Chapter 2

Theoretical Considerations

2.1. Pore structure

A porous material has a wide range of pore spaces known as pores and the narrow connecting regions called as throats. The geometry of pores is the most important property of porous media for various applications. The pores in a porous medium are further classified as open pores, closed pores or blind pores. Pores store a liquid or a gas whereas throats usually help in the transport of fluid between pores. A pore network is obtained in a compacted sample. In a network, the pores can be spherical, cylindrical, square, and triangular. Different regions of a porous body are schematically shown in Figure (2.1).

![Classification of pores in a porous medium.](image)

**Figure 2.1.** Classification of pores in a porous medium.

A porous solid has two phases; a pore phase and a solid phase. The total volume in a porous medium is that due to the total contribution from both the volume of pore ($V_{\text{pore}}$) and volume of solid ($V_{\text{solid}}$):
Porosity $\phi$ in terms of volume is given by the ratio of volume of pore to the total bulk volume of the medium. The fractional volume of pores is given by:

$$V_{total} = V_{pore} + V_{solid}$$

$$\phi = \frac{V_{pore}}{V_{total}}$$ (2.1)

And $(1-\phi)$ is the fractional solid volume in the sample.

### 2.2. Effect of compaction and sintering on pore structure

Particle size, shape, packing and sorting affects the porosity of a porous solid. Arrangement of grains in a porous medium is also responsible for variation of porosity. In order to explain the dependence of porosity on the arrangement of grains, consider a grain of spherical shape. For a cubic packing of identical spherical grains, the maximum theoretical porosity is 47.6 % [Collins R.E., 1976] in which cubic spaces can be fitted into the pores. For a rhombohedral packing of spheres the maximum porosity is 26 % in which tetrahedral spaces can be fitted into the pores. Porosity reduces further if smaller spheres are introduced in the structure as shown in Figure (2.2). Compaction decides the packing type and leads to reduction in volume with externally applied pressure. The variation of porosity with change in pressure is given by:

$$\phi_2 = \phi_1 e^{C_f(P_2-P_1)}$$ (2.2)

Where $\phi_1$ and $\phi_2$ are porosities at pressures $P_1$ and $P_2$, and $C_f$ is the formation compressibility which is a summation of both grain and pore compressibility:

$$C_f = -\frac{1}{V} \frac{dV}{dP}$$
In the case of clay the grains are plate-like and are expected to be susceptible to compaction. Hence the porosity $\phi$ of clay decreases with increasing depth below the Earth’s surface. The variation of porosity in clay with depth is represented by [Athy, 1930].

$$\phi = \phi_0 e^{-az}$$  \hspace{1cm} (2.3)

where $z$ is the depth

![diagram](image)

**Figure 2.2.** a) Cubic packing, b) rhombohedral packing, c) cubic packing with two grain sizes d) floral arrangement.

### 2.3. Theory of flow through porous media

There are three basic equations for a fluid flow through porous media.

#### 2.31. Darcy’s law

The permeability $\kappa$ of a porous material is defined as its fluid conductivity [Collinis R.E., 1976]. Flow through a porous matrix for low Reynolds number ($Re < 1$) is governed by Darcy’s law (1956), which states that the fluid flux $q$ (discharge per unit area) is related to the applied pressure gradient $\nabla p$ by the linear relation [Bear J.,1972].

$$q = -\frac{\kappa}{\mu} \nabla p$$  \hspace{1cm} (2.4)

where $\kappa$ is the permeability, $\mu$ is the dynamic viscosity,
Thus the permeability of a porous material is in units of ‘Darcy’ which is defined as the flow rate of one cubic centimetre per second when a pressure difference of one atmosphere is applied across a cube having unit dimension.

Figure 2.3. Schematic showing definition of Darcy’s law.

