

Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

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Lecture Plan

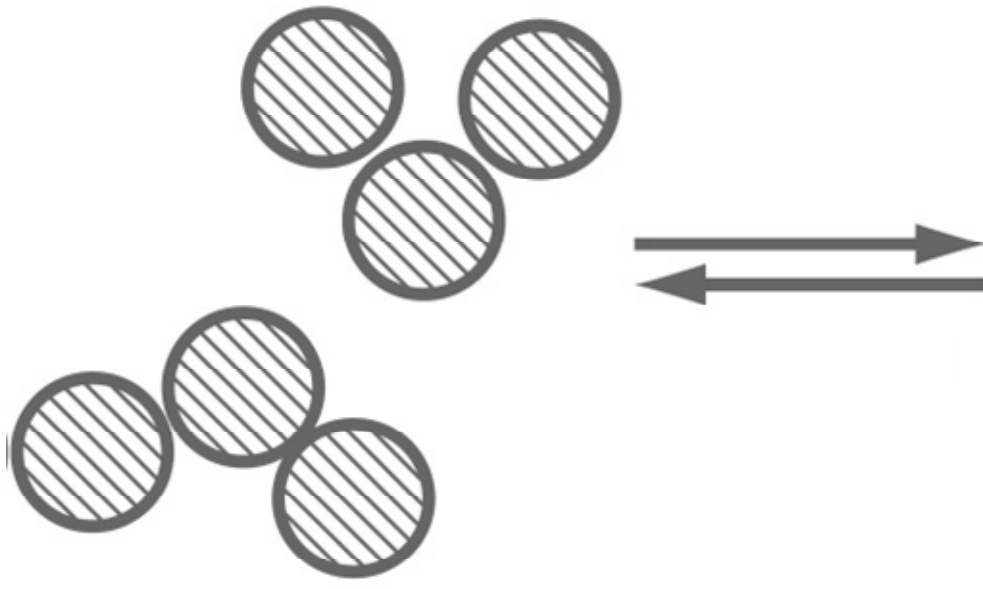
- April 11, Introduction and Physical chemistry
- April 18, Nanoparticles and colloids in our daily experiences
- April 25, Nanoparticles and colloids in our daily experiences
- May 9, Dispersion and aggregation of particles
- May 16, Dispersion and aggregation of particles
- May 23, DLVO theory
- May 30, DLVO theory
- June 6, Theory of monodispersed particles synthesis
- June 13, Liquid-phase synthesis of functional nanoparticles
- June 20, Liquid-phase synthesis of functional nanoparticles
- June 27, Environmental catalysts
- July 4, Adsorption phenomena and catalytic reaction
- July 11, Catalyst preparation methods
- July 18, Catalyst preparation methods
- July 25, Summary

Let's take a look at the colloids around us !

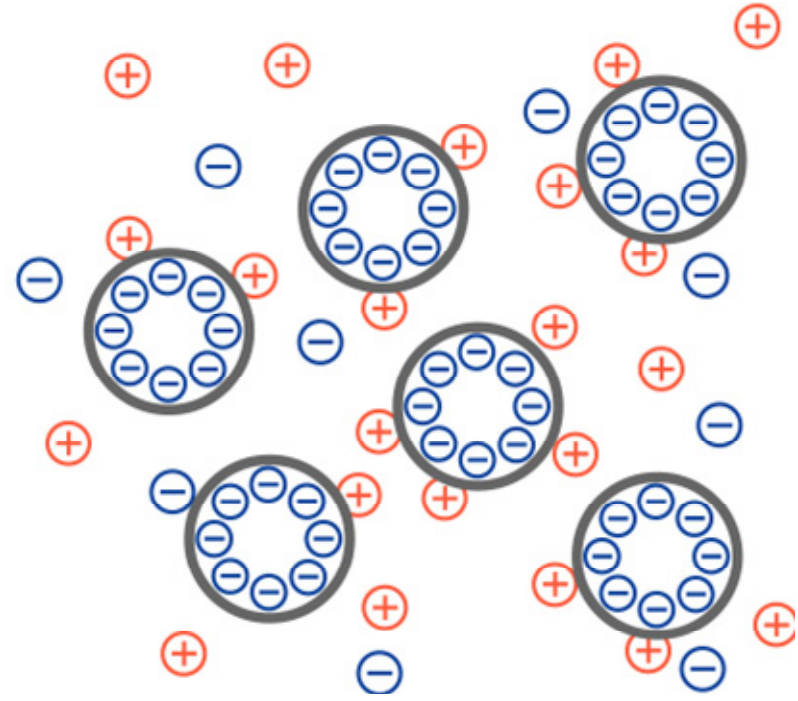
- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?



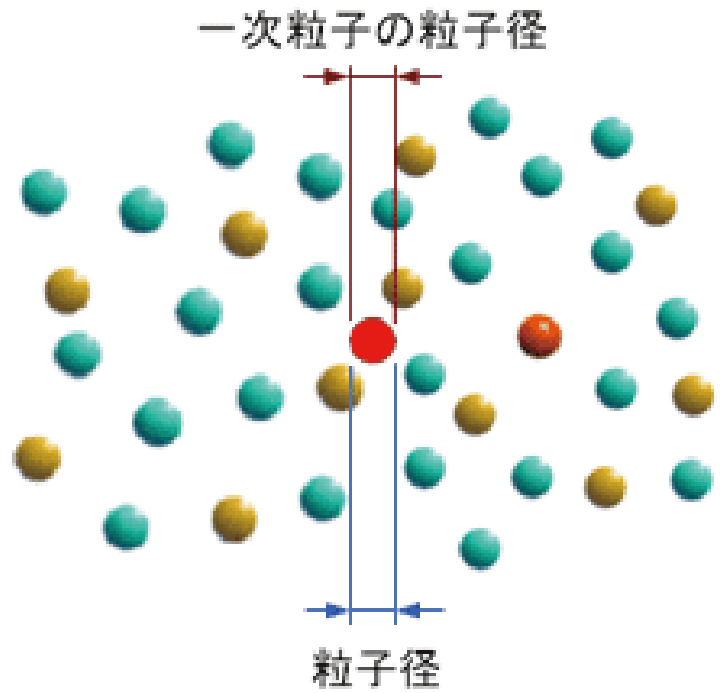
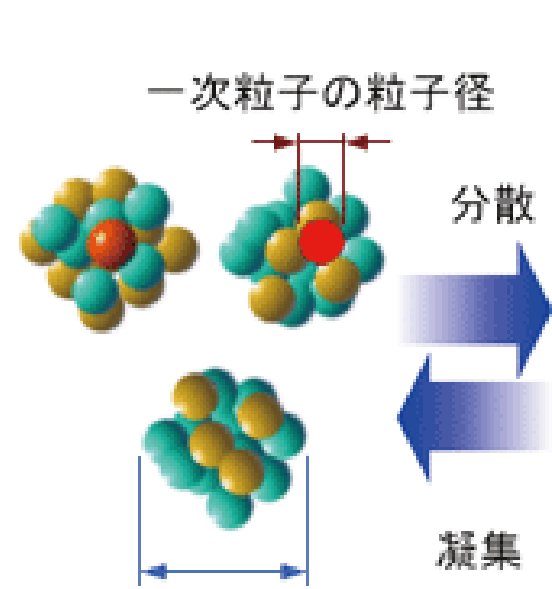
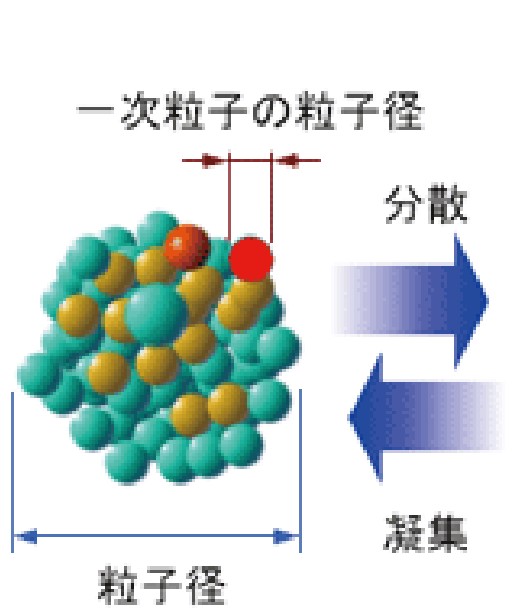
- ▶ If "dispersion" and "aggregation" can be controlled, colloids can be manipulated freely.



Aggregation



Colloidal dispersion



Add salt to coffee milk

Milk fat floating



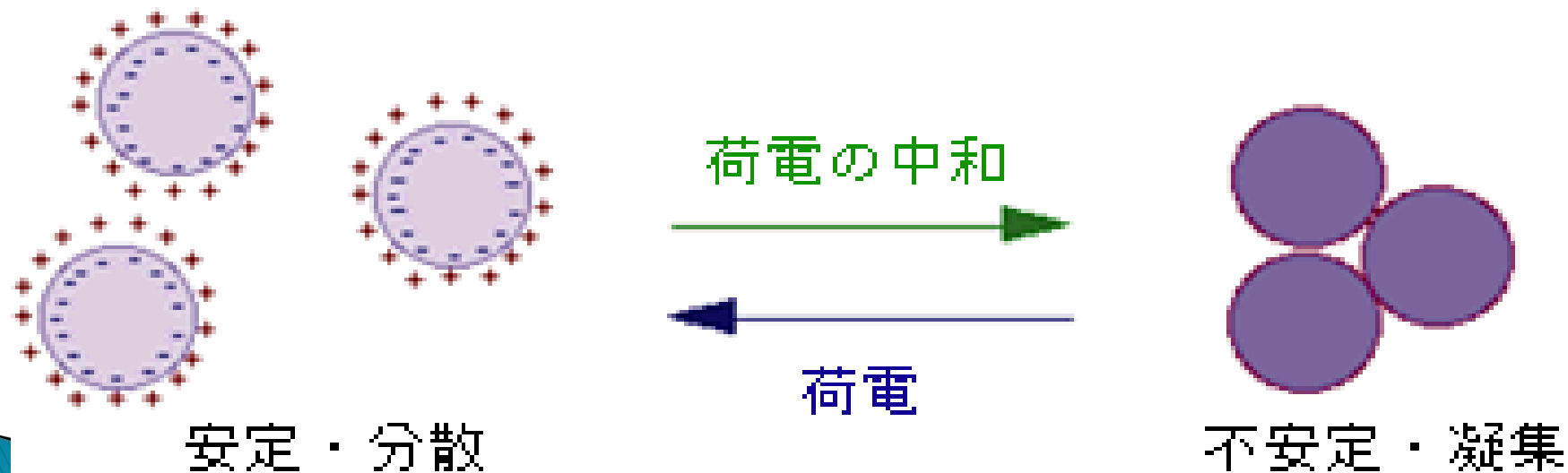
1 mol/L KCl溶液

coffee milk only



Why did milk fat in coffee surface?

- ▶ Milk fat is lighter than water.
 - ▶ Milk is a dispersion of milk fat.
- ↓
- ▶ By adding salt, it "agglomerated" and surfaced.



Dispersion and Aggregation

- ▶ What is dispersion?
 - Particles drift in the solvent without agglomeration.
- ▶ What is aggregation?
 - Particles gather more and form larger flocs.



- ▶ Materials naturally aggregate.
 - Intermolecular force
→ van der Waals force

Dispersion and aggregation (Equilibrium consideration)

- ▶ Aggregation

凝集

- van der Waals interaction

- ▶ Dispersion

分散

- Electrostatic repulsion



- Repulsion due to surface potential

Dispersion or Aggregation?

- ▶ Equilibrium theory
 - electrostatic repulsion
 - due to interfacial potential of colloid
- ▶ Kinetics
 - Collisions between colloids ←
Thermal motion and collision probability

Theory of dispersion & aggregation, and evaluation of dispersion stability

2023/5/30

What is the essence of particle dispersion and aggregation behavior?

intermolecular force

van der waals force

Attractive force acting between any molecule

(The larger the molecular weight, the larger it becomes.)

(Molecular melting point and boiling point increase in proportion to molecular weight.)

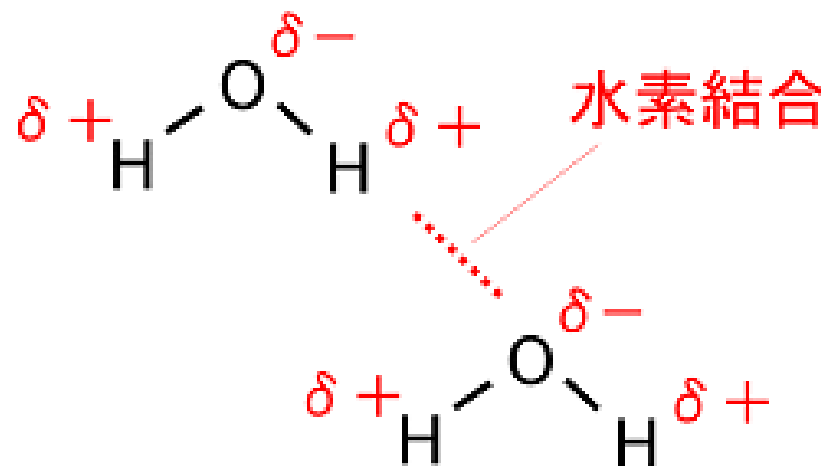
Weak electrostatic force

Works between polar molecules

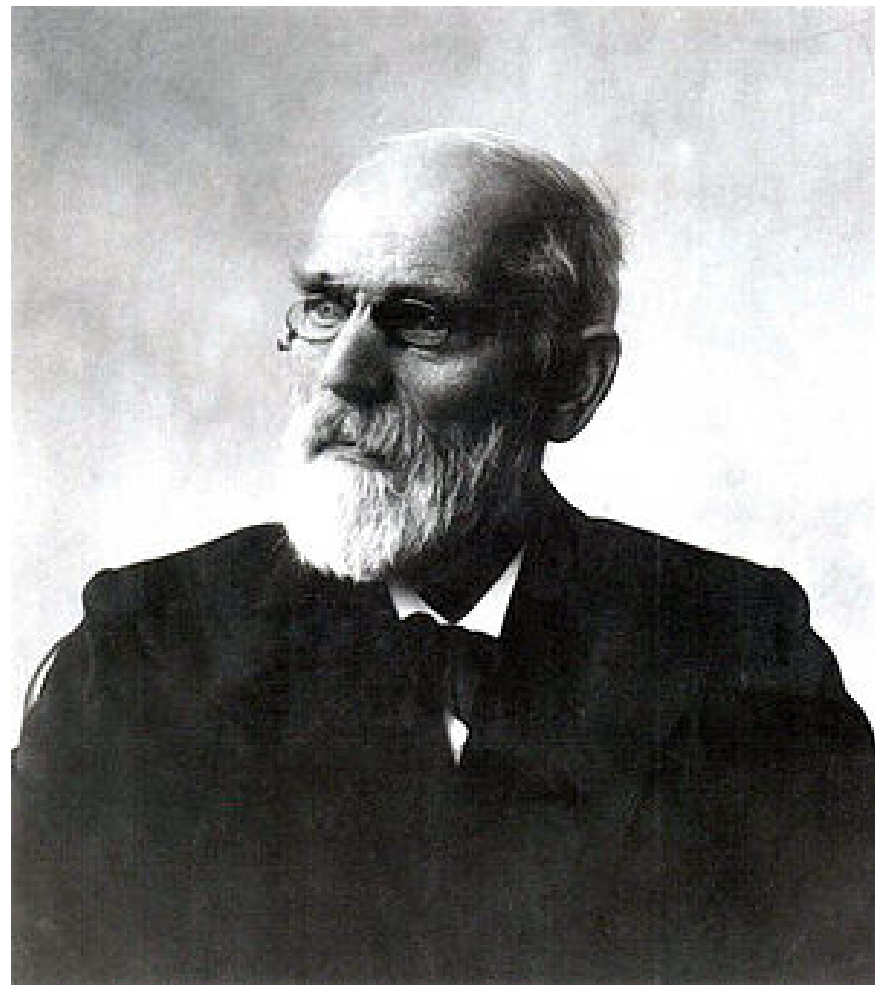
Hydrogen bond

Seen in H_2O , HF , NH_3 , etc.

(O-H, F-H, N-H occur because the polarity is particularly large)



Johannes Diderik van der Waals (23 November 1837 – 8 March 1923) was a Dutch physicist. In 1910, he became the third Dutchman to receive the Nobel Prize in Physics for his discovery of the gas equation of state, which takes into account molecular size and intermolecular forces.



