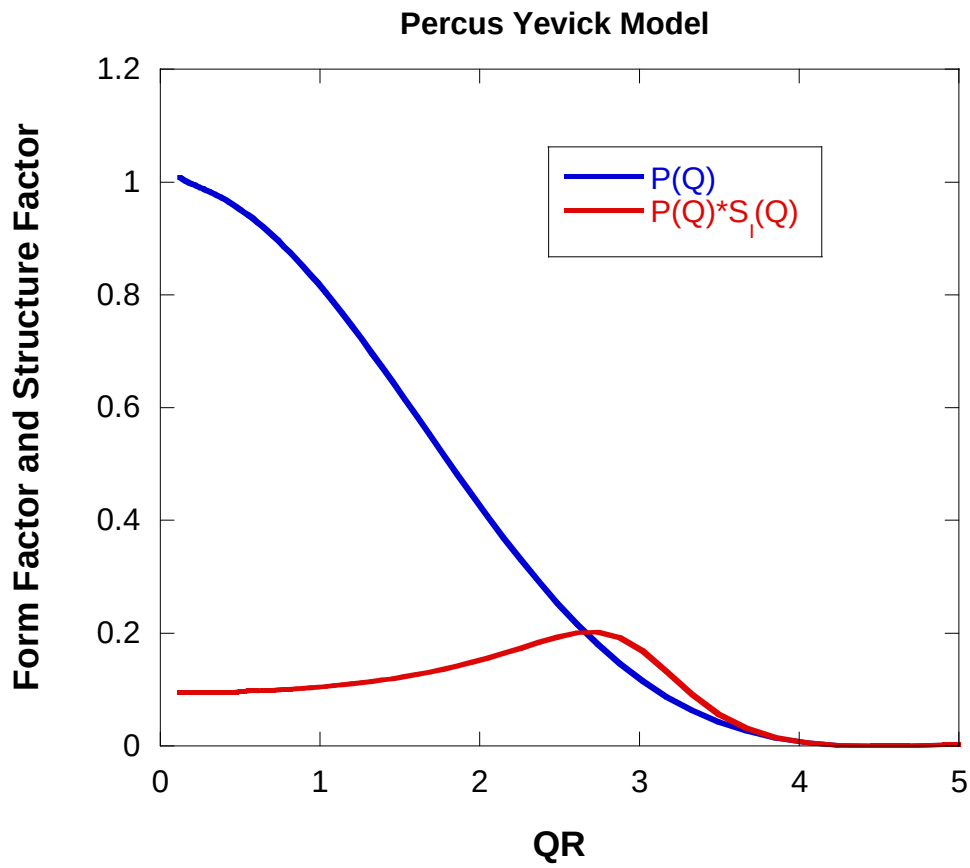

Figure 4: Form factor P(Q) for isolated spheres (infinite dilution limit), and product $P(Q)S_I(Q)$ for a solution of spheres with a volume fraction of $\phi = 0.30$. The Percus-Yevick model (hard sphere potential) has been used to model the inter-particle structure factor $S_I(Q)$.

3. THE MEAN SPHERICAL APPROXIMATION

When Coulomb interactions are present, another closure relation to the OZ equation is applied; the Mean Spherical Approximation (Hayter-Penfold, 1981). Consider a scattering system consisting of macroions (charged positive), counter ions (charged negative) and solvent. The Coulomb interaction potential is defined as:

$$U(r) = \pi\varepsilon_0\varepsilon D^2\psi_0^2\frac{\exp(-\kappa(r-D))}{r} \text{ for } r > D. \qquad (13)$$

The macroion surface interaction potential is given by:

$$\psi_0 = \frac{z_m}{\pi\varepsilon_0\varepsilon(2+\kappa D)}. \qquad (14)$$

The following parameters have been defined:

ε_0: Permittivity of free vacuum
ε: Dielectric constant
D: Macroion diameter
κ : Debye-Huckel inverse screening length
z_m: Macroion electric charge (number of electrons).

The Debye-Huckel screening parameter (inverse length) squared is expressed as follows:

$$\kappa^2 = \frac{e^2}{k_B T} z_m \overline{N} \qquad (15)$$

Here e is the electron charge, $z_m e$ is the macroion charge, $\overline{N}$ is the macroion number density (number per unit volume) and $k_B T$ is the sample temperature in absolute units.

Dimensionless parameters are defined:

$$x = \frac{r}{D}, \; k = \kappa D, \; K = QD \text{ and } \beta = \frac{1}{k_B T}. \qquad (16)$$

Along with the following contact potential (for r = 2D) as:

$$\gamma \exp(-k) = \beta \pi \varepsilon_0 \varepsilon \psi_0^2. \qquad (17)$$

The Mean Spherical Approximation (MSA) closure relation to the Ornstein-Zernike equation is given by:

$$c(r) = -\beta U(r) \qquad \text{for } r > D \qquad (18)$$
$$h(r) = -1 \qquad \text{for } r < D.$$

Note that the limiting case for which $\gamma \to 0$ or $k \to \infty$ yields the Percus-Yevick result.