2.3.2. Kozeny–Carman equation

The relation between permeability $\kappa$ and porosity $\phi$ is given by Koponen [Koponen et al., 1998]. For a tortuous flow through a porous medium, the empirical relation between measurable properties of porous media and fluid permeability is provided by Kozeny [Macieja et al., 2008]

\[ k = C_0 \frac{\phi^3}{T^2 S^2} \]  

(2.5)

$T$ is the hydraulic tortuosity, $S$ is the specific surface area, $C_0$ is a dimensionless Kozeny constant that depends on the geometry of the capillary channel [Bear J., 1972]. Equation (2.5) as modified by Kozeny-Carman is given by:
\[ k = \frac{r_{eff}^2}{8F} \]  

(2.6)

Where \( r_{eff} \) is the effective radius of the capillary channel, \( F \) is the formation factor which, in terms of porosity is given by:

\[ F = \frac{\tau}{\phi} \]

Formation factor is the obstruction offered by a porous medium to the transport of ions or uncharged molecules and is purely a geometric parameter.

### 2.4. Swelling in clay

The interlayer swelling for Na-bentonite and Li-smectite is explained by various authors [Sposito and Prost, 1982; Mielenz and King, 1955; Holtz and Bara, 1965; Parcher and Liu, 1965; Seed et al., 1962]. The linear equation for swelling is given below [Fink, D. H. and Nakayama, 1972; Fink D.H., 1977].

\[
d = \left[ 9.4 - \frac{\mu a}{S_i} \right] + \left[ \frac{\mu (1 - b)}{S_i} \right] W_t \]

(2.7)

where the thickness of the individual platelet is 9.4 Å, \( d \) is the average spacing of the clay platelets and \( W_t \) is the total amount of water present per gm of clay. The plot of \( d \) vs \( W_t \) is linear. The plot gives intercept of \([9.4 - \mu a/S_i]\) and slope of \([\mu(1 - b)/S_i]\). The shrinkage in dried bentonite is mainly due to structural change in the mineral which in turn causes change in porosity.
2.5. Capillary rise in hydrology

In hydrology capillary action is responsible for moving groundwater from a wet area of soil to a dry area. The difference in soil matrix potential drives capillary action. Capillary action is possible when the adhesive intermolecular forces between the liquid and the substance are stronger than the cohesive intermolecular forces inside the liquid. The same effect is responsible for porous material soaking up liquid. The narrower the tube, the higher the rise in water column. The rise in height can be obtained from the following:

\[ h = \frac{2\sigma \cos \alpha}{\rho gr} \]  \hspace{1cm} (2.8)

where \( h \) is the height of rise of fluid in the capillary tube; \( \sigma \) is surface tension of fluid against air; \( \alpha \) is angle of contact of water with the tube; \( \rho \) is the density; \( g \) is the acceleration due to gravity and \( r \) is the equivalent radius of tube.

2.6. Models of porous media

Various mathematical models have been used to understand flow of fluid through porous media. Moisture flow properties of porous media are usually determined based on experiments [Bear J., 1972; Sahima M., 1995; Miguel A., 2000]. The easiest model used to depict the flow through a porous medium assumes the medium to be a bundle of capillary tubes [Scheidegger, 1953]. Several authors have discussed the capillary model and have investigated the correlation of permeability with average pore size or with the pore size distribution curve. A porous material may also be represented by a rectangular network, in which the bonds represent the pores and the nodes the connections between the pores. The connectivity between pores can be found using the equation [Vasconcelos W. L., 1990]:

\[ G_v + N_v = B_v + V_v \]  \hspace{1cm} (2.9)
Where for porous glass if, $G_V$ is the number of connections of pores per unit volume also referred to as connectivity, $N_V$ denotes number of nodes, $B_V$ is the number of branches and $V_V$ is the volume fraction of pores. For cylindrical pores of equal length $L$, and individual diameter $D$, the connectivity may be schematically represented as shown in Figure (2.4).