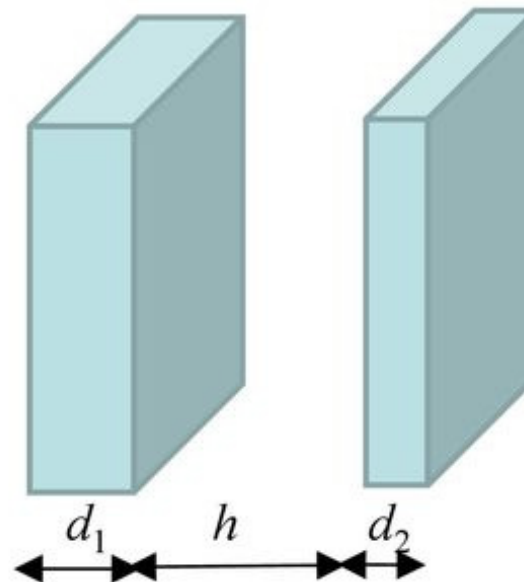
van der Waals force

- ▶ The van der Waals force is an electromagnetic interaction force that acts between electrically neutral molecules. When molecules and atoms approach each other, they are momentarily polarized and an attractive force is generated. This force is called van der Waals force.
- ▶ When molecules or atoms get closer than a certain distance, a strong repulsive force is generated. About 0.2 nm is the minimum surface-to-surface distance.
- ▶ It also occurs when two macroscopic objects, such as particles and particles, or particles and walls, come very close to each other in the same way as molecules and atoms.

van der Waals force: features

- The force is much smaller than that of ionic bonds and covalent bonds.
- In water, the force action is smaller than in air.
- van der Waals forces decrease when moisture is adsorbed on the contact area.
- It becomes smaller in inverse proportion to the surface roughness.
- van der Waals forces exist at all times, independent of the surrounding environment.

van der Waals interaction energy between plates



The Hamaker constant is named after the German scientist H. C. Hamaker. His 1937 paper is famous.

$$V(h) = -\frac{A_{12}}{12\pi} \left[\frac{1}{h^2} - \frac{1}{(h+d_1)^2} - \frac{1}{(h+d_2)^2} + \frac{1}{(h+d_1+d_2)^2} \right] \quad (\text{per unit area})$$

$$A_{12} = \pi^2 C_{12} N_1 N_2 = \pi^2 (C_1 C_2)^{1/2} N_1 N_2 = (A_1 A_2)^{1/2} \text{ は}$$

Hamaker constants for dissimilar substances 1 and 2

(A_i = 物質 i ($i = 1, 2$) 同士の相互作用に対する Hamaker 定数)
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van der Waals forces between particles

$$V_{vdw} = -\frac{A}{6} \left\{ \frac{2}{s^2 - 4} + \frac{2}{s^2} + \ln \left(\frac{s^2 - 4}{s^2} \right) \right\}$$

If h is significantly smaller than a , the potential energy is

$$S = 2a + h$$

$$V_{vdw} = -\frac{Aa}{12h}$$

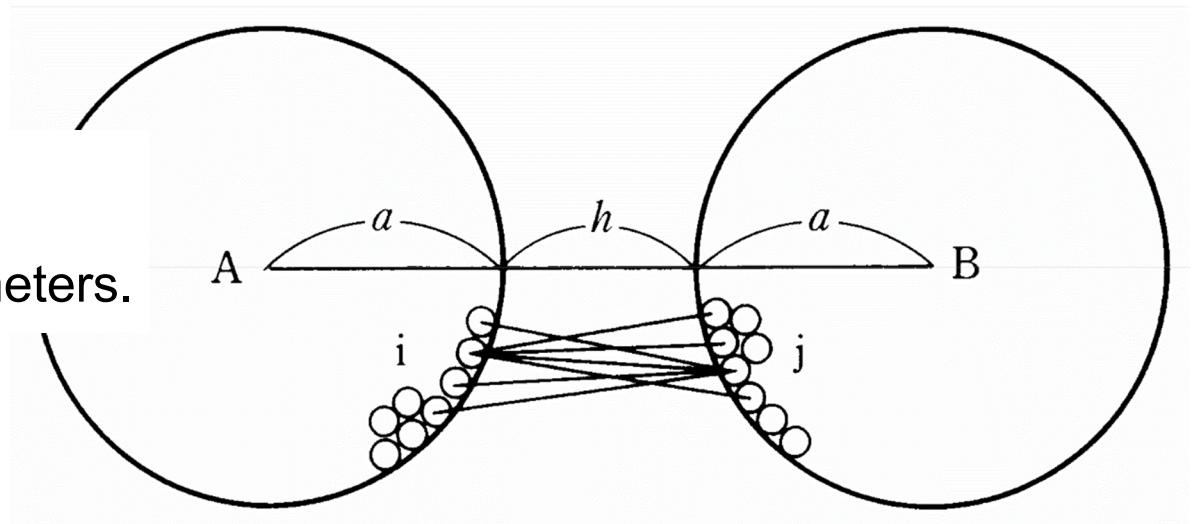
A: Hamaker constant

For particles with different diameters.

$$V_{vdw} = -\frac{Aa_1a_2}{6h(a_1 + a_2)}$$

Between planes.

$$V_{vdw} = -\frac{A}{12\pi h^2}$$



Hamaker constant

From Wikipedia, the free encyclopedia

The **Hamaker constant** A can be defined for a Van der Waals (VdW) body–body interaction:

$$A = \pi^2 \times C \times \rho_1 \times \rho_2,$$

where ρ_1 and ρ_2 are the [number densities](#) of the two interacting kinds of particles, and C is the coefficient in the particle–particle pair interaction.^{[1][2]} It is named after [H. C. Hamaker](#).

The Hamaker constant provides the means to determine the interaction parameter C from the Van der Waals pair potential, $w(r) = -C/r^6$.

Hamaker's method and the associated Hamaker constant ignores the influence of an intervening medium between the two particles of interaction. In the 1950s [Lifshitz](#) developed a description of the VdW energy but with consideration of the dielectric properties of this intervening medium (often a continuous phase).

The [Van der Waals forces](#) are effective only up to several hundred [angstroms](#). When the interactions are too far apart, the dispersion potential decays faster than $1/r^6$; this is called the [retarded](#) regime, and the result is a [Casimir–Polder force](#).

ハーマーカー一定数(はーまーかーていすう) | Hamaker constant

When drawing interaction potential curves between colloidal particles, values of Stem potential ϕ and Hamaker constant A are required. It is assumed that ϕ is approximately equal to the experimentally determined zeta potential. The value of A can be obtained both theoretically and experimentally. According to Hamaker's microscopic theory, the Hamaker constant A of a substance in vacuum is related to the London constant Λ by the following equation.

$$A = \pi^2 q^2 \Lambda$$

Here, q indicates the number of molecules per unit volume of the colloidal particles. The Hamaker constant ($A_{11/3}$) of the colloidal particles (1) dispersed in the liquid medium (3) is expressed by the following equation.

$$A_{11/3} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2$$

Here, A_{11} and A_{33} are Hamaker constants in vacuum for colloidal particles and medium liquids. The method of experimentally obtaining the value of A is to obtain the attractive force between bodies directly, and A is calculated from the value of the critical aggregation concentration. method, and a method of obtaining from the measurement of the surface (interfacial) tension.

(古澤)

Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?



- ▶ The key to controlling "dispersion" and "aggregation" is **zeta potential!**

**There is an electric charge of several tens of mV on
the surface of all “matters“
(“Surface potential” or “Zeta potential”)**

It's on your face, on your desk, on your foam, on everything!

What is the theory behind this?

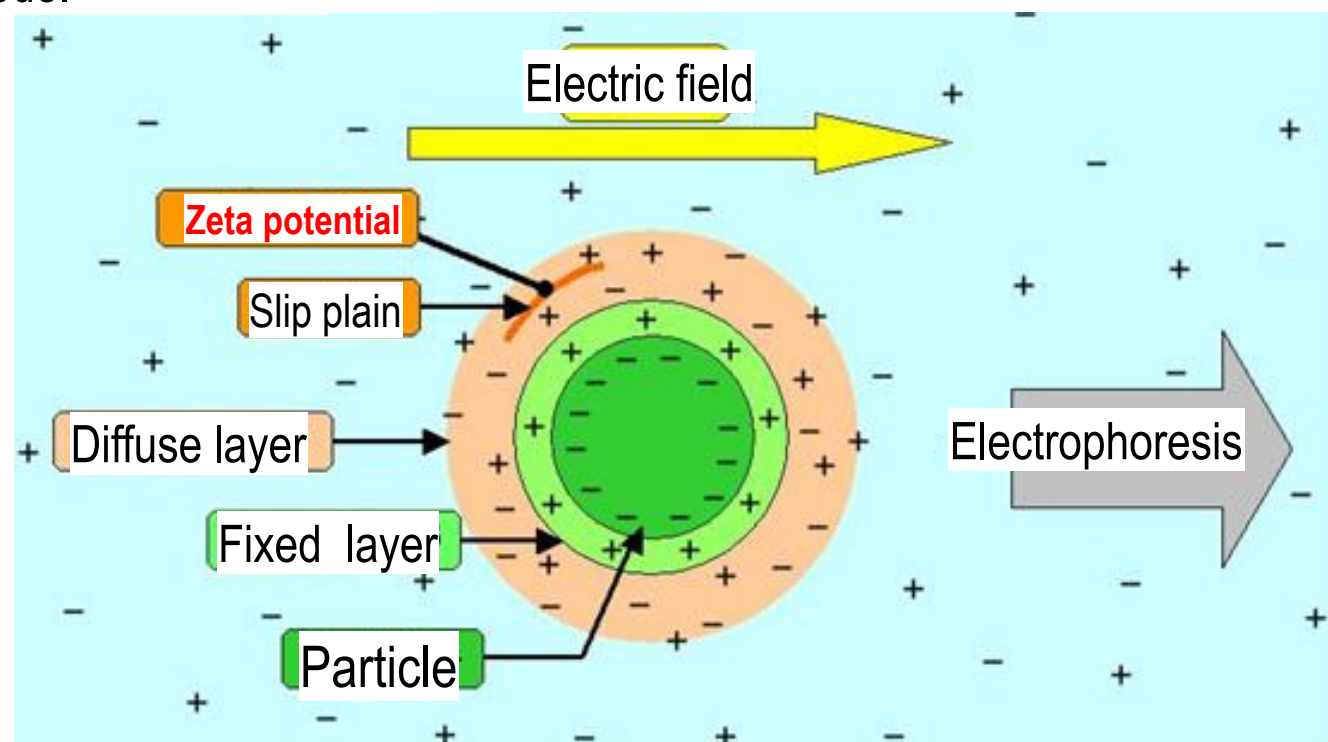
Zeta potential

- ▶ Zeta potential is a unique physical character of each material.
- ▶ Zeta potential changes with pH of aqueous solution.
- ▶ Zeta potential is a clue for dispersion/aggregation.
- ▶ Low zeta potential usually results in aggregation, called homocoagulation.

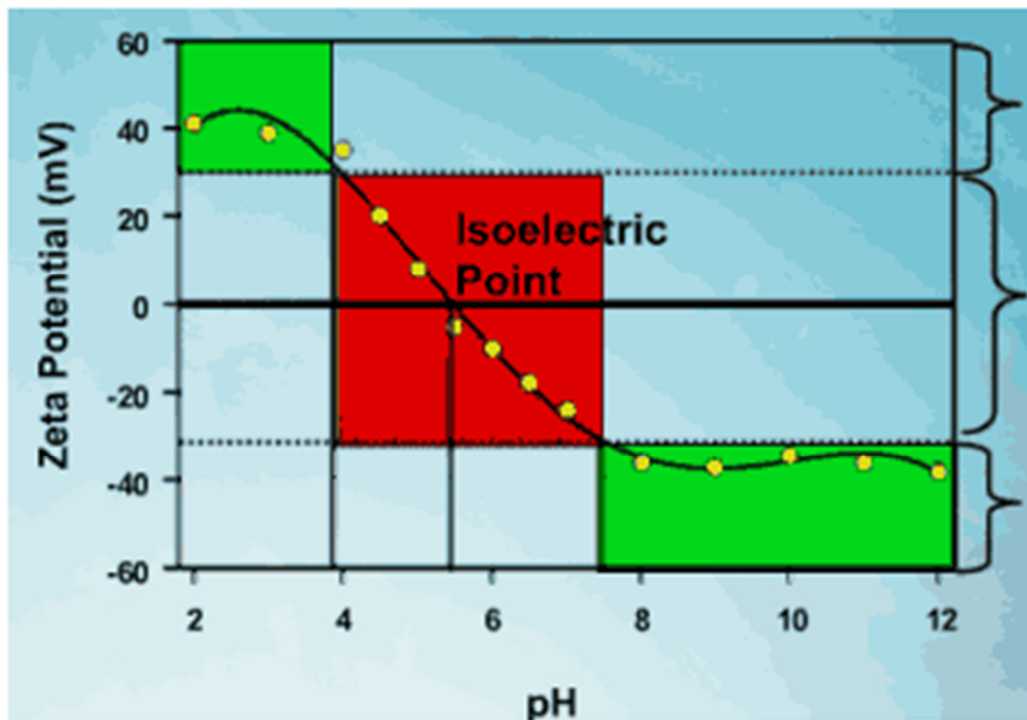
6 Electrophoresis



Particles with the same negative charge are moving to the positive electrode.



Zeta potential as a function of pH

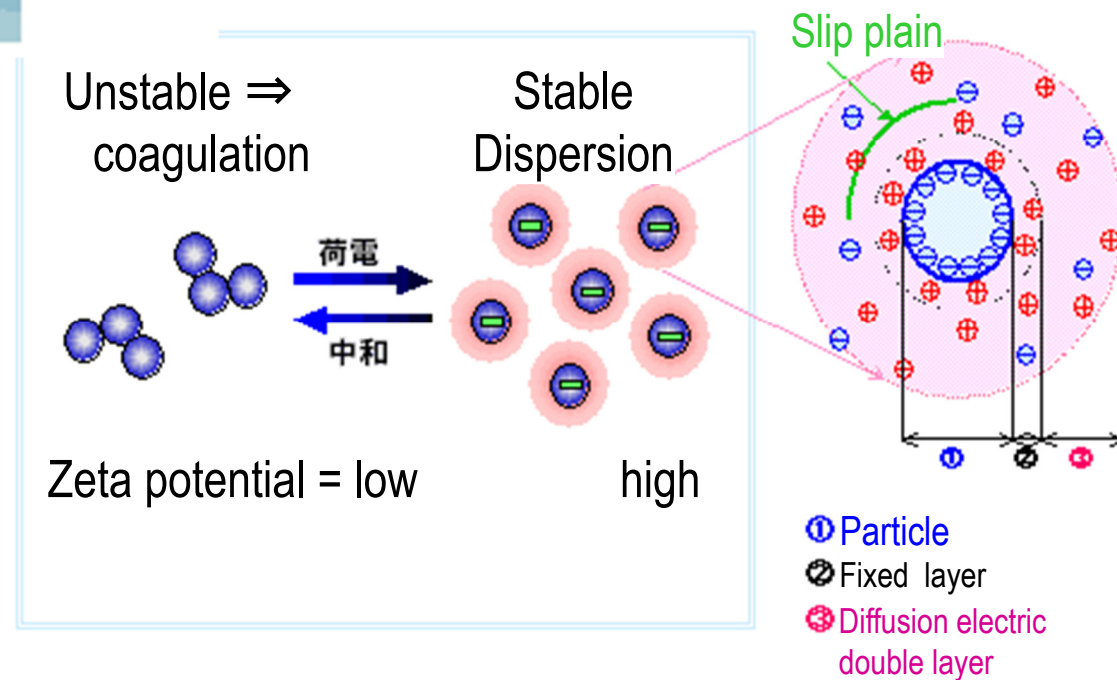


Stable

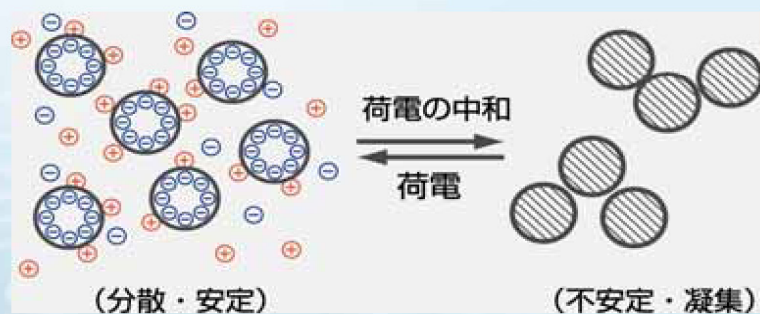
Unstable

Stable

Zeta potential and dispersion



What can we learn from zeta potential?

