

Diffuse Double Layer

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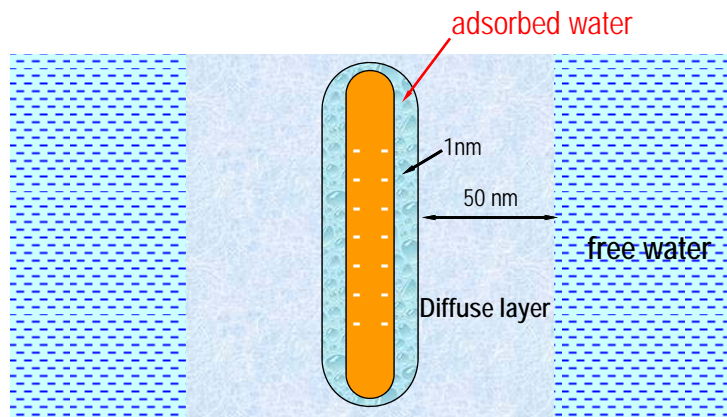
Clay particles are negatively charged due to **isomorphous substitution**, incomplete occupation of the positions available for metal ions and release of protons from hydroxides.

As a consequence of the negative charge at the surface of clay particles, **electrostatic forces exist between the negative surface and exchangeable cations.**

The **strength of these forces** is a function of:

- the charge,
- the position of the charge and
- the valence of the exchangeable cations.

Clay Particle in Water



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Diffuse Double Layers

The surface of a clay particle, being negatively charged, attracts positive ions.

This region of **attracted positive ions in solution** and the **negatively charged surface of the clay** is termed the '**diffuse double layer**'.

The diffuse double layer **occurs at the interface between the clay surface and the soil solution.**

It is **made up of:**

- the **permanent negative charge** of the clay and
- the **cations or counter-ions in the soil solution** that balance the negative charge.

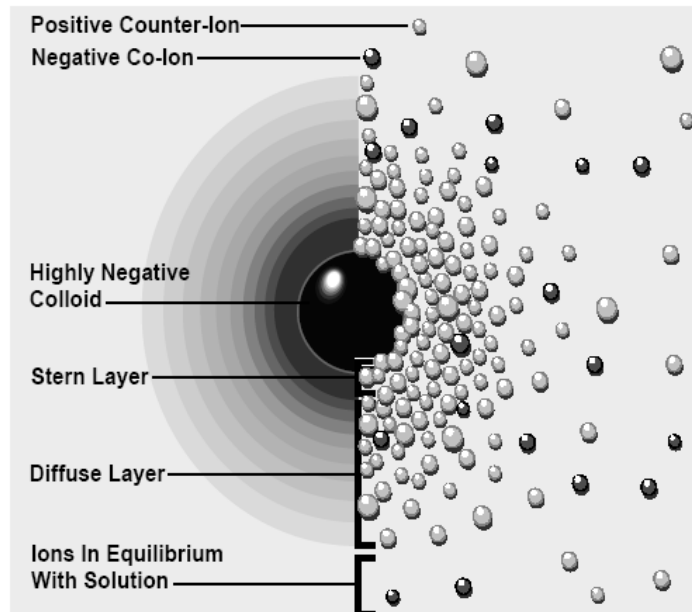
The nature and properties of such layers are highly **dependent on** the type of:

- **mineral and**
- **the chemistry of the pore water.**

Adsorbed Water (Stern Layer)

- **The innermost layer of doublelayer water, which is held very strongly by clay, is known as adsorbed water (Stern layer).**
- **This water is more viscous than is free water.**
- **The orientation of water around the clay particles gives clay soils their plastic properties.**

Initially, attraction from the negative colloid causes some of the positive ions to form a **firmly attached layer around the surface of the colloid;**
this layer of counter-ions is known as the *Stern layer*.



The **attached counter-ions in the Stern layer** and
the **charged atmosphere in the diffuse layer** are
what we refer to as the
double layer.