![Figure 2.4. Schematic of cylindrical pore connectivity.](image)

From the model proposed by Vasconcelos, pore connectivity can be obtained by:

$$G_V = \frac{S_V^3}{32\pi V_V(1 - V_V)} + 1 \quad (2.10)$$

And permeability $K_p$ can be obtained by relation:

$$K_p = \frac{V_V r_p^2}{16c} \quad (2.11)$$

$C$ is a constant and for cylindrical pore is 8.

### 2.7. Small angle scattering in porous media

Various techniques can be used to probe the structure of a porous material: Neutron, X-ray and electron diffraction; Small Angle Neutron Scattering (SANS) [Mazumder et al., 2004] and the similar technique using X-rays (SAXS); optical microscopy; Scanning Electron Microscopy (SEM); and Transmission Electron
Microscopy (TEM). The scales that can be probed by small angle scattering as well as various other instruments are shown in Figure (2.5). Small Angle Scattering (SAS) can be used in the characterisation of nanopores in porous media, as this provides information about geometry and morphology of inhomogeneities, typically in the size range 1 nm to 500 nm.

SAS involves the change in momentum of radiation (X-ray, neutron, light etc) due to the interaction of the beam with the molecules of the sample. When there is change in the direction of the beam without exchange of energy with the molecules of the sample, the scattering is called elastic scattering. In case of SANS, neutrons are scattered whereas it is photons that are scattered in the case of SAXS. The scattering originates due to density fluctuations or structural inhomogeneities in the material. Scattering from nanoporous media have sizes of inhomegeneities that fall within the measureable range of SANS making the method useful in the present study. Scattering is based on the principal that a monochromatic plane wave is scattered by the material through an angle ‘θ’. The scattered intensity is measured as a function of scattering wave vector, Q, which in elastic scattering has the magnitude:

\[ Q = \frac{4\pi}{\lambda} \sin(\theta) \]  

(2.12)

where \( \lambda \) is the incident wavelength of neutrons and \( \theta \) is the scattering angle.
Figure 2.5. Various experimental techniques and their length scales.
2.7.1. **Salient features of neutrons**

The salient features of neutrons that make them suitable for use in a scattering experiment are given below.

1. The absorption of neutrons by matter is small as they do not have charge. Due to their neutral nature and magnetic dipole moment, neutrons can penetrate matter and interact with the atoms via nuclear and magnetic scattering. Thus, properties of the bulk and magnetic structure can both be measured.

2. The neutron’s wavelength is comparable to inter-atomic spacing while its kinetic energy is similar to the energy of excitation in a solid; hence neutrons can be used in the determination of both position and motion of atoms in condensed matter.

3. In the case of X-ray the scattering length increases with atomic number whereas there is a random variation of neutron scattering length with atomic number. Moreover, isotopes of the same element may show different scattering lengths.

4. The feature of the scattering cross section differing for different isotopes is put to good use in the technique known as contrast matching in SANS.

2.7.2. **Scattering length and scattering cross section**

The neutron scattering length is related to how strongly a particular nucleus will scatter neutrons. Scattering length per unit volume (scattering length density ‘ρ’) for a homogeneous sample consisting of ‘n’ isotopic species is given by

\[
\rho = \frac{\sum_{i} b_i}{V}
\]  

(2.13)
where \( \rho \) is the scattering length density, \( b_i \) is scattering length of a particular atom and \( V \) is volume occupied by \( n \) atoms. For a monochromatic incident plane wave \( e^{ik_0r} \) interacting with the scatterer the scattered wave is represented as \( \psi = -\frac{b}{r} e^{ikr} \) where \( k_0 \) and \( k \) are incident and scattered wave vectors respectively, \( b \) is the bound scattering length.

The momentum transfer vector \( \mathbf{Q} \) for elastic scattering \( k = k_0 \) is given by Figure (2.6)

\[
Q = |\mathbf{k} - \mathbf{k}_0| = \frac{4\pi \sin \theta}{\lambda}
\] (2.14)

Where \( \lambda \) is the incident wavelength of neutrons.