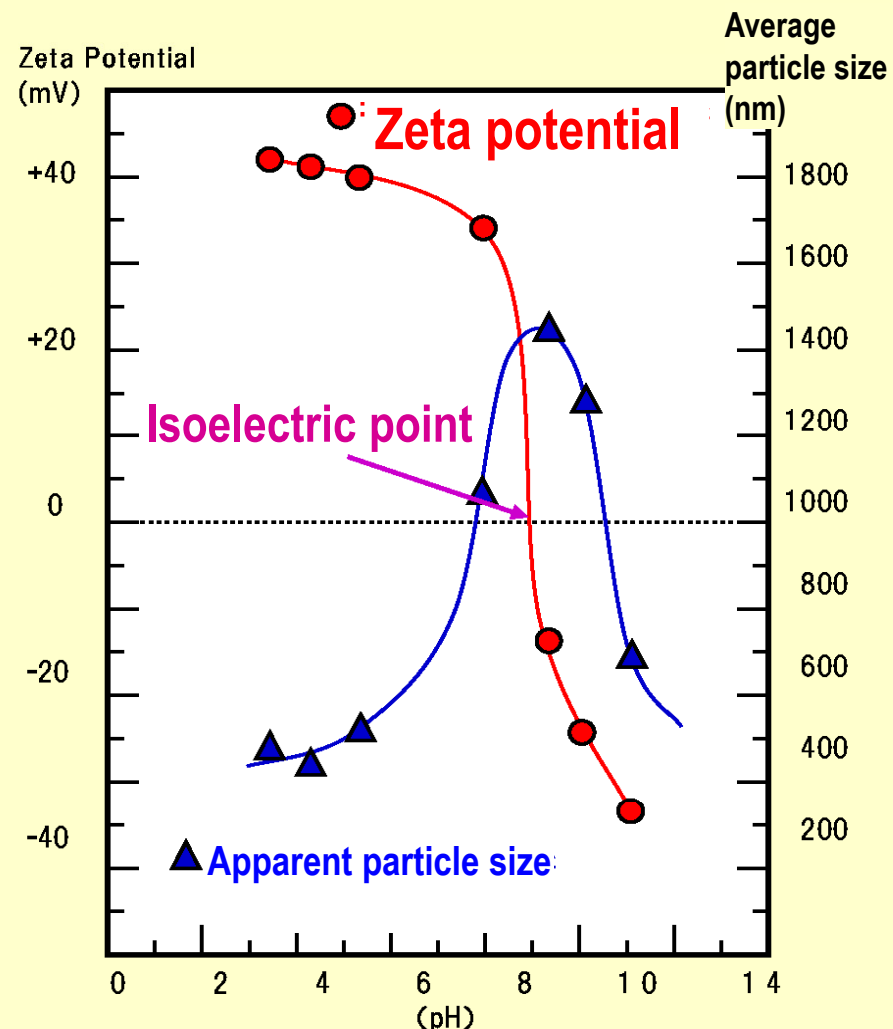


The larger the absolute value of the zeta potential, the better the dispersibility. However, if it is small, it is unstable and tends to aggregate.

The alumina particles in the right figure have a **positive charge** on the acidic side. The isoelectric point is around pH 9. It has a **negative charge** on the alkaline side.

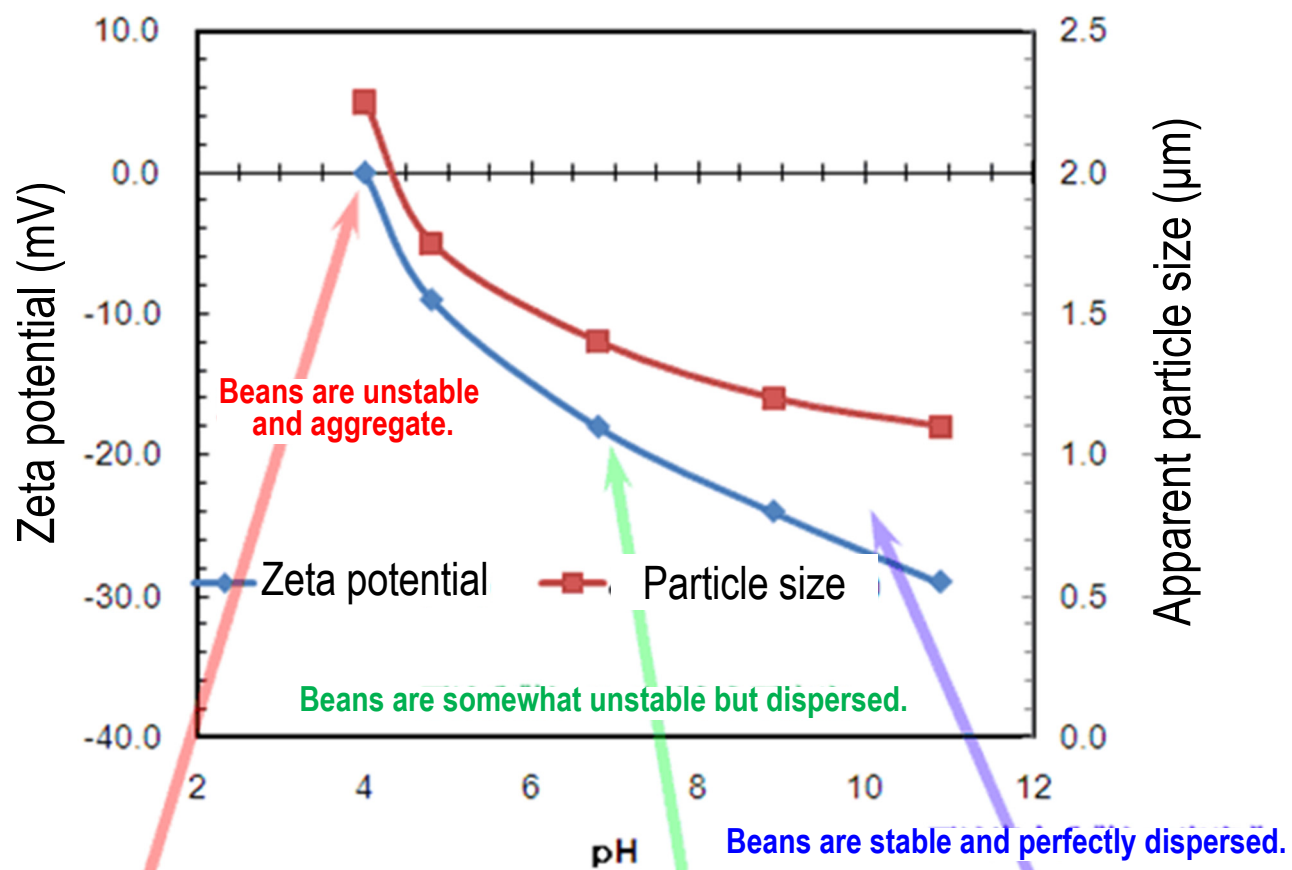
The average particle size is small in the pH region where the absolute value of the zeta potential is large. In the vicinity of the isoelectric point, they aggregate and have a large particle size.

The larger the absolute value of the zeta potential, the better the dispersibility. If it is small, it is unstable and tends to aggregate.



Tea, black tea, and coffee are colloids.

Zeta potential of coffee bean particles



What is electrokinetic phenomenon?

A so-called electric double layer is formed at the phase interface of substances in the liquid phase.

An electric double layer is approximately represented by two electric layers with different signs, like a capacitor.

However, since one layer has the property of being diffusively movable (diffusion layer), only one layer has the property of deforming when subjected to external mechanical stimulation.

Due to this property, the motion of the electric double layer is always accompanied by electrical strain. The phenomenon caused by this electrical strain is the electrokinetic phenomenon (Electrokinetic Phenomena).

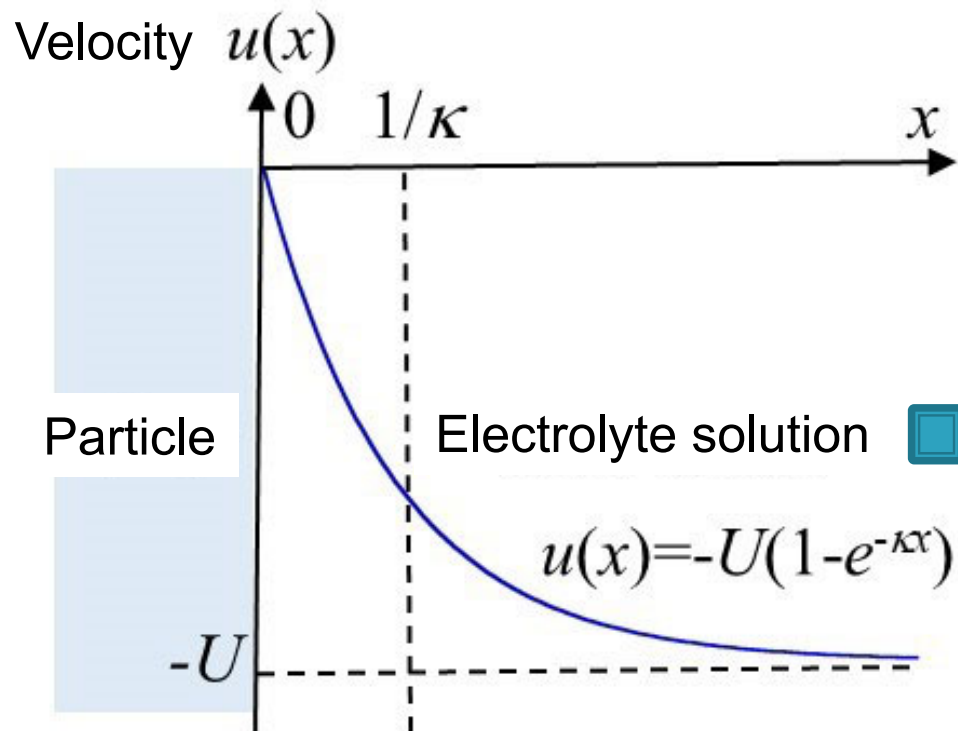
The following electrokinetic phenomena are generally known.

Electrophoresis, electroosmosis, streaming potential, zeta potential, electrorheological effect, oscillating potential

Electrokinetic Phenomenon ~Electrophoresis~

- ▶ Suppose that a DC electric field E is applied from the outside parallel to the solid-liquid interface with an electric double layer on the solution side. Since the solid surface is stationary, a laminar flow on the solution side causes a distribution of velocities along the interface. Now, assuming a microcube in the solution, the electric force and the viscous force acting on the cube must balance in the steady state. If the average charge density in the cube is ρ , the electric force is ρE , which is balanced with the viscous force ($\eta d^2u/dx^2$) in the steady state (SI unit system) (equation 6).

$$\rho E = \eta \frac{d^2u}{dx^2} \dots \dots \dots (6)$$



When laminar flow occurs on the solution side, a velocity distribution occurs along the interface.

Now, assuming a microcube in the solution, the electric force and the viscous force acting on the cube must balance in the steady state.

$$\rho E = \eta \frac{d^2 u}{dx^2}$$

Electric field E

Mobility U

Potential $\psi(x)$

ψ_0

Particle

surface
charge
density, ρ

Electrolyte solution

$$\psi(x) = \psi_0 e^{-\kappa x}$$

0 $1/\kappa$

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Electrokinetic Phenomenon ~Electrophoresis~

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Electrophoresis and zeta potential

- ▶ u ($u = V/E$) is the relative velocity of the interface or particle and solution, i.e. the electrophoretic mobility. After substituting Poisson's formula into this relation and rearranging it, the following formula is obtained by integrating both sides twice.

$$V = (\epsilon_0 \epsilon_r / \eta) \phi_0 E \dots\dots\dots (7)$$

The potential in the diffusion layer is obtained based on Poisson's equation.

$$\Delta \psi = \text{div} (\text{grad } \psi) = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho}{\epsilon_r \epsilon_0}$$

ϵ_r : Dielectric constant of solution

ϵ_0 : Dielectric constant in vacuum

ρ : Charge density

Smoluchowski formula

- ▶ Electrophoretic mobility, $u = V/E$ is represented by

$$u = (\epsilon_0 \epsilon_r / \eta) \zeta \dots\dots\dots (8)$$
- ▶ where η indicates viscosity. Also, in equation (8), the surface potential ψ_0 is replaced with the zeta potential ζ . This equation is called the Smoluchowski equation and is the most widely used electrophoretic equation. Although this formula was derived for flat plates, it can be applied to spherical particles where the particle radius (a) is larger than the thickness of the electric double layer ($1/\kappa$) ($a \gg 1/\kappa$, or $ka \gg 1$). It can also be used for cylindrical particles with large radii. Furthermore, it can be said that it is a very useful formula because it can be applied to large particles of any shape.
- ▶ In particular, in water at 25°C ($\epsilon_r = 78.5$, $\eta = 0.89\text{mPa}$), it can be expressed as follows.

$$\zeta = 12.8 u \text{ (mV)}$$

Hückel formula

- ▶ The second method is to think of the external electric field as “acting on a point charge”, which is the opposite limit of the Smoluchowski equation, i.e., the limit of small particle radius a or thick double layer ($a \ll 1$), which is called Hückel's formula.

$$u = \frac{2\varepsilon_0 \varepsilon_r \zeta}{3\eta} \dots\dots\dots (10)$$

- ▶ Like Smoluchowski's equation (8), Hückel's equation does not depend on the particle radius, a , but differs in that it has a factor of $2/3$.

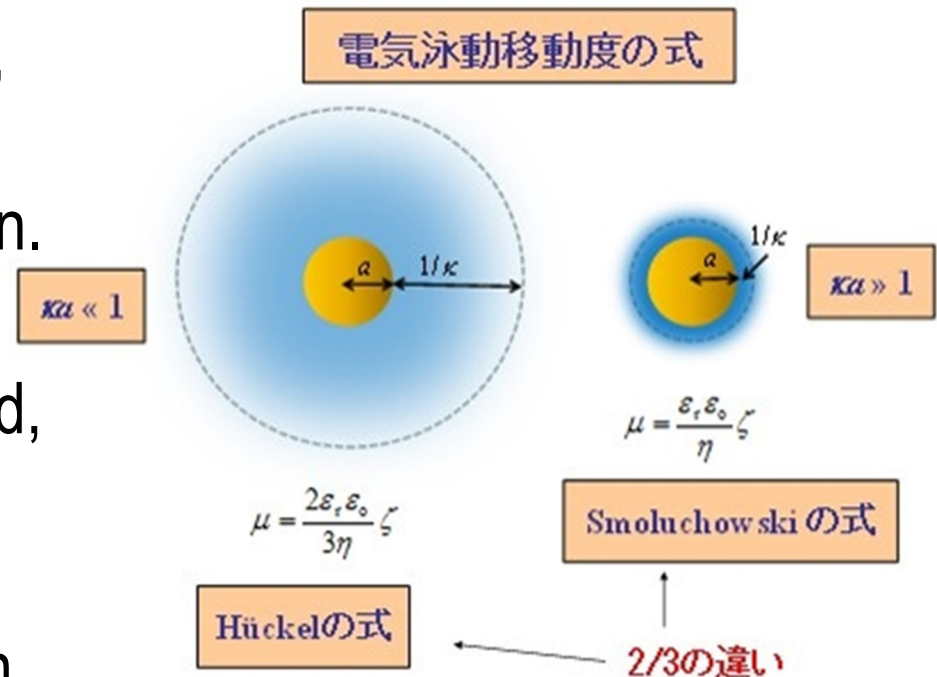
Henry formula

- ▶ Henry thought about this contradiction as follows. The Smoluchowski equation takes into account the distortion of the electric field due to the presence of particles (the electric field acts parallel to the interface), whereas the Hückel equation ignores the distortion of the external electric field due to the presence of very small particles. . This distortion of the electric field is strictly treated as a function of κa , and the effect (retarding effect) due to the movement of counterions in the liquid flowing in the opposite direction, rather than the particles migrating in the stationary liquid, is also considered. and derived the following equation.

$$u = (\epsilon_0 \epsilon_r / \eta) \zeta \cdot f(\kappa a) \dots\dots\dots (12)$$

Henry coefficient

- ▶ The function $f(\kappa a)$ is called Henry's coefficient and expresses the degree of distortion of the external electric field due to the presence of particles. Here, when $\kappa a \rightarrow 0$, $f = 2/3$ and the Henry equation becomes the Hückel equation.
- ▶ Conversely, when $\kappa a \rightarrow \infty$, $f = 1$ and the Smoluchowski equation is obtained, and in this limit the external electric field is completely distorted. The intermediate values of κa are shown in the figure on the next slide.