The **thickness of this layer** depends upon

- **the type and**
- **concentration**

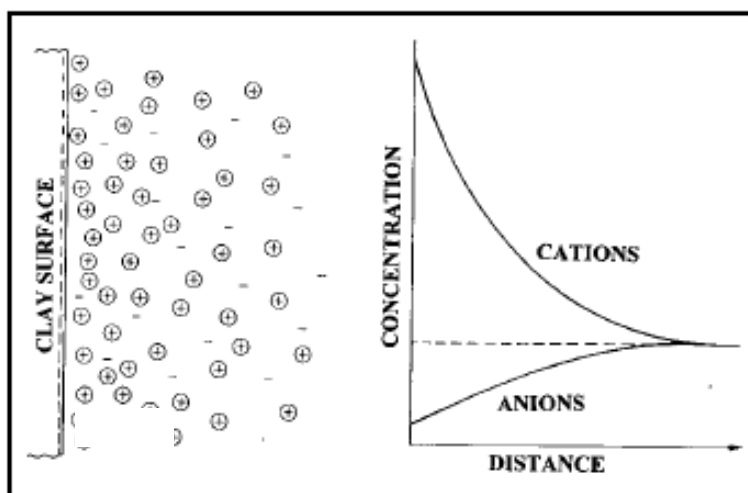
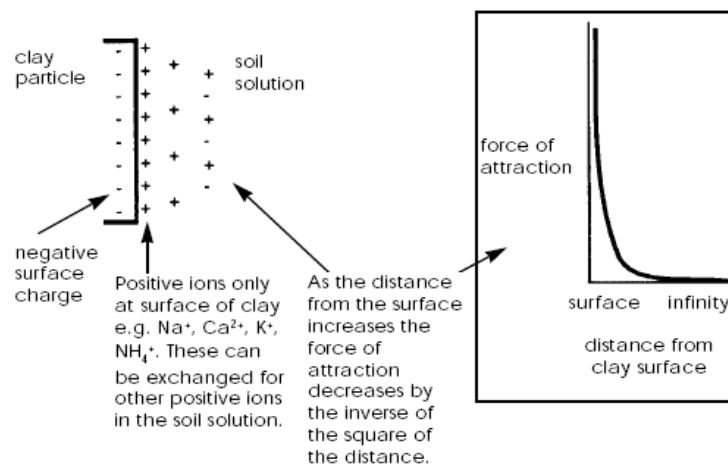
of ions in solution.

The **diffuse layer is called 'diffuse'**,
because a net positive
charge of ions **extends away from the**
surface.