![Figure 2.6. Schematic of momentum transfer vector Q.](image)

The scattering cross section is the effective area of collision. The differential scattering cross section \( d\sigma/d\Omega \) gives the probability of scattering into the solid angle \( d\Omega \).

In a scattering experiment at small momentum transfer values, the measured differential scattering cross-section from a sample of volume \( V \), referred to as the scattered
intensity $I(Q)$ or the macroscopic differential scattering cross-section $d\Sigma/d\Omega$, may be written in terms of the scattering length density difference (per unit volume) between a scattering particle $\rho_p$ and its surrounding matrix $\rho_m$:

$$I(Q) = \frac{(\rho_p - \rho_m)^2}{V} \left\langle \frac{1}{V_p} \int \exp(-iQ \cdot r) \, dr \right\rangle^2$$  \hspace{1cm} (2.15)

In the context of a material having pores whose dimensions are of the order of the incident wavelength, $\rho_p$ refers to the scattering length density of the pore (typically air or vacuum) while $\rho_m$ refers to the scattering length density of the material (sum of scattering length values of each of the constituent atoms of the composition unit multiplied by the number of such units in an unit volume).

If $R_k$ is the position vector of the $k^{th}$ pore and $F_k(Q)$ is the form factor associated with a pore then equation (2.15) can be written as

$$I(Q) = (\rho_p - \rho_m)^2 V_p^2 \left\langle \sum_k F_k(Q) \exp(-iQ \cdot R_k) \right\rangle^2$$  \hspace{1cm} (2.16)

Where \( F(Q) = \frac{1}{V} \int_P \exp(-iQ \cdot r) \, dr \)

For monodispersed pores or particles the equation can be expressed as [Glatter and Kratky, 1982]:

$$I(Q) = \frac{N_p(\rho_p - \rho_m)^2 V_p^2}{V_{\text{sample}}} \langle |F(Q)|^2 \rangle \cdot \frac{1}{N_p} \left\langle \sum_k \exp(-iQ \cdot R_k) \right\rangle^2$$  \hspace{1cm} (2.17)

The equation can be simplified as
\[ I(Q) = \frac{N_p (\rho_p - \rho_m)^2 V_p^2}{V_{\text{sample}}} P(Q) S(Q) \]  \hspace{1cm} (2.18)

where \( P(Q) \) is the single particle structure factor and \( S(Q) \) is the inter particle structure factor.

\[ P(Q) = \langle |F(Q)|^2 \rangle \]  \hspace{1cm} (2.19)

and

\[ S(Q) = \frac{1}{N_p} \left| \sum_k \exp(iQ \cdot R_k) \right|^2 = \frac{1}{N_p} \left\langle \sum_k \sum_k \exp(iQ \cdot (R_k - R_k')) \right\rangle \]  \hspace{1cm} (2.20)

\( P(Q) \) depends on the shape and size of the inhomogeneities/scattering centres, while the interparticle correlation is determined by \( S(Q) \). For a dilute system where the inhomogeneities are spaced far enough apart that the correlation between them is negligible [\( S(Q) \approx 1 \)], if \( N_p \) is the number density of inhomogeneities or pores, the above equation can be written as:

\[ I(Q) = \frac{N_p (\rho_p - \rho_m)^2 V_p^2}{V_{\text{sample}}} P(Q) \]  \hspace{1cm} (2.21)

The variations of \( P(Q) \) and \( S(Q) \) with \( Q \) for a hypothetical sample are sketched below Figure (2.7) together with the case when both functions are significant in a given sample.
Figure 2.7. The sketch of $P(Q)$ and $S(Q)$. 
2.7.3. Form factor of simple geometric objects

The expressions for $P(Q)$ of some standard shapes are listed below [Glatter and Kratky, 1982; Guinier and Fournet, 1955]:

1. Sphere shaped particles of radius $R$ the form factor is given by:

$$P(Q) = \left[ \frac{3(sin QR - QR cos QR)}{QR^3} \right]^2 \quad (2.2)$$

2. Cylindrical particle with radius $R$ and length $2l$

$$P(Q) = \int_0^{\pi} \frac{\pi \sin^2(Q l \cos \theta) 4 J_1^2(Q R \sin \theta)}{Q^2 l^2 \cos^2 \theta \ Q^2 R^2 \sin^2 \theta} \sin \theta d \theta \quad (2.23)$$

$J_1(x)$ is a Bessel function and $\theta$ is the angle subtended by the principal axis of the cylinder with $Q$.