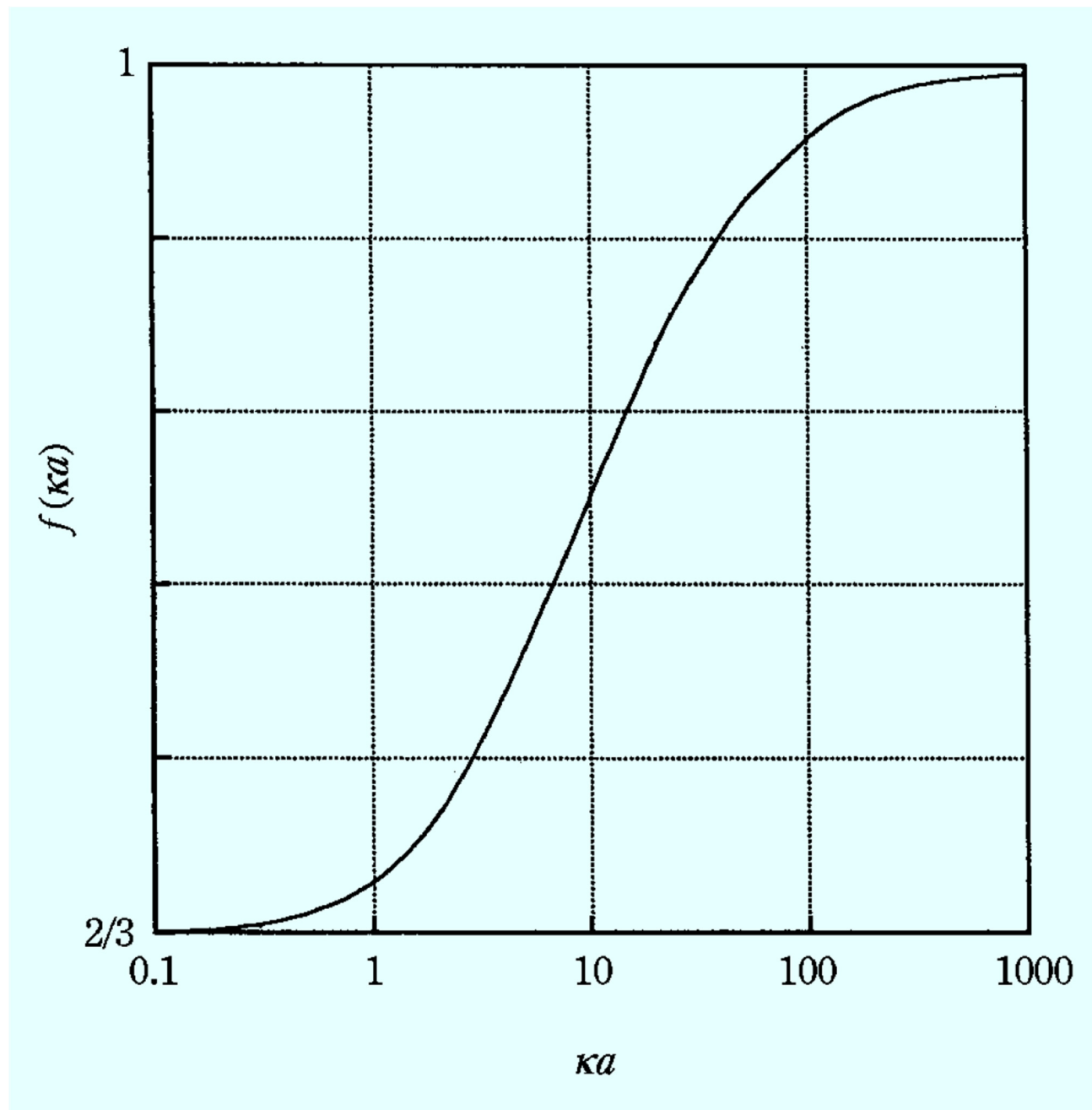


図2 Henry 係数 f の ka による変化
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Relaxation effect

- ▶ One problem still remains in the relationship between electrophoretic mobility and ζ potential. It is a well-known relaxation effect in the theory of electrical conduction in strong electrolytes. It is the effect that the opposite electric force acts on the particles because the double layer is deformed by an external electric field and becomes asymmetric.
- ▶ a) In colloidal electrophoresis with a ζ potential of 50 mV or less, the relaxation effect is negligible.
- ▶ b) In colloidal systems satisfying $\kappa a \gg 1$ or $\kappa a \ll 1$, the effect of the relaxation effect is small.
- ▶ c) In colloidal systems with $1 < \kappa a < 100$ and a ζ potential of 75 mV or more, u is greatly affected by the relaxation effect, making it difficult to estimate the ζ potential from the value of u .

Electrophoresis measurement

- ▶ A major problem with performing electrophoretic measurements in thin glass cells is the electroosmotic effect that occurs on the glass walls. Since the glass wall is negatively charged with respect to the aqueous solution, the solution flows due to the electroosmotic effect when an electric field is applied, and this flow u_{osm} is superimposed on the true electrophoretic mobility, u , of the colloidal particles. That is, the apparent particle migration mobility, u_{app} , observed under a microscope and u are related as follows.

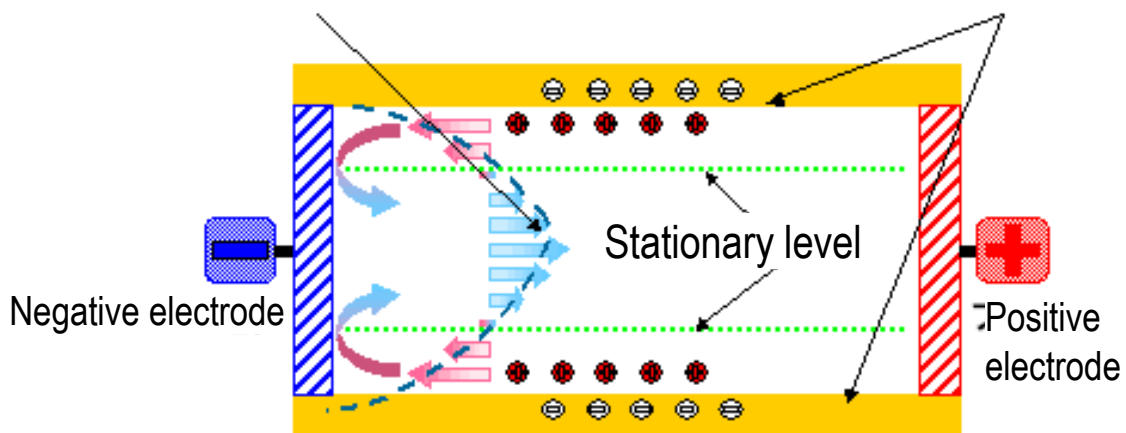
$$u_{\text{app}} = u + u_{\text{osm}} \dots \dots \dots (14)$$

- ▶ u_{app} varies parabolically with cell depth h and is given by the following equation when $k = (\text{cell width}/\text{cell depth}) \gg 1$.

$$u_{\text{osm}} = \frac{u_0}{2} \left(\frac{3h^2}{b^2} - 1 \right) \dots \dots \dots (15)$$

- ▶ b : 1/2 of the cell thickness, u_0 is the electrophoretic mobility at the wall surface ($h = \pm b$)

Electroosmotic flow curve Negative charge inside the cell

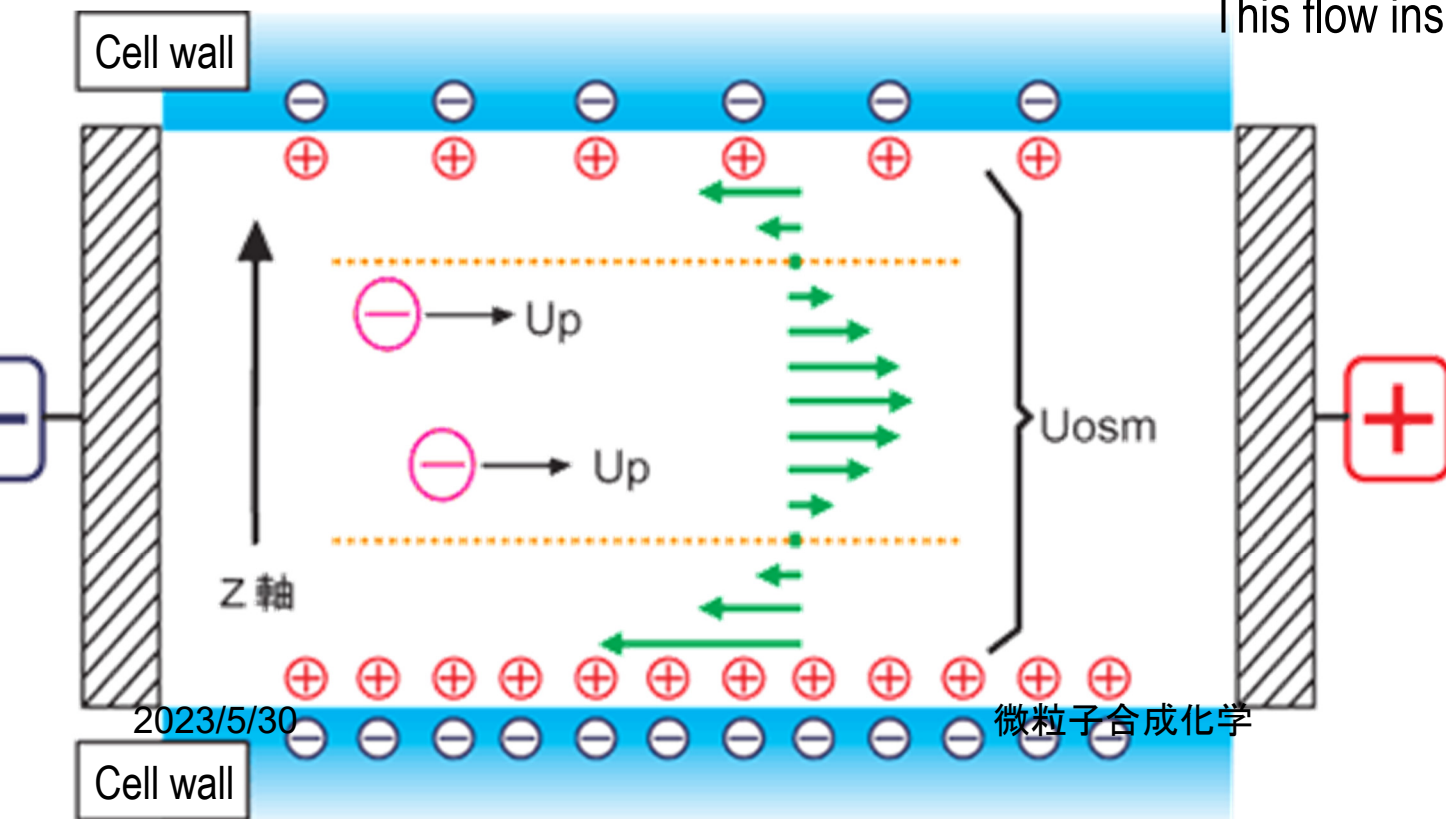


Electroosmotic flow

Quartz cells are generally used as measurement cells. The isoelectric point of quartz is 2 ~ 3, and the surface of the cell is usually negatively charged. There are many ions.

When a voltage is applied to the cell, the positive ions near the cell wall are pulled toward the cathode and move, creating a flow. Since the cell is normally a closed system, the flow in the vicinity of the cell wall is circulated, and the flow in the opposite direction occurs in the vicinity of the cell center.

This flow inside the cell is called electroosmotic flow.



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Electrophoresis measurement

- ▶ u_{app} at level h_s , giving $u_{\text{osm}}=0$, gives the true electrophoretic mobility u . This h_s is called the stationary level and given by the following equation.

$$h_s = \pm \frac{b}{\sqrt{3}} = \pm 0.577b$$

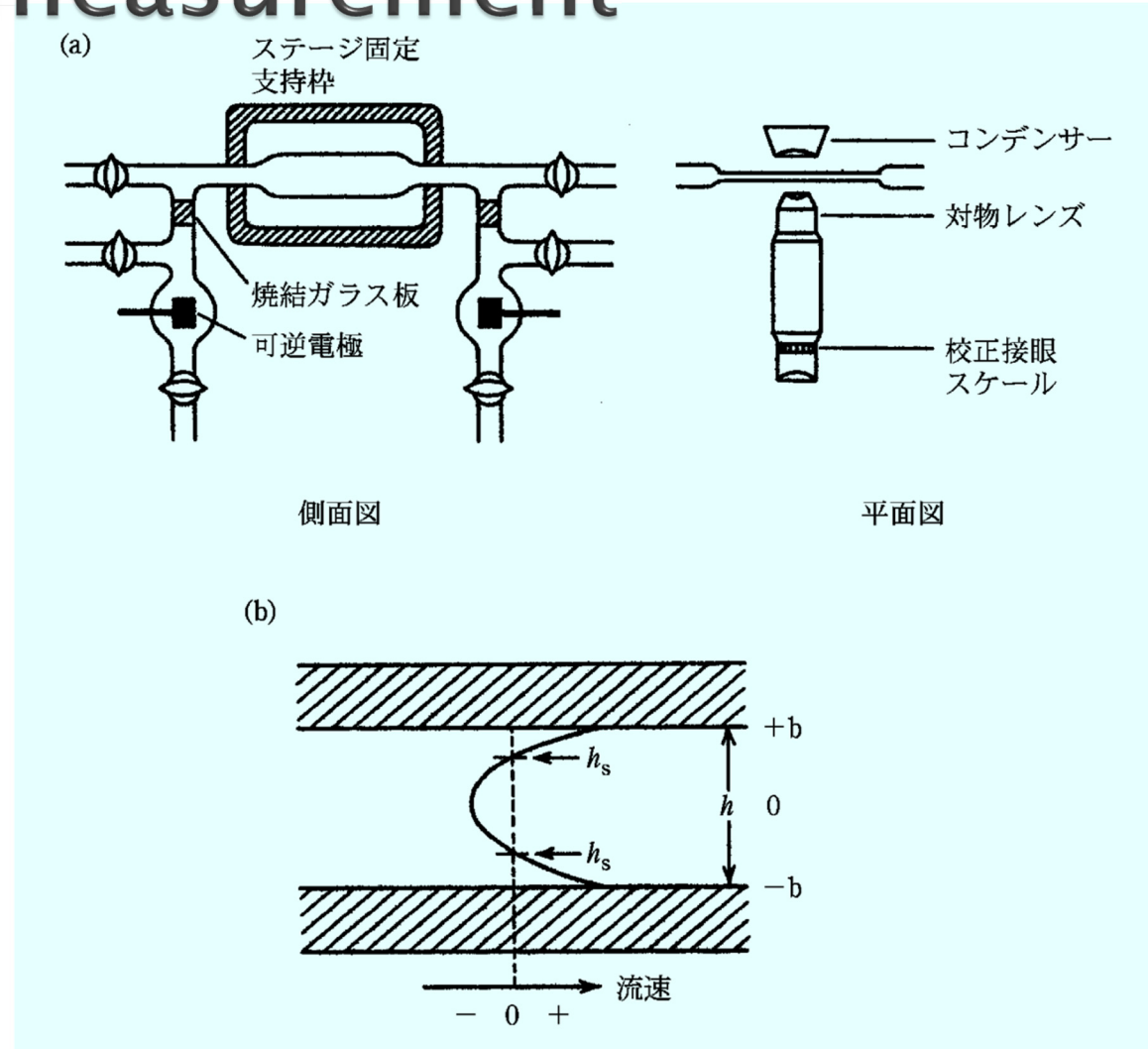
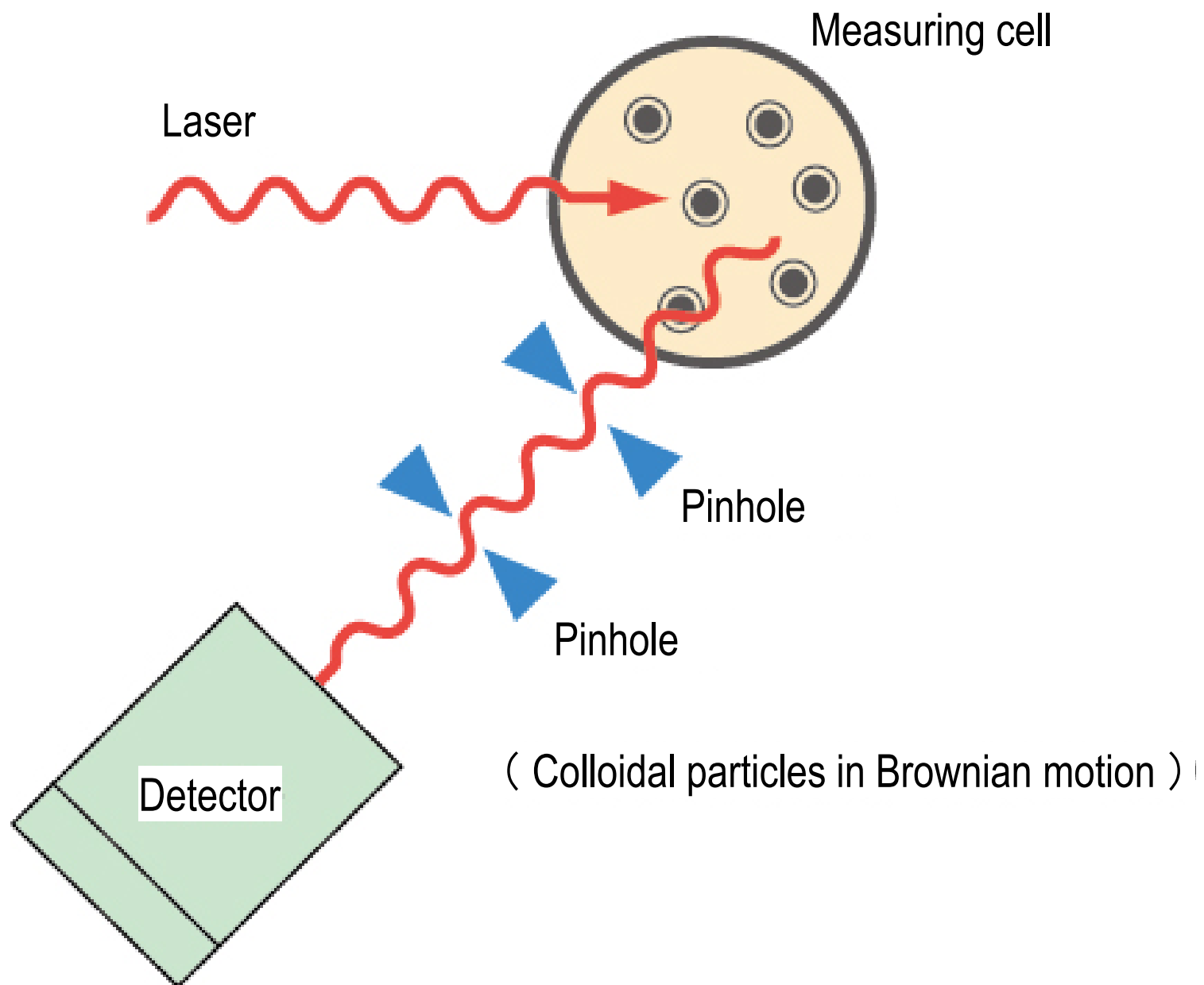