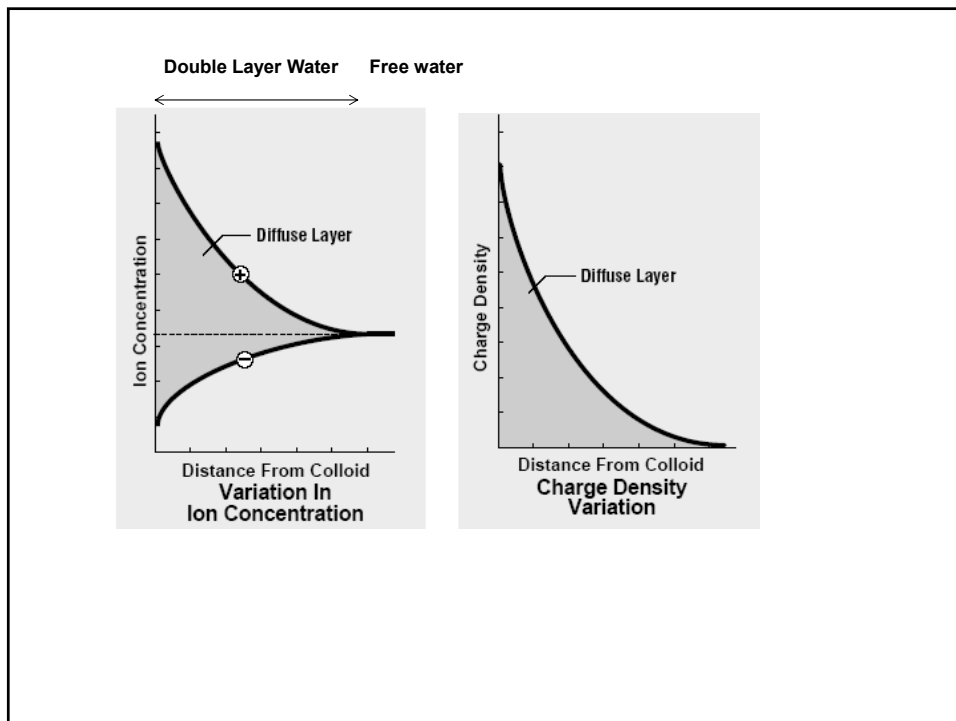
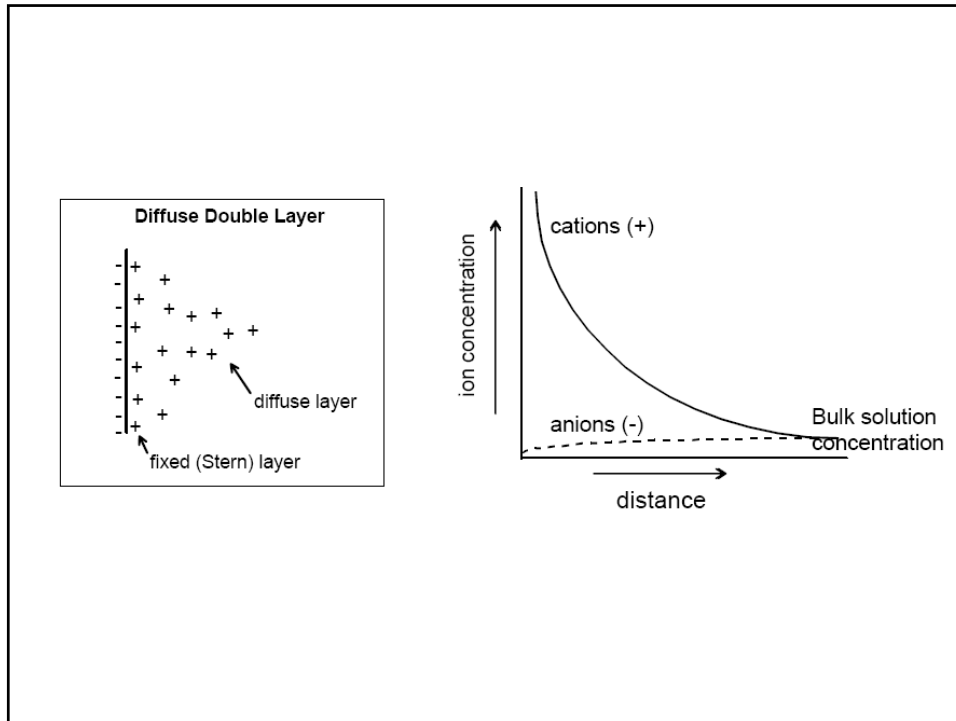
The **further from the surface, the less is**
the net positive charge of the solution.

Force of Attraction

The double layer at the face of a clay particle.



The Distribution of Cations and Anions Adjacent to a Clay Particle.



- The **force of attraction** between water and clay **decreases with distance from the surface** of the particles.
- All of the **water held to clay particles by force of attraction** is known as double-layer water.
- For one cation to leave the double layer **it must be replaced by** another from the soil solution.

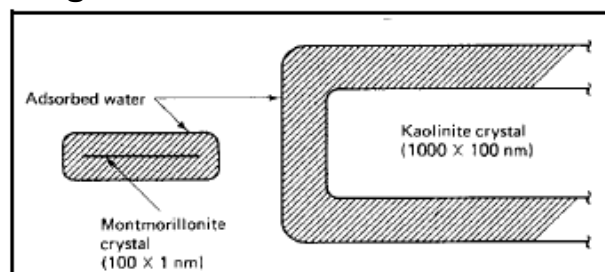
The **amount of adsorbed water** in the double layer relative to the total volume of pores **varies greatly with mineral type** (van Olphen, 1963).

This variation is clearly illustrated in the table given by Quigley and Fernandez, 1989.

The table indicates **the volumes of water adsorbed in 1 nm thick double layers** for saturated clays at a void ratio of 2.5 (Quigley and Fernandez, 1989).

CLAY MINERAL	SPECIFIC SURFACE (m ² /g)	VOL. OF ADSORBED H ₂ O IN DBL LAYER (% PORE VOLUME)
Kaolinite	20	2
Illite	100	9
Montmorillonite	800	70

The figure shows a **sodium montmorillonite and kaolinite crystal** with layers of adsorbed water. The **thickness of the adsorbed water is approximately the same**, but **because of the size differences**, the montmorillonite will have much greater activity, higher plasticity, and greater swelling, shrinkage, and volume change due to loading.



Relative sizes of adsorbed water layers on sodium montmorillonite and sodium kaolinite (after Lambe, 1958a).