The MSA closure is used to solve for c(r):

$$c(r) = A + Bx + \frac{1}{2}\phi A x^3 + \frac{C \sinh(kx)}{x} + \frac{F(\cosh(kx) - 1)}{x} \qquad \text{for } x<1$$
$$c(r) = -\gamma \frac{\exp(-kx)}{x} \qquad \text{for } x>1. \qquad (19)$$

The structure factor is obtained as:

$$S_I(Q) = \frac{1}{1 - \overline{N}C(Q)} \tag{20}$$

With:

$$\begin{aligned}\frac{\overline{N}C(Q)}{24\phi} = {} & \frac{A\left(\sin(K) - K\cos(K)\right)}{K^3} + \frac{B\left[\left(\frac{2}{K^2} - 1\right)K\cos(K) + 2\sin(K) - \frac{2}{K}\right]}{K^3} \\ & + \frac{\phi A\left[\frac{24}{K^3} + 4\left(1 - \frac{6}{K^2}\right)\sin(K) - \left(1 - \frac{12}{K^2} + \frac{24}{K^4}\right)K\cos(K)\right]}{2K^3} \\ & + \frac{C\left(k\cosh(k)\sin(K) - K\sinh(k)\cos(K)\right)}{K\left(K^2 + k^2\right)} \\ & + \frac{F\left[k\sinh(k)\sin(K) - K\left(\cosh(k)\cos(K) - 1\right)\right]}{K\left(K^2 + k^2\right)} \\ & + \frac{F\left(\cos(K) - 1\right)}{K^2} - \frac{\gamma\exp(-k)\left(k\sin(K) + K\cos(K)\right)}{K\left(K^2 + k^2\right)}.\end{aligned} \tag{21}$$

The macroion volume fraction $\phi = \pi\overline{N}D^3/6$ has been expressed in terms of the macroion number density $\overline{N}$. The forward scattering limit is given by $S_I(0) = -1/A$.

Note that expressions for the constants A, B, C, and F are too lengthy to reproduce here. They can be found in the original publication (Hayter-Penfold, 1981). F is the solution of a 4th power polynomial equation.

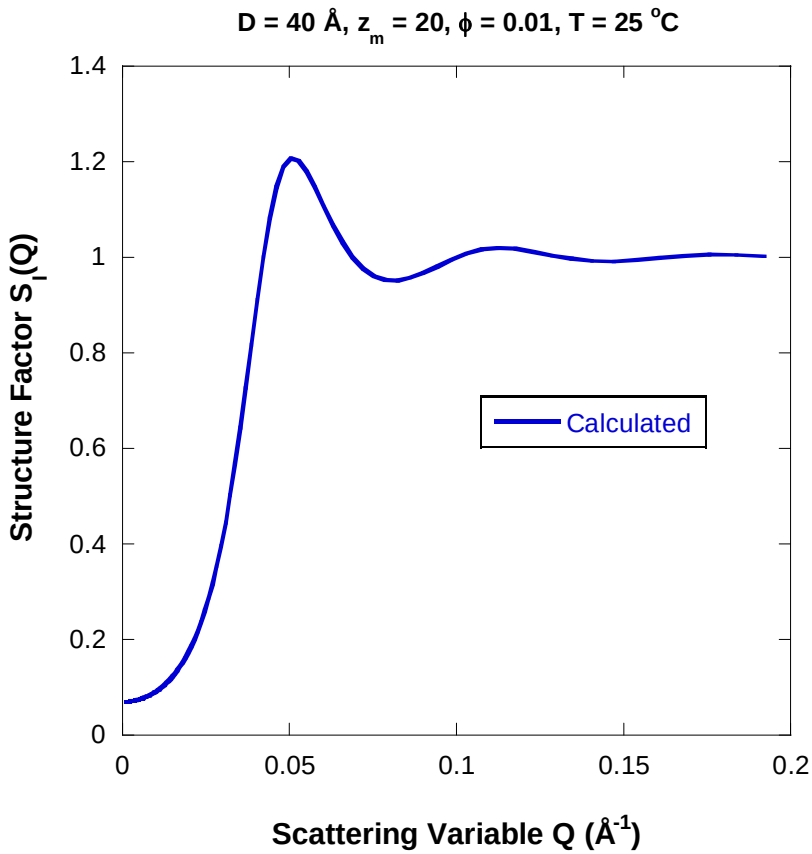

Figure 5: Variation of the structure factor $S_I(Q)$ obtained from the MSA for a spherical macroion diameter of D = 40 Å, macroion charge of z_m = 20 electrons, a volume fraction of ϕ = 0.01 and at T = 25 ^oC. The dielectric constant ε = 78 is for D_2O at 25 ^oC.