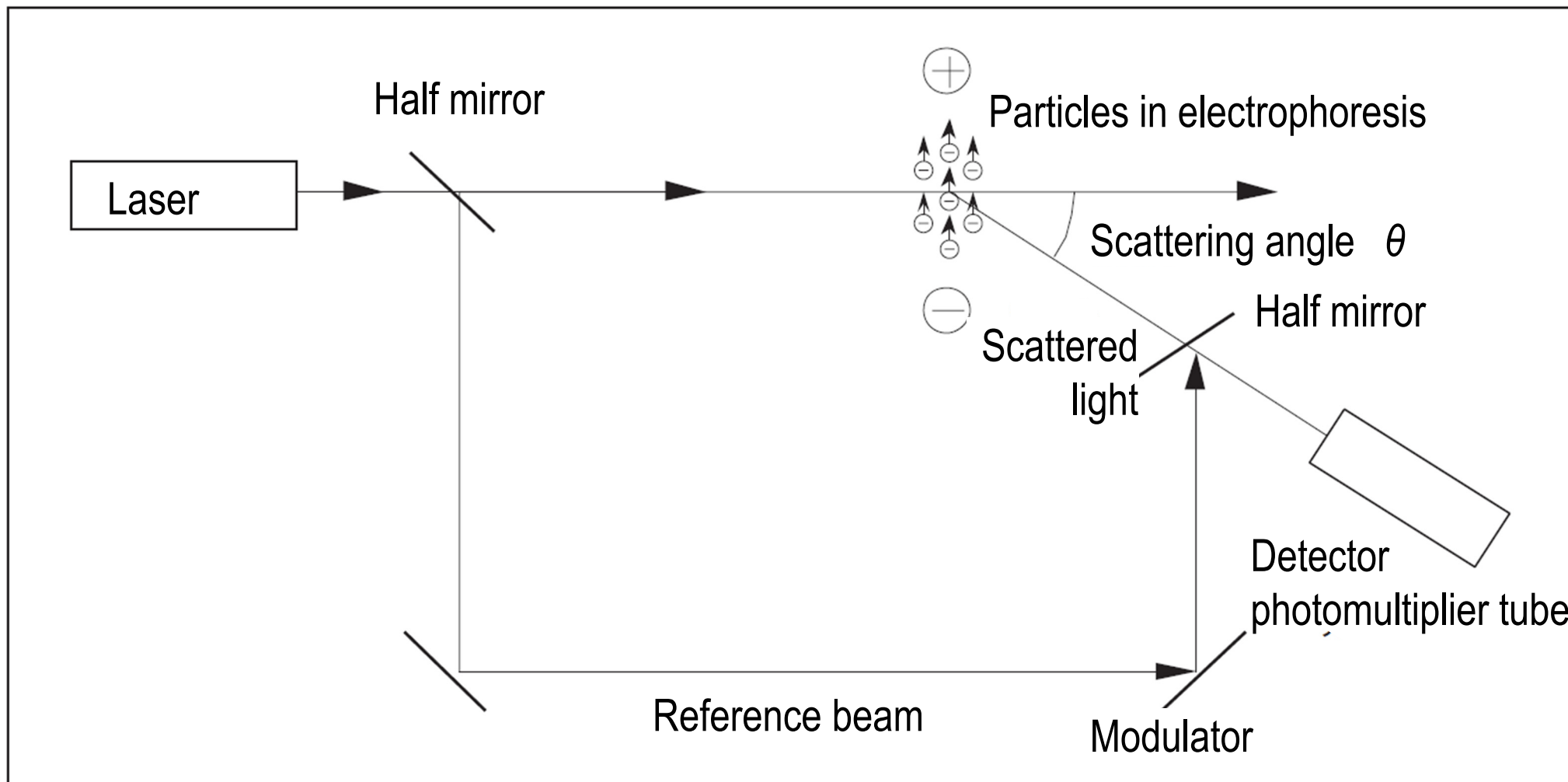
図4 顕微鏡電気泳動測定装置(a)とセル中の流速の分布と座標の取り方(b)

Electrophoretic light scattering measurement method

- ▶ The electrophoretic light scattering measurement method is also called the laser Doppler method. This is a method that uses the “Doppler effect” to give the migration velocity of particles. The Doppler effect is the phenomenon that when light or sound waves strike a moving object and are reflected or scattered, the frequency of the light or sound wave changes in proportion to the speed of the object. When electrophoretic particles are irradiated with laser light, the scattered light from the particles undergoes a frequency shift due to the Doppler effect. We can see the migration speed of the particles.



Electrophoretic light scattering measurement method



ヘテロダイン法による電気泳動光散乱光度計の光学系

Isoelectric point, i.e.p.

- ▶ Normally, the isoelectric point is the pH at which the ζ potential becomes zero under the condition where specific adsorption (chemisorption) does not occur.
- ▶ In oxide particles, the isoelectric point is on the acidic side for acidic oxides and on the alkaline side for basic oxides.
- ▶ When specific adsorption occurs, the isoelectric point changes even for the same material.
- ▶ On the other hand, the pH at which the true surface potential becomes 0 is called the point of zero charge. When chemisorption of sign ions occurs, the isoelectric point changes even though the surface potential is zero.

3. Theory of dispersion & aggregation, and evaluation of dispersion stability

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DLVO theory

DLVO理論

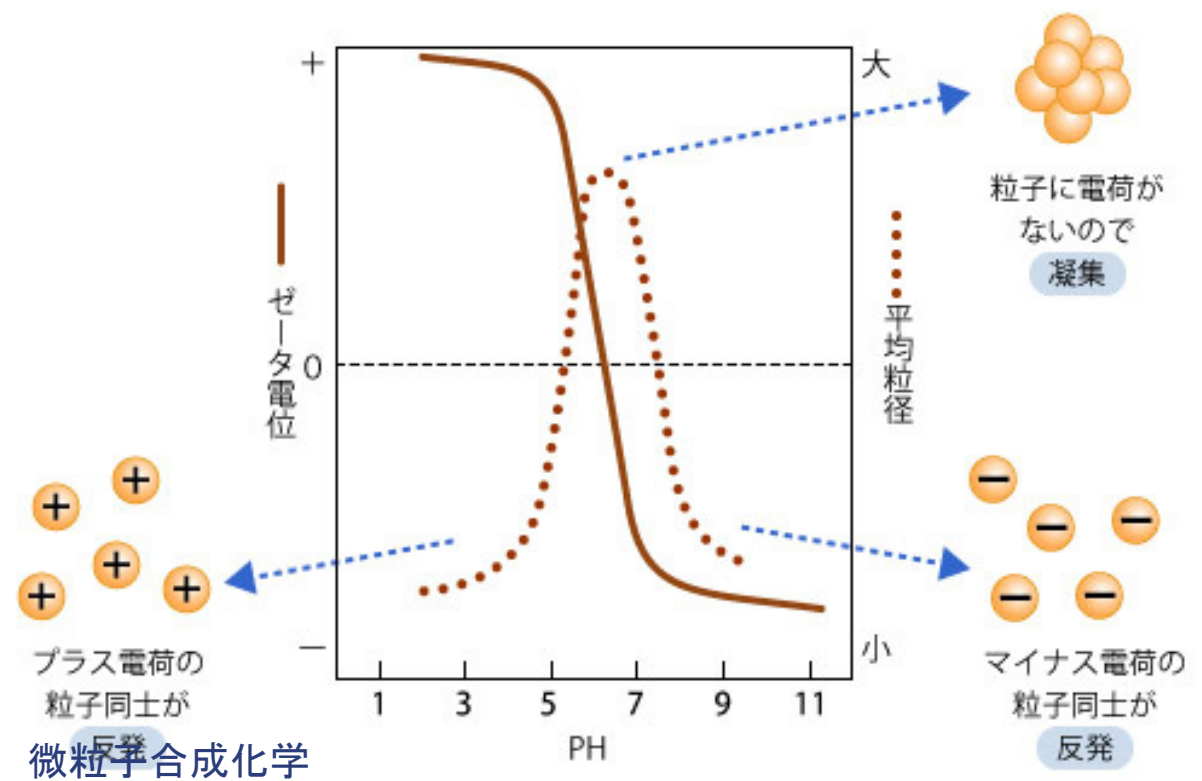
Derjaguin-Landau-Verwey-Overbeek theory



Derjaguin, B.; Landau, L. (1941), “Theory of the stability of strongly charged lyophobic sols and of the adhesion of strongly charged particles in solutions of electrolytes”, *Acta Physico Chemica URSS* **14**: 633.

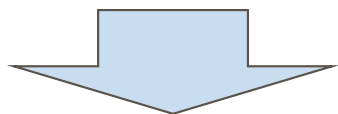
Verwey, E. J. W.; Overbeek, J. Th. G. (1948), *Theory of the stability of lyophobic colloids*, Amsterdam: Elsevier.

Dispersion and Aggregation



Dispersion and Aggregation

- What is dispersion?
 - Particles drift in the solvent without agglomeration.
- What is aggregation?
 - Particles gather more and form larger flocs.



- Materials naturally aggregate.
 - Intermolecular force
 - van der Waals force

Dispersion and aggregation (Equilibrium consideration)

- Aggregation

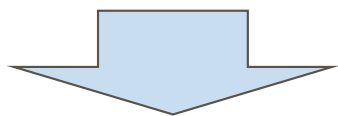
- van der Waals interaction

凝集

- Dispersion

- Electrostatic repulsion

分散



- Repulsion due to surface potential

Way to think

Dispersion and aggregation

- Interaction due to van der Waals forces
- electrostatic repulsion

$$V_{\text{total}} = V_{\text{H}} + V_{\text{el}}$$

V_{H} : interaction energy due to van der Waals force

V_{el} : interaction energy due to electrostatic repulsion

Dispersion and aggregation

Way to think

$$V_{\text{total}} = V_{\text{H}} + V_{\text{el}}$$

V_{H} : interaction energy due to van der Waals force

V_{el} : interaction energy due to electrostatic repulsion

V_{total} Positive \rightarrow Dispersion

V_{total} Negative \rightarrow Aggregation

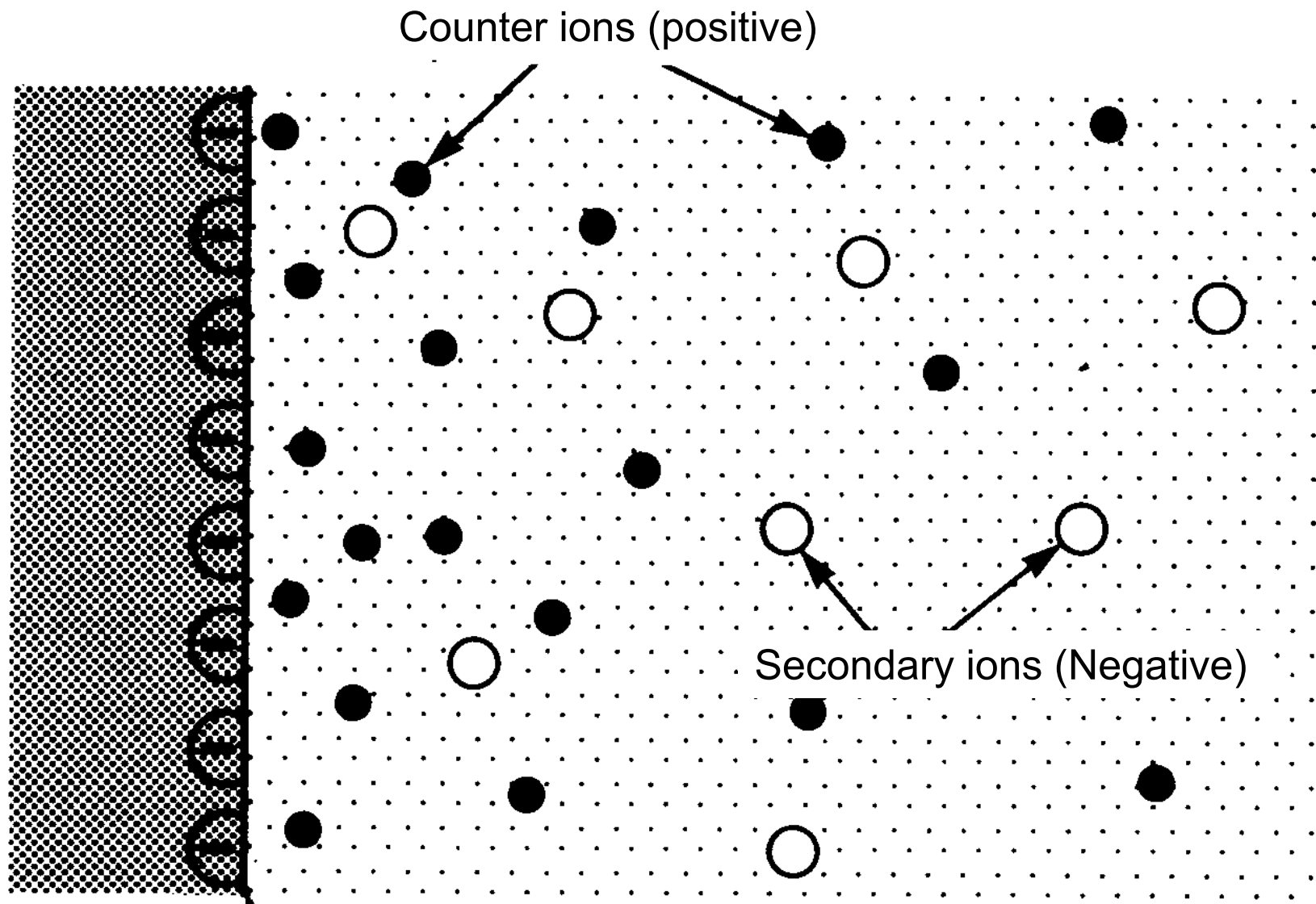
Electrostatic repulsion



Electrostatic repulsion

- Particle surface is charged
 - Electrostatic phenomena
- Could this be the source of the electrostatic repulsion?

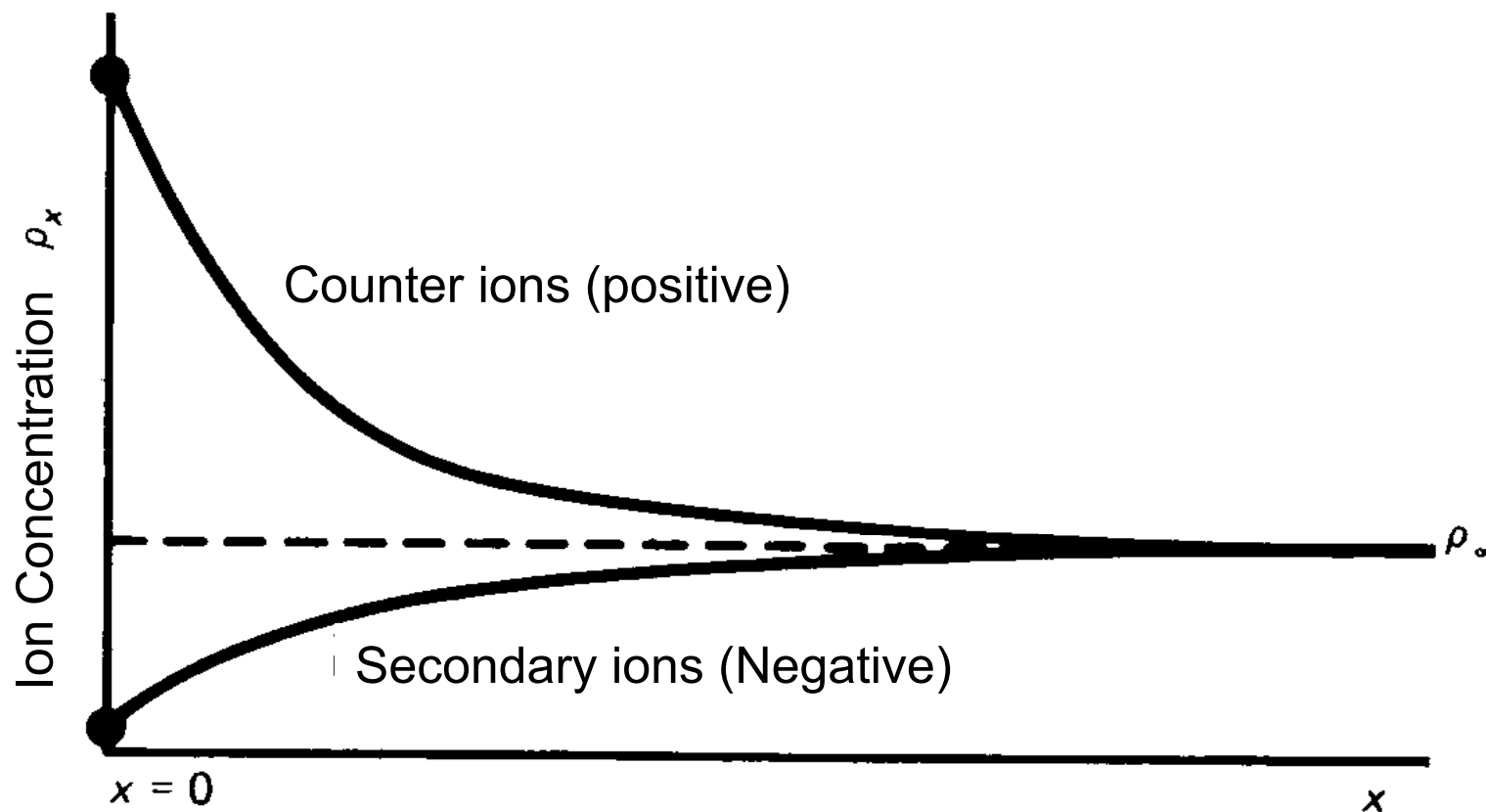
- Start here



Counter ions (positive)