- The negative surface and the distributed charge in the adjacent phase are together termed the “diffuse double layer”.
- Several theories have been proposed for the description of diffuse double layer.
- The Gouy Chapman Theory of the diffuse double layer is considered as the most successful.

Quantitative treatment of the diffuse double layer presents
an extremely difficult
and, in some respects,
unsolved problem.

The **simplest quantitative treatment** is that due to

Gouy (1910) and Chapman (1913),

which incorporates numerous assumptions including

the treatment of ions in the double layer as point charges (van Olphen, 1963).

Following **from the theory,**

the thickness of the diffuse double layer can be related

to the major pore fluid properties as follows:

The Gouy Chapman Theory

Double layer thickness is expressed as:

$$\frac{1}{K} = \left(\frac{\varepsilon_0 D k T}{2 n_0 e^2 v^2} \right)^{1/2}$$

or

$$\frac{1}{K} = \left(\frac{D k T}{8 \pi n_0 \varepsilon^2 v^2} \right)^{1/2}$$

k= Boltzman constant (1.38x10⁻¹⁶ erg/K°)
 ε : unit electronic charge
 : 4.80x10⁻¹⁰ esu or 16.0x10⁻²⁰ coulomb.

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n₀: Electrolyte concentration, (ions/cm³)

v: Effect of cation valency

T: Temperature

D: Effect of dielectric constant.

Factors Affecting the Double Layer Thickness

1. Electrolyte concentration, n_0 (ions/cm³)

$$n_0 \uparrow \quad \frac{1}{K} \downarrow$$

2. Effect of cation valency (v)

$$v \uparrow \quad \frac{1}{K} \downarrow$$

3. Effect of dielectric constant (D)

$$D \uparrow \quad \frac{1}{K} \downarrow$$

(The dielectric constant is a measure of the ease with which molecules can be polarized and oriented in an electric field)

4. The effect of temperature (T)

$$T \uparrow \quad \frac{1}{K} \uparrow$$

However as $T \uparrow$ $D \downarrow$ so $DT \approx$ same.

T°C	T°K	D	DT
0	273	88.0	2.4×10^4
20	293	80.0	2.34×10^4
25	298	78.5	2.34×10^4
60	333	60.	2.20×10^4

5. Effect of ion size

as size \uparrow Thickness \uparrow

6. pH

pH \uparrow Thickness \uparrow

The **higher the pH, the greater the tendency for the H^+ to go into solution,** and the greater the effective negative charge of the particle.

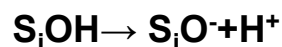
pH

$\text{pH} = -\log_{10} H^+ \text{ concentration}$

$\text{pH} < 7$ is acid. \rightarrow High H^+ concentration

$\text{pH} > 7$ is basic. \rightarrow Low H^+ concentration

Clay particles have hydroxyls (OH^-) exposed on their surfaces and edges. The tendency for the hydroxyls **to dissociate (separate) in water** is strongly influenced by the pH.



The higher the pH,
the greater the negative charge
 of the particle
 so the **higher the thickness of**
the double layer.

<u>H⁺</u>	<u>pH</u>	
0.3	0.53	as H ⁺ ↑ pH ↓
0.2	0.69	
0.1	1.0	

Attractive and Dispersive Forces

The counter-ions (**positive ions**) are influenced by two equal but opposing forces:

- **Attractive Forces**

the **electrical force** attracting the **positive ion** to the negative surface, and

- **Dispersive Forces**

the **diffusive** or thermal **forces** (responsible for Brownian motion) which tend to move the **cations away from the surface.**

The **binding force on to and between the clay plates** depends on a number of factors including:

- the **charge of the cations**
- the **size of the cations**, including their hydration shell
- the **thickness of the double layer** outside the surface of the clay particles.

Strength of Attraction of Exchangeable Cations

The **cations adsorbed on to the surface of the clay particles** can **greatly affect how the clay behaves.**

The **cations act as a link** between the clay particles.

Similarly, dispersive organic matter (with negatively charged edges) can be linked strongly by positively charged cations.