3. For an ellipsoidal core-shell model of inner radius $R_1$ and outer radius $R_2$

$$P(Q) = \left[ (\rho_c - \rho_{shell}) V_1 \frac{3 J_1(Q R_1)}{Q R_1} + (\rho_{shell} - \rho_m) V_2 \frac{3 J_1(Q R_2)}{Q R_2} \right]^2 \quad (2.24)$$

Where $\rho_c$, $\rho_{shell}$ and $\rho_m$ are the scattering length densities of core, shell and solvent and $J_1(x)$ is a Bessel function.

2.7.4. Contrast Matching

For a system having two phases as in porous media viz. a pore and a matrix having scattering length densities $\rho_p$ and $\rho_m$, the scattered neutron intensity will be proportional to the contrast factor i.e. $(\rho_p - \rho_m)^2$. The scattering contrast can be varied by using isotopes of
constituent elements of either the matrix or the particle. In the case of pores as the “particles”, an appropriate fluid can be made to fill the pores such that there is a match with the scattering length density of the matrix in which case the scattering profile should either go to zero or to the combined incoherent level of fluid and matrix. For example, as the scattering length densities of hydrogen and deuterium are of opposite sign, \((b_H = -3.741 \text{ fm} \text{ and } b_D = 6.664 \text{ fm})\) there will be a combination of the two in different proportions which would exactly match the scattering length density of the matrix.

2.7.5. Guinier and Porod approximations

**Guinier Approximation**

At lower Q for a dilute solution of non-interacting monodispersed particles the scattered intensity \(I(Q)\) is given by the Guinier approximation which in terms of the radius of gyration is:

\[
I(Q) = I_0 \exp \left( -\frac{Q^2 R_g^2}{3} \right)
\]

where \(I_0\) is the scattering at \(Q = 0\).

\(R_g\) is obtained from the slope of the plot of \(\ln(I(Q))\) vs. \(Q^2\). The approximation is applicable provided \(Q R_g \leq 1\).

**Porod scattering**

Information concerning surface and volume irregularities in the medium can also be obtained by SANS. The approximation due to Porod deals with scattering from well defined volumes with clear boundaries. Many materials exhibit scattering at the higher Q range of the measured space. The proportionality of the intensity to \(Q^4\) is termed Porod’s
law [Porod G., 1951]. This is due to the fact that other structural features do not contribute to scattering in this region of \( Q \). The approximation is valid in the range \( lQ \gg 1 \)

\[
\lim_{Q \to \infty} I(Q) \propto A_s Q^{-4}
\]  

(2.26)

Where \( l \) is the reciprocal length.

\[
\lim_{Q \to \infty} I(Q) \propto A_s Q^{-(6-d)}
\]  

(2.27)

In the case of a rough surface having a fractal character (as in clusters and aggregates) the dimension \( d \) lies between 2 and 3 and the intensity follows a power law. The power law relation is given by:

\[
I(Q) \propto Q^{-D_m}
\]  

(2.28)

This gives a linear plot on a log \( I(Q) \) verses \( Q \). \( D_m \) is called the mass fractal dimension is obtained in the range \( 1 < D_m < 3 \).

The measured scattered intensity \( I(Q) \) of an ensemble of poly-dispersed spherical particles under a local monodisperse approximation can be expressed as [Pedersen J. S., 1994]

\[
I(Q) = C \int P(Q, r) r^6 D(r) S(Q, r) dr
\]  

(2.29)

where \( C \) is a scaling factor, \( D(r) \) is the pore size distribution of pores with radii \( r \).