Secondary ions (Negative)

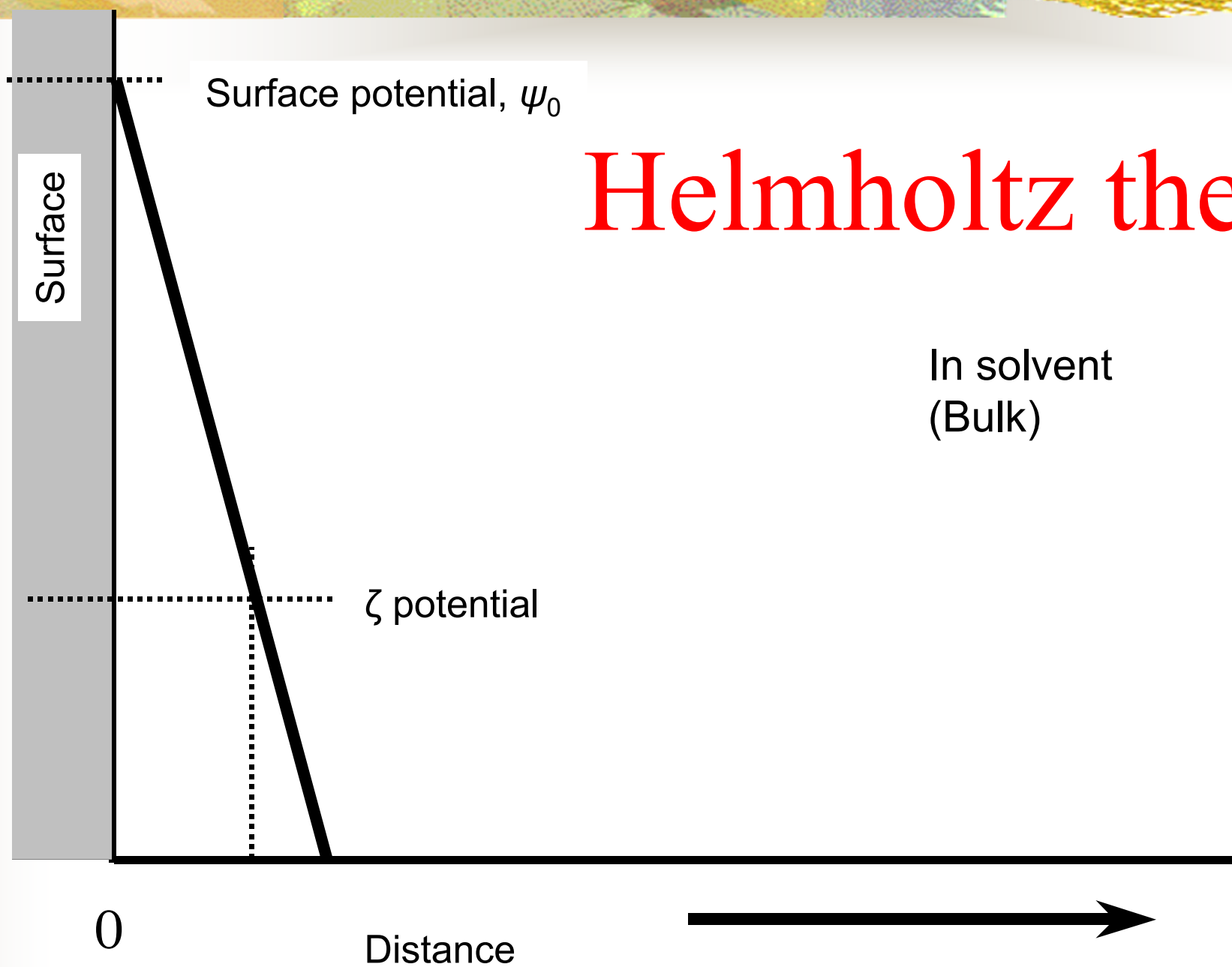
負に帯電した表面



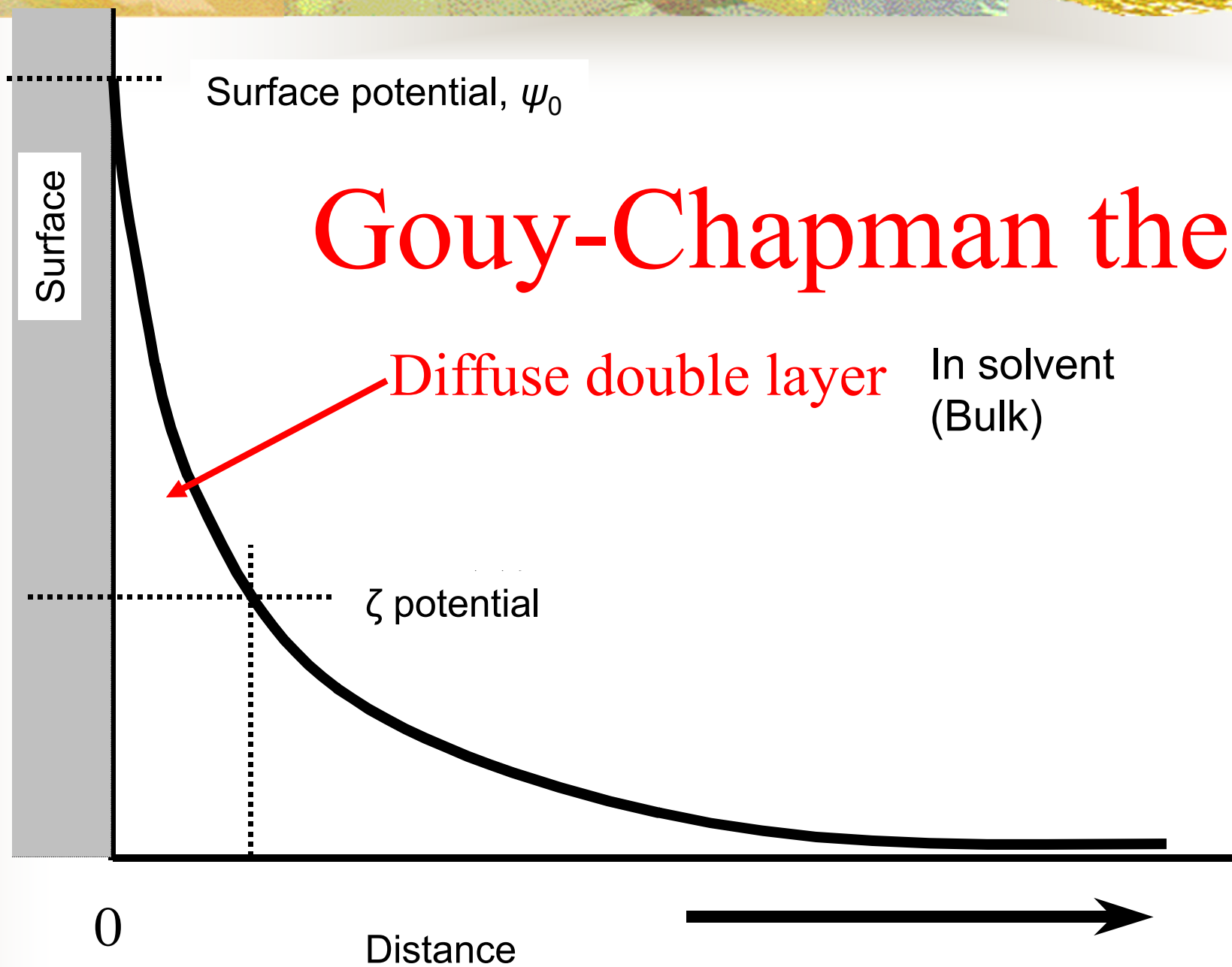
Near charged surfaces, counter ions (charges of the opposite to the surface charge) accumulate, while secondary ions are scarce. This graph is for the 1-1 electrolyte.

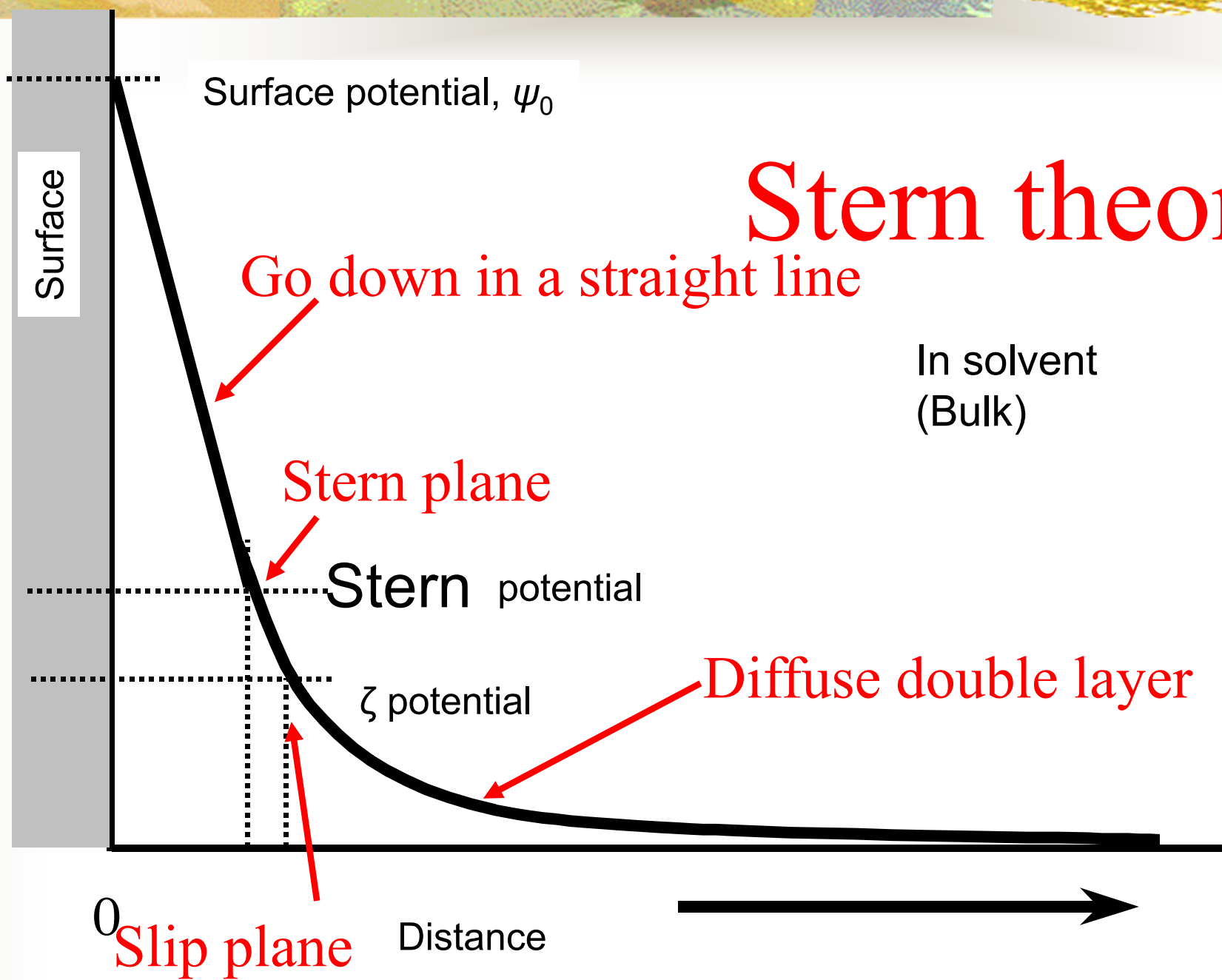
Potential drops with distance

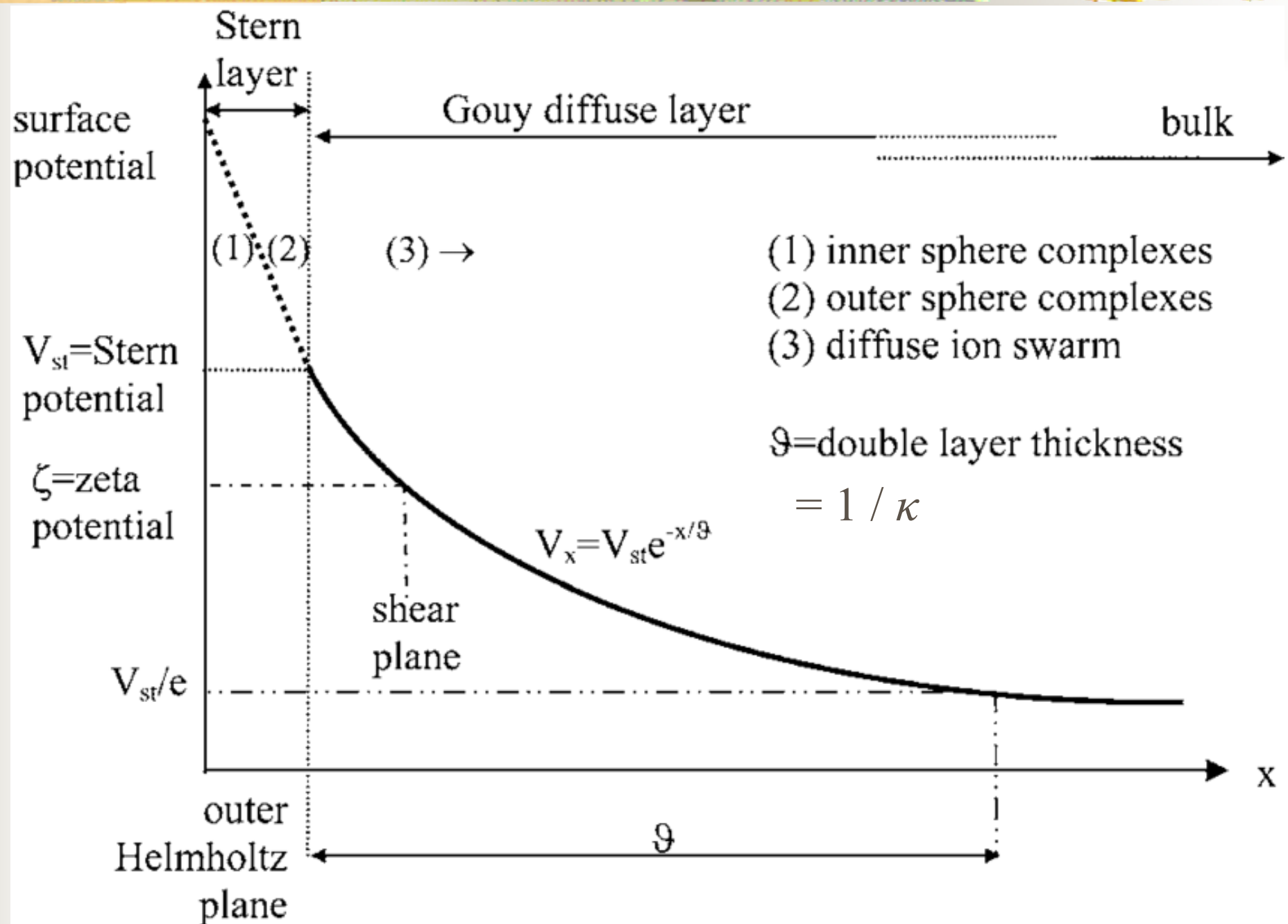
- Helmholtz theory
- Gouy-Chapman theory
- Stern theory