The strength of the bond depends on the cations present

Sodium

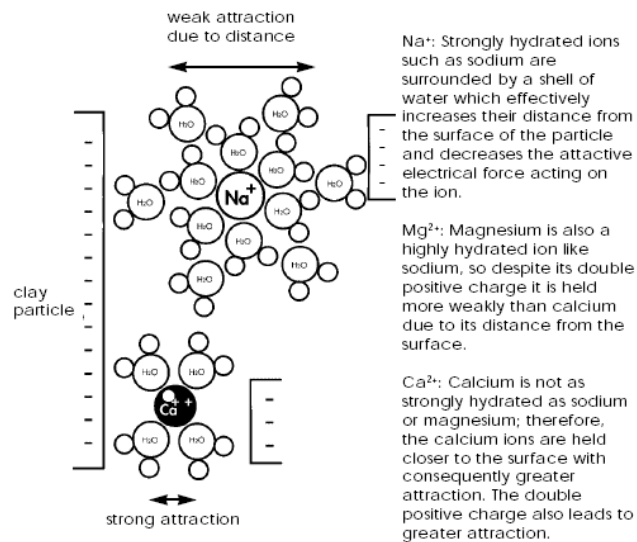
ions have a **single positive charge**, so their clay-binding ability is **poor**.

Calcium ions have a **double positive charge**, so their clay-binding ability is **good**.

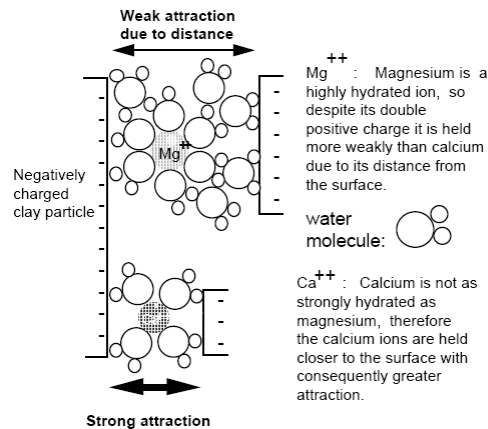
Magnesium

is **intermediate** because, although it has a double positive charge like calcium, **when hydrated it is larger than a hydrated calcium ion**.

Figure E4-6. Strength of attraction of common soil cations



Strengths of attraction of common soil cations.



In a dispersive soil with a large exchangeable sodium percentage and **small concentrations of water-soluble salts**, the weak bonding of the clay particles by sodium ions **can be broken**.

As water enters between the clay **particles it hydrates the sodium ions**. This in turn forces the plates away from the ions and **lowers the attractive force between the particles and the ions**.

The plates may move far enough **apart for attraction forces** to be overcome.

The result is dispersion.

Rate of Cation Exchange

The rate of cation exchange varies with:

- clay type,
- solution concentration,
- temperature, etc.

In general, however, exchange reactions in the kaolin minerals **are almost instantaneous**.

In illite, a few hours may be needed for completion,

because a small part of the exchange sites may be between unit layers.

A longer time is required **in smectite** because the major part of the exchange capacity is **located in the inter-layer regions** (Mitchell, 1993a).

Exchangeable Sodium Percentage (ESP)

Exchangeable sodium percentage (ESP) is a measure of the

number of sodium ions adsorbed onto the surface of the clay particles,

compared with other positive ions.

Soils with **low ESP** generally have **better aggregate stability** in water than soils with high ESP.

Since the doubly charged **calcium ions are more strongly attracted to the clay surface** than sodium, **the thickness of the double layer is less** and the tendency to swell is correspondingly less.

Much more importantly, the particular organisation of the clay particles where they overlap **restricts the swelling**, due to diffuse double layers.

Individual particles are linked to each other by:

- **Cementation:**
calcite, silica and oxides. These cements are more or less stable at ambient pressure, temperature and/or pore fluid chemistry encountered in regular geotechnical engineering.
- **Interlocking of particles**, which occurs in metamorphosed or otherwise **compressed clayey soils.**
- **Electrostatic forces:**
These forces depend strongly on the **pore fluid chemistry and the charge at the particle surfaces.**

The thickness of DDLs around clay particles is governed by the **concentration of salt and type of cation(s)** in the soil water.

It also depends on the degree of expansion of the DDLs, which is controlled by **soil-water content;**

the **DDLs expand fully only in the abundance of water.**

In dry soils, the thickness of the **DDLs is very small** since the DDLs cannot expand fully, and most clay particles remain isolated resulting in **discontinuous pathways** for the flow of electrical current .

Electrostatic Double Layer