2.8. Quasi-elastic neutron scattering

In neutron scattering one could measure the change of momentum transfer \( Q \) and the energy exchange due to interaction of the neutron beam with the nuclei of the specimen. If \( E_i \) and \( E_f \) are the initial and final energies and \( p_i \) and \( p_f \) are similarly the corresponding momentum values, then;
\[ \Delta E = E_i - E_f \]

\[ \Delta p = p_i - p_f \]

If \( \omega \) is the angular frequency corresponding to the energy transfer and \( k_i \) and \( k_f \) are the initial and final wave vectors:

\[ \Delta E = \hbar \omega \]

\[ \Delta p = \hbar (k_i - k_f) = \hbar Q \]

Two types of scattering can occur when neutrons scatter from the sample:

1. Elastic scattering - Atoms interact with the neutrons without changing their energy. Here we get information about the position of atoms, \( \Delta E = (k_i - k_f) = 0. \)

2. Inelastic scattering - there is exchange of neutron energy with the sample. From this type of scattering we can get information about the diffusion of atoms. \( \Delta E \neq 0. \) When there is a broadening of the elastic peak due to either gain or loss of energy, it is called quasielastic scattering.

In a Quasielastic Neutron Scattering (QENS) experiment, the scattered intensity is analyzed as a function of both energy and momentum transfer. The measured intensity is proportional to the double differential scattering cross section, which is the probability that the neutron is scattered with energy change \( dE = \hbar \omega \), which in turn is proportional to the incoherent scattering law \( S(Q,\omega) \) due to the large incoherent scattering cross section of hydrogen.

In general, this scattering law can be written as:
where $\sigma$ is the scattering cross-section, $S(Q, \omega)$ is the scattering law and the suffices “coh” and “inc” are coherent and incoherent components of scattering. For a hydrogenous system $\sigma_{coh} << \sigma_{inc}$ (hydrogen), hence the double differential cross section is given by [Bee M., 1988] :

$$\frac{d^2 \sigma}{d\Omega d\omega} \propto \left| \frac{k}{k_0} \right| \left[ \sigma_{coh} S_{coh}(Q, \omega) + \sigma_{inc} S_{inc}(Q, \omega) \right]$$  \hspace{1cm} (2.30)

In general the dynamical structure factor $S(Q, \omega)$ can be written as [Pradeep et al., 2004]:

$$S(Q, \omega) = A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma, \omega)$$ \hspace{1cm} (2.32)

where the first term on the right hand side is the elastic part while the second is the quasielastic part. In the second term on the right hand side, $L(\Gamma, \omega)$ is a Lorentzian function with a half width at half maxima (HWHM) $\Gamma$. The variation of (HWHM) $\Gamma$ provides information about the time scale of the motion. Out of the total scattered spectrum the contribution from elastic scattering is called the Elastic Incoherent Structure Factor (EISF) designated as $A(Q)$. EISF is the space Fourier transform of the particle distribution, taken in infinite time and averaged over all the possible initial positions. A negligible contribution of EISF generally corresponds to the presence of pure long-range translational motion. However, for localized motion e.g., rotational motion, this term is expected to have a non-zero value and the variation of EISF with $Q$ is used to determine the information about the geometry of the molecular motion.
2.9. Diffusion through a porous medium

In diffusion, atomic or molecular size particles move randomly from a region of higher to a lower concentration. Fick’s law relates the particle mass flux to the concentration gradient. It states that the flux for a steady state system moves from regions of higher to lower concentration with a magnitude proportional to the concentration gradient and is expressed as:

\[ F = -D \frac{\partial C}{\partial x} \]  \hspace{1cm} (2.33)

Where \( F \) is the diffusive flux, that measures the amount of material that will flow, through a small area, for a small time interval. \( D \) is the diffusion coefficient that describes the rate at which molecules flow. \( C \) is the pore water concentration which depends on time \( t \) and distance \( x \).