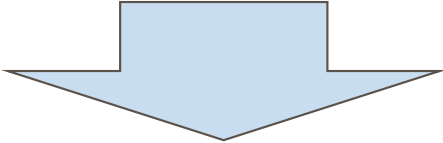
Helmholtz theory

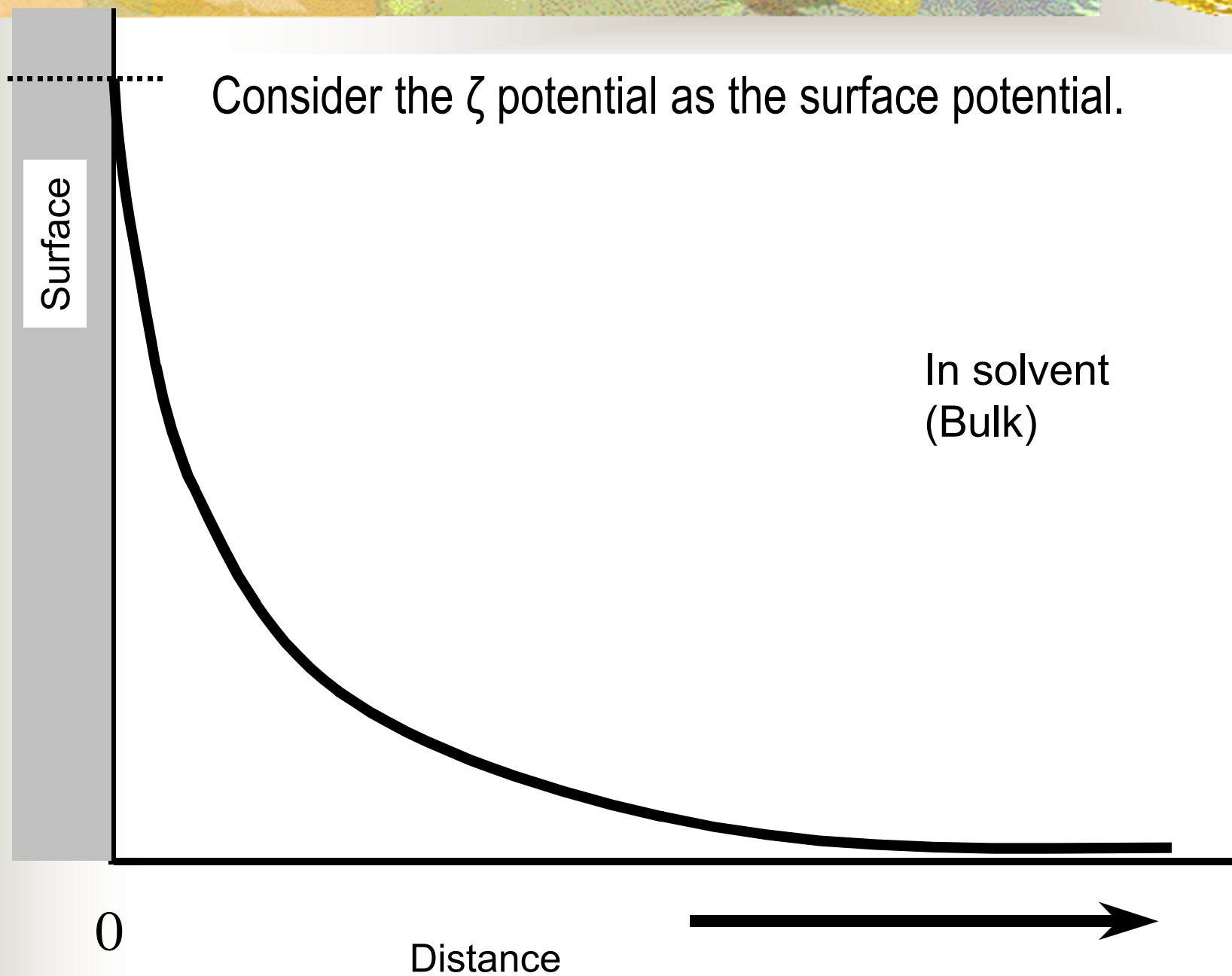






How to think realistically

- Only the ζ potential can be measured
 - The ζ potential is considered equal to the Stern potential.
 - Then, consider the ζ potential as the surface potential.
- 
- Instead of Stern theory, let us apply Gouy-Chapman's diffuse double layer theory in reality.



1. The ion concentration in the diffuse layer follows the Boltzmann distribution.

$$n_+ = n_{0+} \exp\left(\frac{-z_+ e \psi}{kT}\right) \quad (1)$$

$$n_- = n_{0-} \exp\left(\frac{z_- e \psi}{kT}\right)$$

n : number concentration of ions in diffusion layer

n_0 : number concentration of ions in bulk solution

z : Ion valence

k : Boltzmann constant

T : Temperature

ψ : Potential at distance x

$+$, $-$: Positive ions or negative ions

Surface potential:

ψ_0 is defined by bulk activity c of potential determining Ion:

$$\psi_0 = \frac{RT}{zF} \ln \frac{c}{c_0} \quad (2)$$

R : Gas constant

c_0 : c at $\psi_0 = 0$

Potential in diffuse layer is defined as Poisson equation:

$$\Delta \psi = \text{div} (\text{grad } \psi) = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = -\frac{\rho}{\epsilon_r \epsilon_0} \quad (3)$$

ϵ_r : Dielectric constant of solution

ϵ_0 : Dielectric constant in vacuum

ρ : Charge density

ρ : Charge density is defined by

symmetrical electrolyte $(z_+ = z_- = z, n_{0+} = n_{0-} = n)$

$$\begin{aligned}\rho &= ze(n_+ - n_-) \\ &= nze \left\{ \exp\left(-\frac{ze\psi}{kT}\right) - \exp\left(\frac{ze\psi}{kT}\right) \right\} \\ &= -2nze \sinh\left(\frac{ze\psi}{kT}\right)\end{aligned}\quad (4)$$

Therefore,
the Poisson-Boltzmann equation for the flat electric double layer is derived from Eqs. (3) and (4), considering only x-axis.

$$\frac{d^2\psi}{dx^2} = \frac{2nze}{\epsilon_r\epsilon_0} \sinh \frac{ze\psi}{kT} \quad (5)$$

It is obtained by integrating Eq. (5).

$$\tanh \frac{ze\psi}{4kT} = \tanh \left(\frac{ze\psi_0}{4kT} \right) \exp(-\kappa x) \quad (6)$$

$ze\psi/kT \ll 1$ then, eq.(5) is simplified as

$$\frac{d^2\psi}{dx^2} = \kappa^2\psi \quad (7)$$

where
$$\kappa^2 = \frac{2nz^2e^2}{\epsilon_r\epsilon_0kT} \quad (8)$$

In an aqueous solution at 25° C, the following is obtained.

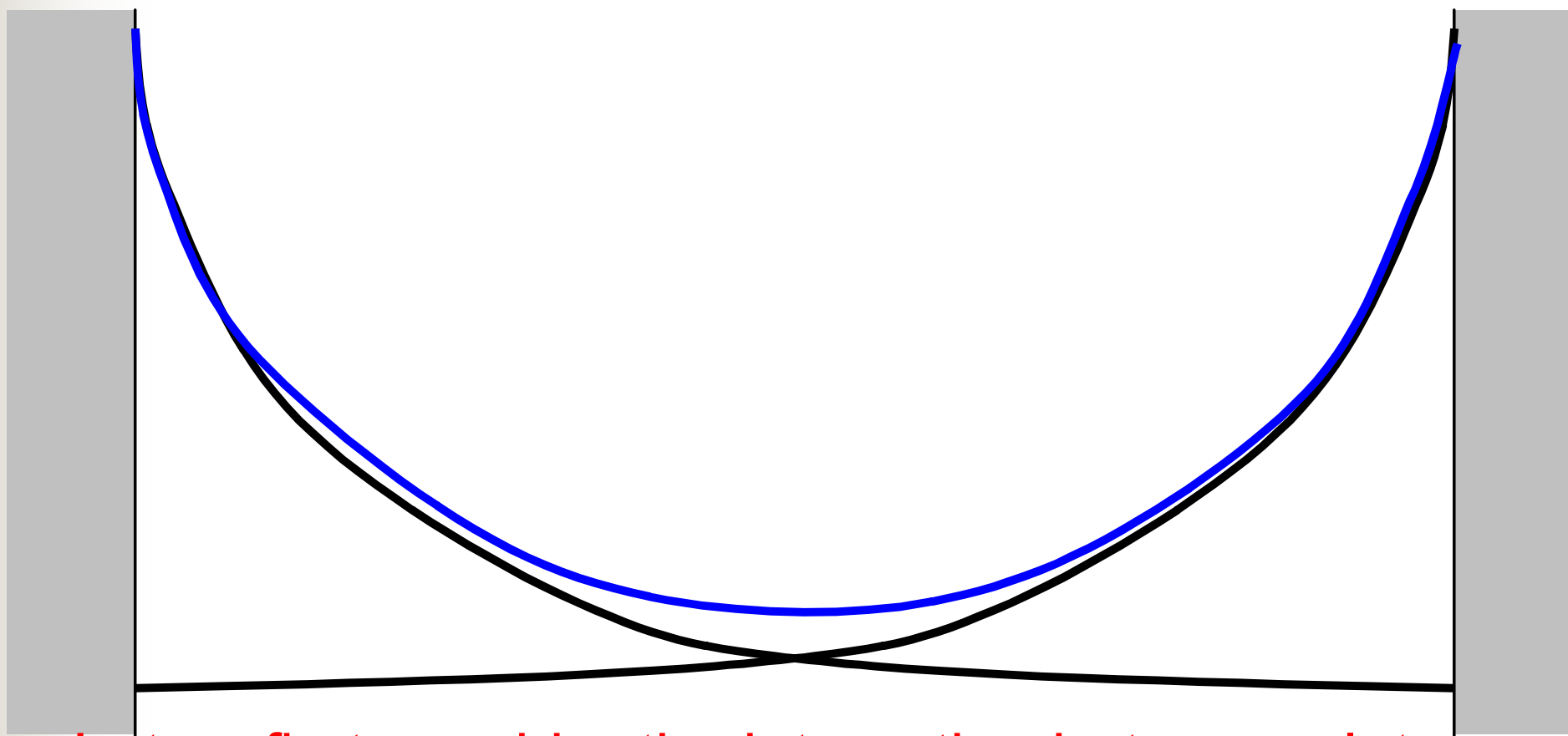
$$\kappa = 3.3 \times 10^9 z\sqrt{c} \quad (9)$$

Solving equation (7) yields the following.

$$\psi = \psi_0 \exp(-\kappa x) \quad (10)$$

κ is called as Debye-Huckel parameter.

Next, consider the interaction between the flat plate electric double layers.



Let us first consider the interaction between plates

The force acting on two parallel plates (distance between plates: h) in a solution is

$$P = P_E + P_O \quad (15)$$

The electrostatic component P_E is the force that is attracted inward by the electric lines of force.

The osmotic pressure component, P_O , is the force pushed outward by the osmotic pressure of the counterions.

$$P_E = -\frac{\epsilon_r \epsilon_0}{2} \left(\frac{d\psi}{dx} \right)^2$$

$$P_O = (n_+ + n_-)kT - 2nkT \quad (16)$$

P_O is always larger than P_E , and the plate receives a repulsive force. If the surface potential does not change during the approaching process of the plate, the repulsive force received by the plate per unit area is given by the following formula from Eqs. (1) and (16), ignoring the contribution of P_E .

Let's supplement.

Consider the plane exactly halfway between the two planes and the plane at infinity.

For the former, due to symmetry, the electric field is zero. For the latter, the electric field is zero. Therefore, only the osmotic pressure component should be taken into account.

$$P_R(h) = 2nkT \left\{ \cosh \frac{ze\psi_{h/2}}{kT} - 1 \right\} \quad (17)$$

$\psi_{2/h}$: potential at exactly the middle between two plates

If the interaction is weak, $\psi_{h/2}$ can be thought of as twice the potential, $\psi_{s(h/2)}$, of a single electric double layer.

$$ze\psi / 4kT \ll 1 \text{ then } \tanh(ze\psi / 4kT) \cong ze\psi / 4kT$$

(This approximation holds when $\psi < 20\text{mV}$, as will be described later.)

Eq. (6) is transformed as follows.

$$\psi_{(h/2)} = \frac{8kT}{ze} \gamma \exp\left(-\kappa \frac{h}{2}\right) \quad (18)$$

$$\gamma = \tanh\left(\frac{ze\psi_0}{4kT}\right) \quad (19)$$

Eq. (17) is transformed as follows.

$$ze\psi_{h/2}/kT \ll 1 \text{ then } P_R(h) \cong nkT\{ze\psi_{h/2}/kT\}^2$$

Substituting eq. (18) into here yields the following.

(This approximation holds when $\kappa h > 1$, that is, when h is larger than the thickness of the electric double layer.

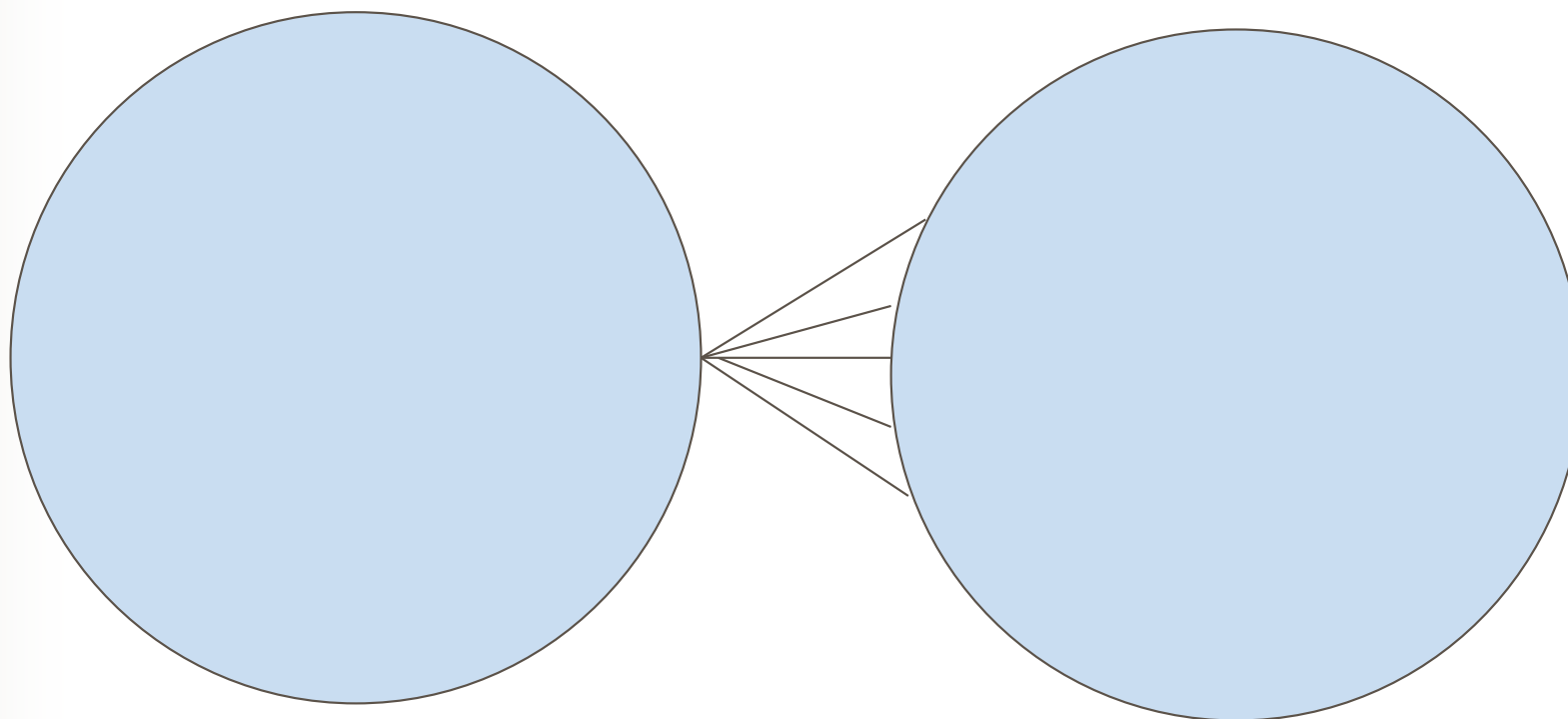
For approximation, $\cosh y = 1 + y^2$ was used.)

$$P_R(h) = 64nkT\gamma^2 \exp(-\kappa h) \quad (20)$$

Therefore, the interaction energy of the electric double layer between the plates is as follows.

$$V_R(h) = -\int_{\infty}^h P_R(h) dh = \frac{64nkT}{\kappa} \gamma^2 \exp(-\kappa h) \quad (21)$$

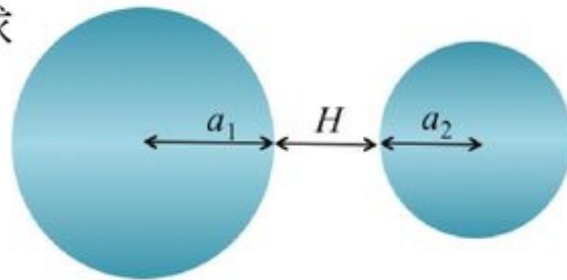
Next, consider the interaction
between spherical particles



Next, let us consider the interaction between spherical particles.