4. THE RANDOM PHASE APPROXIMATION

Consider now particles with internal structure or polymers made out of spherical monomeric units. Note that spheres are assumed to fill the particles or replace the monomers in polymers. The Random Phase Approximation (RPA) provides another closure relation used to solve the OZ equation. The RPA assumes that $c(r) = -w(r)/k_B T$. Note that within the RPA, different notation is used for interaction potentials. By convention, these are called w(r) for polymers and U(r) for particulate systems.

The intra-particle contributions are included in the Ornstein-Zernike equation as follows (in Fourier space):

$$H(Q) = S_0(Q)C(Q)S_0(Q) + S_0(Q)C(Q)\overline{N}H(Q). \qquad (22)$$

Along with the RPA closure relation:

$$\overline{N}C(Q) = -\frac{W(Q)}{k_B T}. \tag{23}$$

This closure is reminiscent of the MSA closure relation for r > σ. Note the following relations for particles with internal structure (or polymers with spherical monomers):

$$S_I(Q) = \frac{1}{1 - S_0(Q)\overline{N}C(Q)} \tag{24}$$

$$S(Q) = S_0(Q)S_I(Q) = \frac{S_0(Q)}{1 - S_0(Q)\overline{N}C(Q)}$$

It follows that:

$$S^{-1}(Q) = S_0^{-1}(Q) + \frac{W(Q)}{k_B T}. \tag{25}$$

This is the Random Phase Approximation result obtained for compressible polymer mixtures. The scattering cross section is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \Delta\rho^2 S(Q). \tag{26}$$

Note that this approach can be extended to the multi-component case by changing the various structure factors to matrices.

The scattering factor for polymer mixtures S(Q) and the structure factor for particulate systems $S_I(Q)$ are related by the relationship:

$$S(Q) = \phi_1 V_1 P_1(Q) S_I(Q). \tag{27}$$

Here ϕ_1, V_1 and $P_1(Q)$ are the volume fraction, polymer volume and form factor for polymer component 1. Recall that within the incompressible RPA, the structure factor $S_I(Q)$ is given by:

$$S_I(Q) = \frac{S_{22}^0(Q)}{S_{11}^0(Q) + S_{22}^0(Q) - 2\frac{\chi_{12}}{v_0} S_{11}^0(Q) S_{22}^0(Q)}. \tag{28}$$

The scattering factor S(Q) is therefore proportional to $\phi_1\phi_2$ as it should.

Note also that the mean field approximation does not model the local interactions properly for inter-particle inter-distances smaller than particle sizes since packing effects on thermodynamics and phase separation are neglected. For this reason, the g(r) obtained from such a mean field approach does not show realistic oscillations for the neighboring coordination shells. The appeal of this approach, however, is that it gives simple analytical results.

REFERENCES

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L.S. Ornstein and F. Zernike, Phys. Z. 19, 134 (1918)

J.K. Percus, G.J. Yevick, “Analysis of Classical Statistical Mechanics by Means of Collective Coordinates”, Phys. Rev. 110 1 (1958).

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QUESTIONS

1. Does a numerical solution to the Ornstein-Zernike integral equation (with a realistic closure relation) describe local packing adequately? How about a mean field analytical solution (using the mean spherical approximation)?
2. Can the scattering cross section for a concentrated solution of particles (colloidal suspension for example) be described as the product of a single-particle and an inter-particle structure factors?
3. Name the closure relation that yields an analytical solution to the OZ integral equation in the case of hard sphere interaction potential.
4. What approach gives the most realistic solution to the Ornstein-Zernike equation?
5. What is the Mean Spherical Approximation (so called MSA)? What systems are well described by the MSA?
6. Are the Random Phase Approximation (used to describe polymer systems) and the Ornstein-Zernike equation (used to describe particulate systems) related at all?

ANSWERS

1. A numerical solution to the Ornstein-Zernike integral equation along with a realistic closure relation describes local packing well. A mean field analytical solution is too simplistic and yields correct overall trends but incorrect local packing information.

2. The scattering cross section for a concentrated solution of particles can be described as the product of a single-particle and an inter-particle structure factors provided that the particles are not elongated (i.e., are isotropic).
3. The Percus-Yevick closure relation yields a simple analytical solution to the OZ integral equation for the hard sphere interaction potential.
4. A numerical solution to the Ornstein-Zernike equation along with one of the closure relations gives more realistic results than highly approximated analytical solutions.
5. The Mean Spherical Approximation (MSA) is a closure relation used to solve the Ornstein-Zernike equation. Charged systems are well described by the MSA since Coulomb interactions are included. The MSA yields analytical (albeit lengthy) results.
6. The Random Phase Approximation (used to describe polymer systems) is a mean-field closure relation to the Ornstein-Zernike equation. The RPA closure is a simplified form of the MSA closure.