Fick’s second law relates the time rate of concentration changes to the second derivative of the concentration gradient:

\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \]  \hspace{1cm} (2.34)

In porous media diffusion is affected by the length of the diffusion path, tortuosity (\( \tau \)), the pore geometry, constrictivity (\( \delta \)). The pore diffusion coefficient \( D_p \) is related to diffusion in free (bulk) water \( D_w \) by relation

\[ D_p = \frac{\delta}{\tau^2} D_w \]  \hspace{1cm} (2.35)

Here, tortuosity (\( \tau^2 \)) [Brakel and Heertjes, 1974] is defined as the square of the ratio of the length of actual diffusion paths to the length of their projection on the \( x \)-axis, and constrictivity (\( \delta \)) as a factor accounting for the variable shape and diameter of the pores. In
most of the cases it is not possible to determine \( \delta \). The geometric factor \( G \) may be written as

\[
\frac{\delta}{\tau^2} = \frac{1}{G}
\]  

Diffusion studies of clay by quasielastic neutron scattering at microscopic scale are least influenced by geometrical particle arrangement. Movement of water in such an environment is different from bulk water motion [Cebula et al., 1981]. In this case the diffusion constant within the pore is given by:

\[
D_p = \frac{q}{G}
\] 

where \( q \) is the electrostatic constraint and \( G \) is geometric factor. At microscopic scale, geometrical restrictions are negligible \( G \approx 1 \).

Quasi-elastic Neutron Scattering (QENS) is a technique by which the broadening of the elastic diffraction peak due to scattering from a particular molecular species in a fluid is measured and related to the diffusion of such a molecular unit. The method has been successfully applied to the diffusion of propane water in the bulk as well as in enclosed volumes such as pores in zeolites [Mukhopadhyay and Mitra, 2006]. The microscopic diffusion coefficient measured by QENS can be expressed as:

\[
D_p \, (QENS) = D_{\text{clay}}(QENS) = D_w \times Q
\] 

The \( Q \) and \( G \) can be obtained by comparing macroscopic \( D_p \), microscopic \( D_p \, (QENS) \) and \( D_w \). In a porous medium all the volume is not available for diffusion; the flux flow is proportional to porosity \( \phi \). The effective diffusion coefficient \( D_e \) is given by

\[
D_e = \phi
\]
Fick’s law is modified [Crank, 1975] as:

\[ F = -D_p \varepsilon \frac{\partial C_p}{\partial x} \]  

(2.40)

\( C_p \) is the concentration of diffusion species.

### 2.10. Models of Diffusion

Various models are used in the study of diffusion of molecules in a confined region.

#### 2.10.1. Jump Diffusion Models

Jump diffusion models were developed by [Hall and Ross, 1981; Singwi and Sjölander, 1960] for short distance diffusion. In this model it is assumed that a water molecule oscillates with a certain mean square amplitude \( \langle u^2 \rangle \) around an equilibrium position and for an average time \( (\tau) \) before it jumps a distance \( l \) to another equilibrium position, where \( l^2 \gg \langle u^2 \rangle \). For this type of diffusion, the scattering function is a single Lorentzian [Bée, 1988; Jobic, 2000]. The following models differ in the jump length distribution and also in the broadening \( \Gamma_i(Q) \) of the Lorentzian curve [Jobic and Theodorou, 2007].

**a) Hall and Ross model (HR) [Hall and Ross, 1981]**

In this model the jump length distance follows a Gaussian distribution given by:

\[ \rho(r) = \frac{2r^2}{r_0^3(2\pi)^{1/2}} e^{-\frac{r^2}{2r_0^2}} \]  

(2.42)

with \( r_0 \) and \( r \) the initial and final position of the water molecule. The scattering function is given by a Lorentzian whose half-width at half-maximum (HWHM) is:
\[ \Gamma(Q) = \frac{\hbar}{\tau_t} \left[ 1 - \exp \left( - \frac{Q^2 \langle d^2 \rangle}{6} \right) \right] \] (2.42)

Where \( Q \) is the momentum transfer vector, \( \langle d^2 \rangle \) is the mean square of the jump length and \( \tau \) is the residence time of a molecule at a quasi equilibrium position with diffusion constant \( D = \frac{l^2}{6\tau_t} \); before it rapidly jumps to the next quasi equilibrium position.

b) **Singwi and Sjölander model (SS)** [Singwi and Sjolander, 1960]:

Based on the assumption that a molecule executes an oscillatory motion for a mean time \( \tau_0 \) and diffuses for mean time \( \tau_1 \) continuously repeating such a motion. If the time taken to jump in between equilibrium positions is much shorter than the residence time (\( \tau_1 \ll \tau_0 \)), the jump length distribution according to Singwi and Sjölander model is:

\[ \rho(r) = \frac{r}{r_0^2} e^{\left( \frac{r}{r_0} \right)} \] (2.43)

which leads to a broadening defined by:

\[ \Gamma_t(Q) = \frac{\hbar D Q^2}{1 + D Q^2 \tau_t} \] (2.44)

and the mean square jump length

\[ l^2 = 6r_0^2 \] (2.45)

c) **Chudley - Elliot model (CE)** [Chudley and Elliott, 1961]

Here the jump distance \( l \) is fixed in all the neighbouring sites between which the atoms vibrate.

\[ \Gamma_t(Q) = \frac{\hbar}{\tau} \left( 1 - \frac{\sin(Q.l)}{Q.l} \right) \] (2.46)
d) **Jobic model** [Jobic, 2000]

This model is an extension of the Hall and Ross model. The molecule jumps from one site to the other and is delocalised over a length. This model can be used, if the jump length is small compared to the amplitude of the delocalized vibration. The jump length distribution is given by:

\[
\rho(r) = \frac{x}{l_0 r_0 (2\pi)^{\frac{3}{2}}} e^{\left(\frac{(r-l_0)^2}{2r_0^2}\right)}
\]

(2.47)

Where the distance between two sites is \( l_0 \). The parameter \( r_0 \) accounts for the delocalization of the molecule. The mean jump length is then given by

\[
l^2 = l_0^2 + 3r_0^2
\]

The resultant broadening is given by:

\[
\Gamma_r(Q) = \frac{\hbar}{\tau} \left(1 - \frac{\sin(Q.l_0)}{Q.l_0} e^{\left(\frac{Q^2 r_0^2}{2}\right)}\right)
\]

(2.48)

All models lead to Fick’s law at low \( Q \).

### 2.10.2. Rotational motion

The model used for the rotational motion of molecules is due to Sears [Sears, 1966]. This model assumes isotropic rotation of hydrogen atoms on a spherical surface, i.e. water molecules rotate around their center of gravity. This model is expressed as:

\[
S_{rot}(Q, \omega) = j_0^2(Qa).\delta(E) + \frac{1}{\pi} \sum_{n=1}^{\infty} (2n + 1)j_n^2(Qa) \frac{l(l+1)D_R}{\omega^2 + [l(l+1)D_R]^2}
\]

(2.49)
The term $\delta(E)$ is the Dirac delta function, $j_n$ are the spherical Bessel functions, $\alpha$ is the radius of rotation of the water molecule taken as 0.98 Å (OH distance of the water molecule). $j_0^2(Qa)$ is the elastic incoherent structure factor (EISF) and $(2n + 1)j_n^2(Qa)$ are the quasi-elastic incoherent structure factors corresponding to the spherical Bessel functions $j_l(x)$, and $D_R$ is the rotational diffusion constant. $D_R$ can be obtained by the relation:

$$D_R = \frac{\hbar}{6\tau} \quad (2.50)$$