Derjaguin approximation

2球

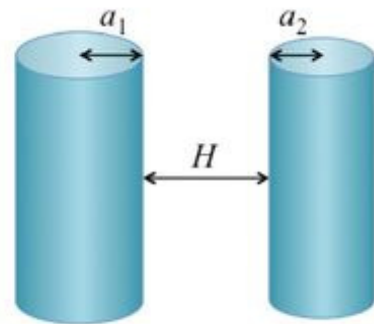


Sphere 1

Sphere 2

$$V_{sp}(H) = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_H^\infty V_{pl}(h) dh$$

平行2円柱



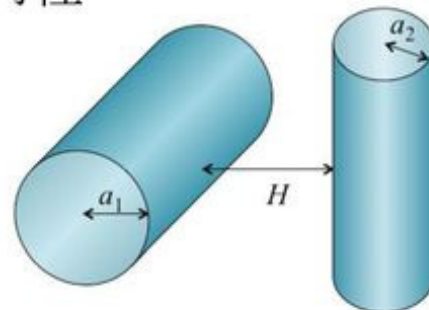
Cylinder 1

Cylinder 2

$$V_{cyl}(H) = \sqrt{\frac{2a_1 a_2}{a_1 + a_2}} \int_H^\infty V_{pl}(h) \frac{dh}{\sqrt{h - H}}$$

(per unit length)

交差2円柱



Cylinder 1

Cylinder 2

$$V_{cy\perp}(H) = 2\pi \sqrt{a_1 a_2} \int_H^\infty V_{pl}(h) dh$$

From the Derjaguin approximation, the interaction force of spherical particles can be obtained.

The interaction force between two spherical particles with radii a_1 and a_2 , when the closest distance is H , is:

$$(H \ll a_1, a_2)$$

$$P_R(H) = 2\pi \left(\frac{a_1 a_2}{a_1 + a_2} \right) V_R(H) \quad (22)$$

when $a_1 = a_2 = a$, the following eq.(23) is obtained.

$$P_R(H) = \frac{64\pi a n k T}{\kappa} \gamma^2 \exp(-\kappa h) \quad (23)$$

Therefore, the interaction energy acting between two spherical particles with radius a is obtained as follows.

$$\begin{aligned} V_R(H) &= -\int_{\infty}^H P_R(H) dH \\ &= \frac{64\pi a n k T}{\kappa^2} \gamma^2 \exp(-\kappa h) \end{aligned} \quad (24)$$

Derivation of approximation formula.

$ze\psi_0 / 4kT \ll 1$ then $\tanh(ze\psi_0 / 4kT) \cong ze\psi_0 / 4kT$

Hence, Eqs. (23) and (24) is changed to Eqs. (25) and (26).

($ze\psi_0 = 4kT$ then

$\psi_0 = 103$ mV at 25°C for 1:1 electrolyte.

$\psi_0 = 20$ mV or more, then $ze\psi_0 / 4kT$ to $\tanh\{ze\psi_0 / 4kT\}$ has, more than 1% difference.

Therefore, this approximation is allowed less than 20 mV.)

$$P_R(H) = 2\pi\alpha\epsilon_r\epsilon_0\kappa\psi_0^2 \exp(-\kappa h) \quad (25)$$

$$V_R(H) = 2\pi\alpha\epsilon_r\epsilon_0\psi_0^2 \exp(-\kappa h) \quad (26)$$

$$P_R(H) = 2\pi a \varepsilon_r \varepsilon_0 \kappa \psi_0^2 \exp(-\kappa h) \quad (25)$$

$$V_R(H) = 2\pi a \varepsilon_r \varepsilon_0 \psi_0^2 \exp(-\kappa h) \quad (26)$$

Using Eq. (13),

$$P_R(H) = \frac{2\pi a \sigma^2}{\kappa \varepsilon_r \varepsilon_0} \exp(-\kappa H) \quad (27)$$

$$V_R(H) = \frac{2\pi a \sigma^2}{\kappa^2 \varepsilon_r \varepsilon_0} \exp(-\kappa H) \quad (28)$$

$$\sigma_0 = \varepsilon_r \varepsilon_0 \kappa \psi_0 \quad (13)$$

van der Waals Interaction

Aggregation

van der Waals force and energy are

$$P_A(H) = -\frac{aA}{12H^2} \quad (29)$$

$$V_A(H) = -\frac{aA}{12H} \quad (30)$$

A is Hamaker constant.

The total energy is given below.

$$P_T(H) = \frac{2\pi a \sigma^2}{\kappa \epsilon_r \epsilon_0} \exp(-\kappa H) - \frac{aA}{12H^2} \quad (31)$$

$$V_T(H) = \frac{2\pi a \sigma^2}{\kappa^2 \epsilon_r \epsilon_0} \exp(-\kappa H) - \frac{aA}{12H} \quad (32)$$

Or

$$V_T(H) = 2\pi a \epsilon_r \epsilon_0 \psi_0^2 \exp(-\kappa h) - \frac{aA}{12H} \quad (33)$$

Consider the meaning of the formula.



How does it change depending on the solution conditions?

$$V_T(H) = 2\pi a \varepsilon_r \varepsilon_0 \psi_0^2 \exp(-\kappa H) - \frac{aA}{12H}$$

$\varepsilon_r, \varepsilon_0, \psi_0, A$ are constants.

a is a particle radius.

Changing parameter is only κ .

$$\kappa^2 = \frac{2nz^2e^2}{\epsilon_r\epsilon_0kT}$$

e elementary charge. $\epsilon_r\epsilon_0$ dielectric constants.

k Boltzmann constant.

n number concentration of ions

z ion valence

T temperature

n number concentration of ions is increased

z ion valence is increased

T temperature is decreased



K is increased

$$V_T(H) = 2\pi a \varepsilon_r \varepsilon_0 \psi_0^2 \exp(-\kappa H) - \frac{aA}{12H}$$

Let's draw a diagram.

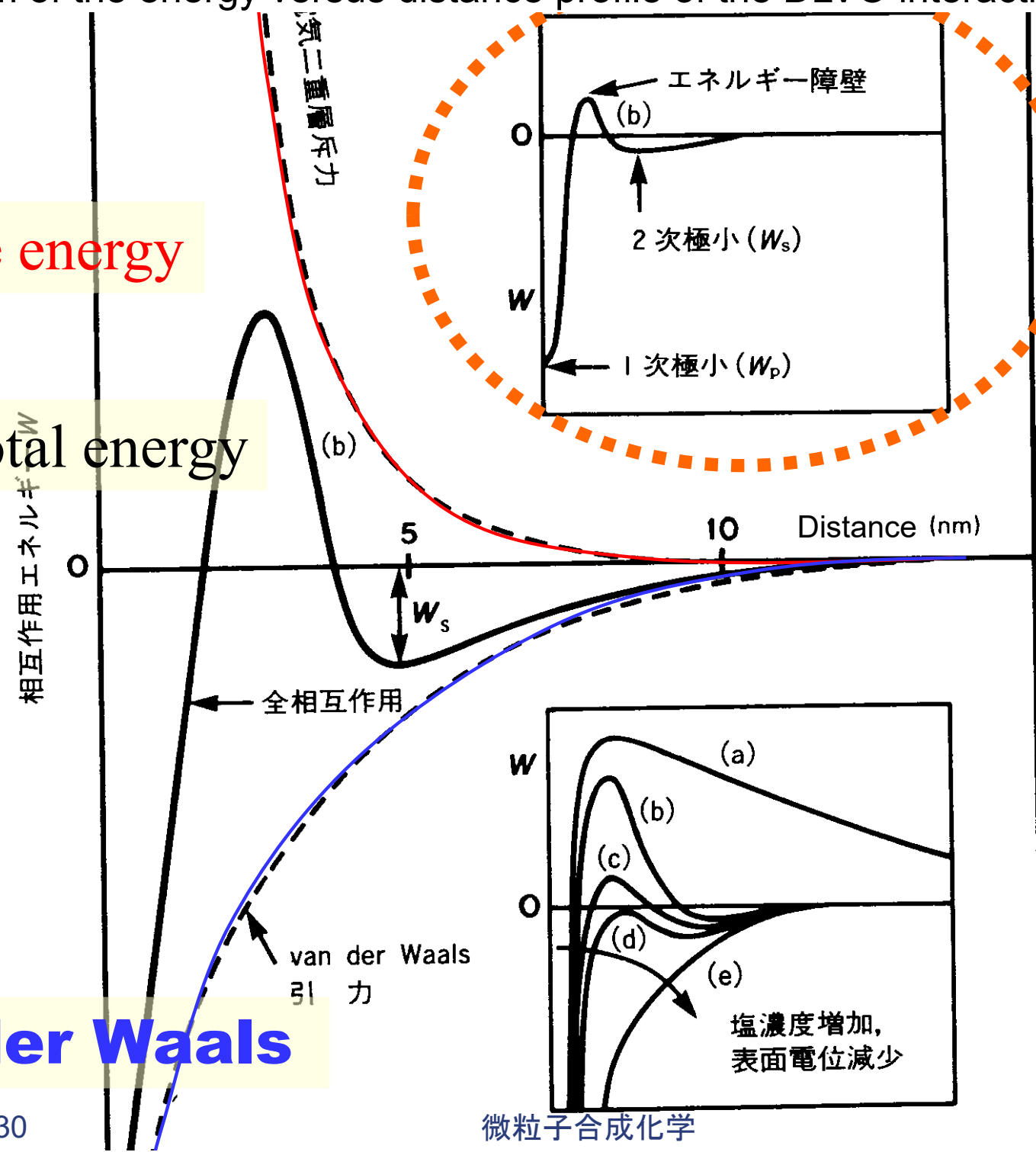
Schematic diagram of the energy versus distance profile of the DLVO interaction

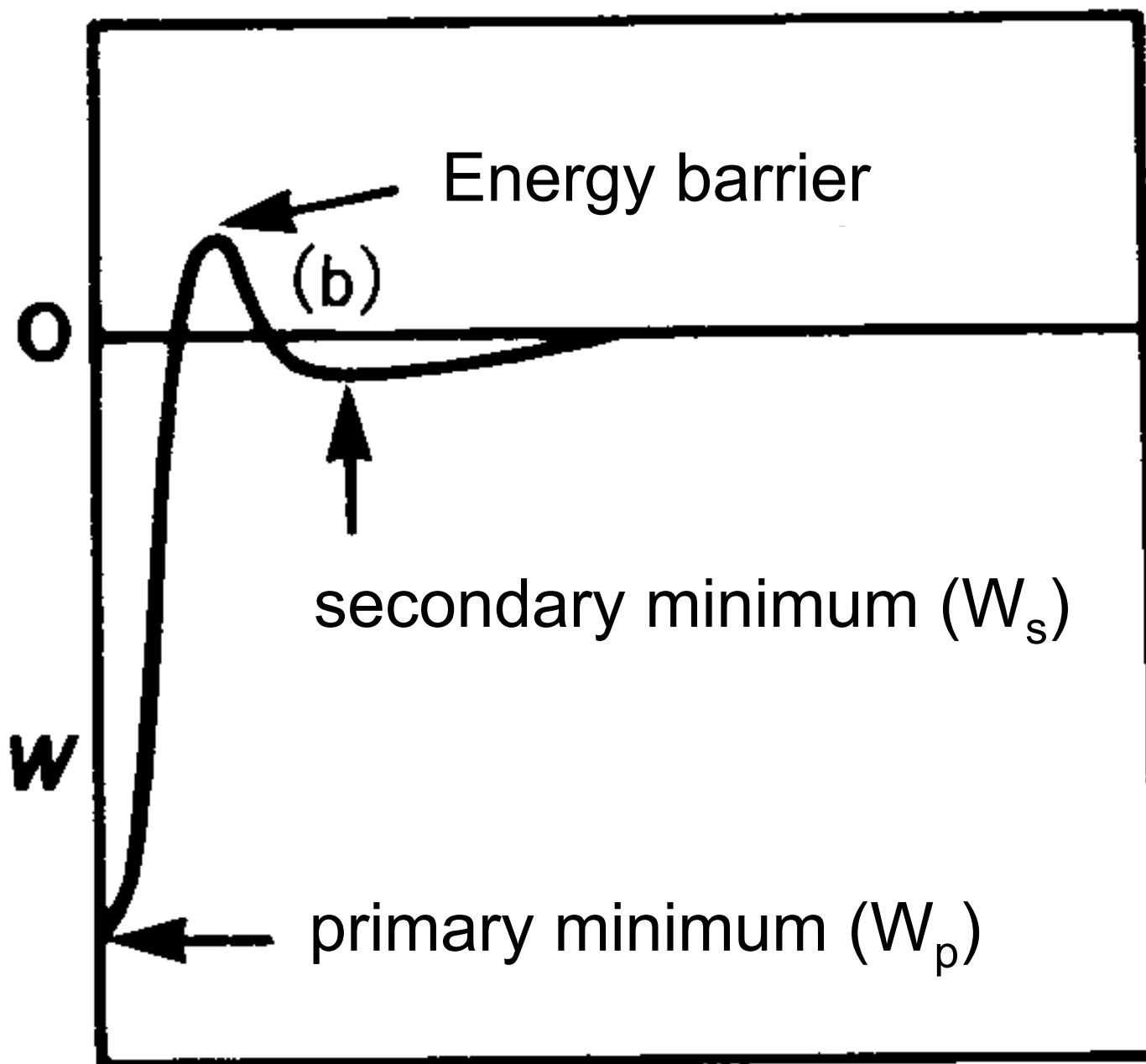


Repulsive energy

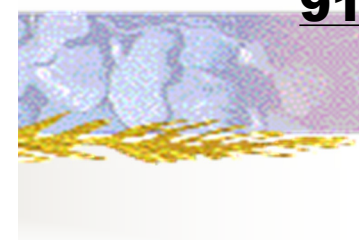
Total energy

van der Waals





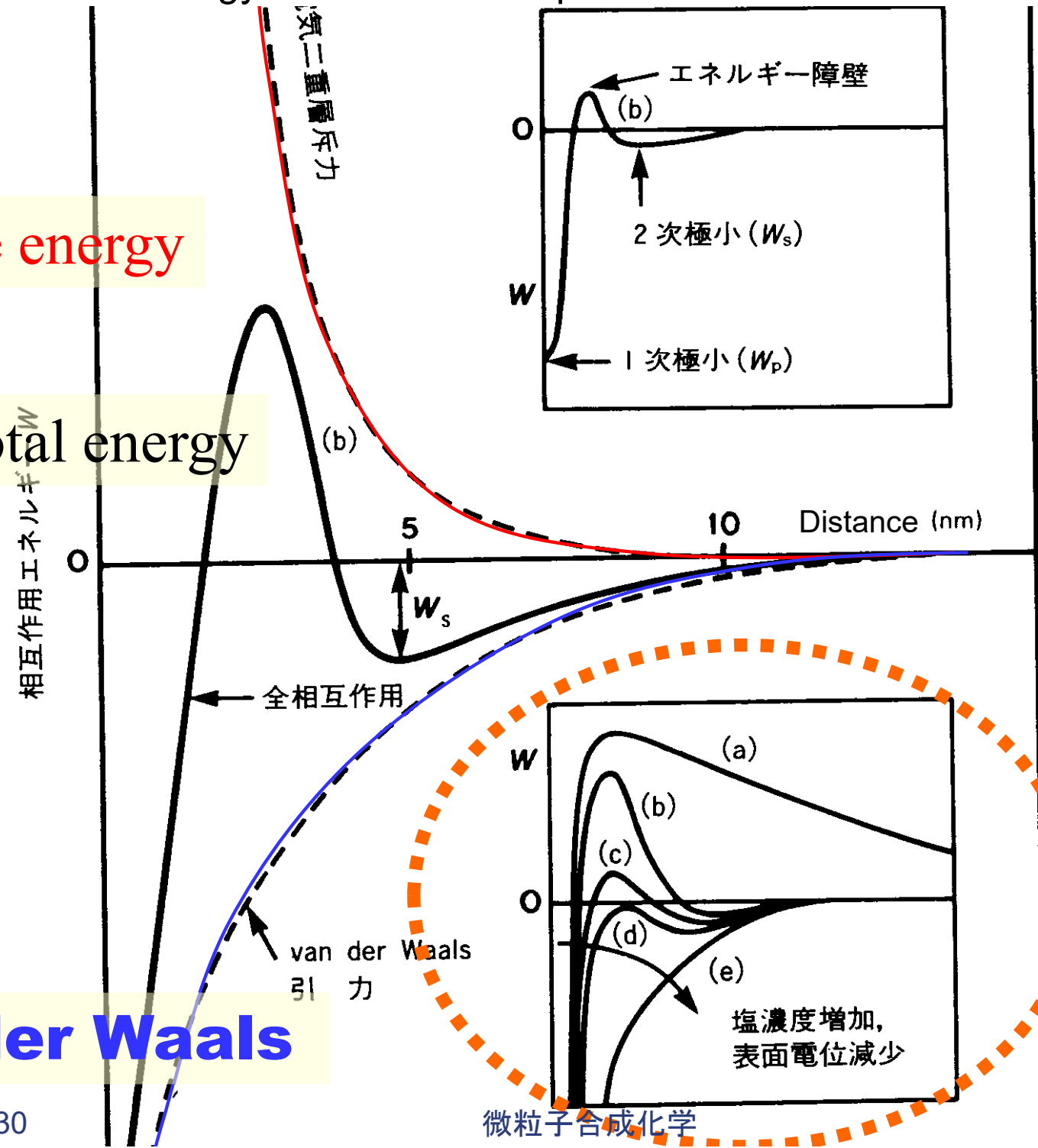
Schematic diagram of the energy versus distance profile of the DLVO interaction

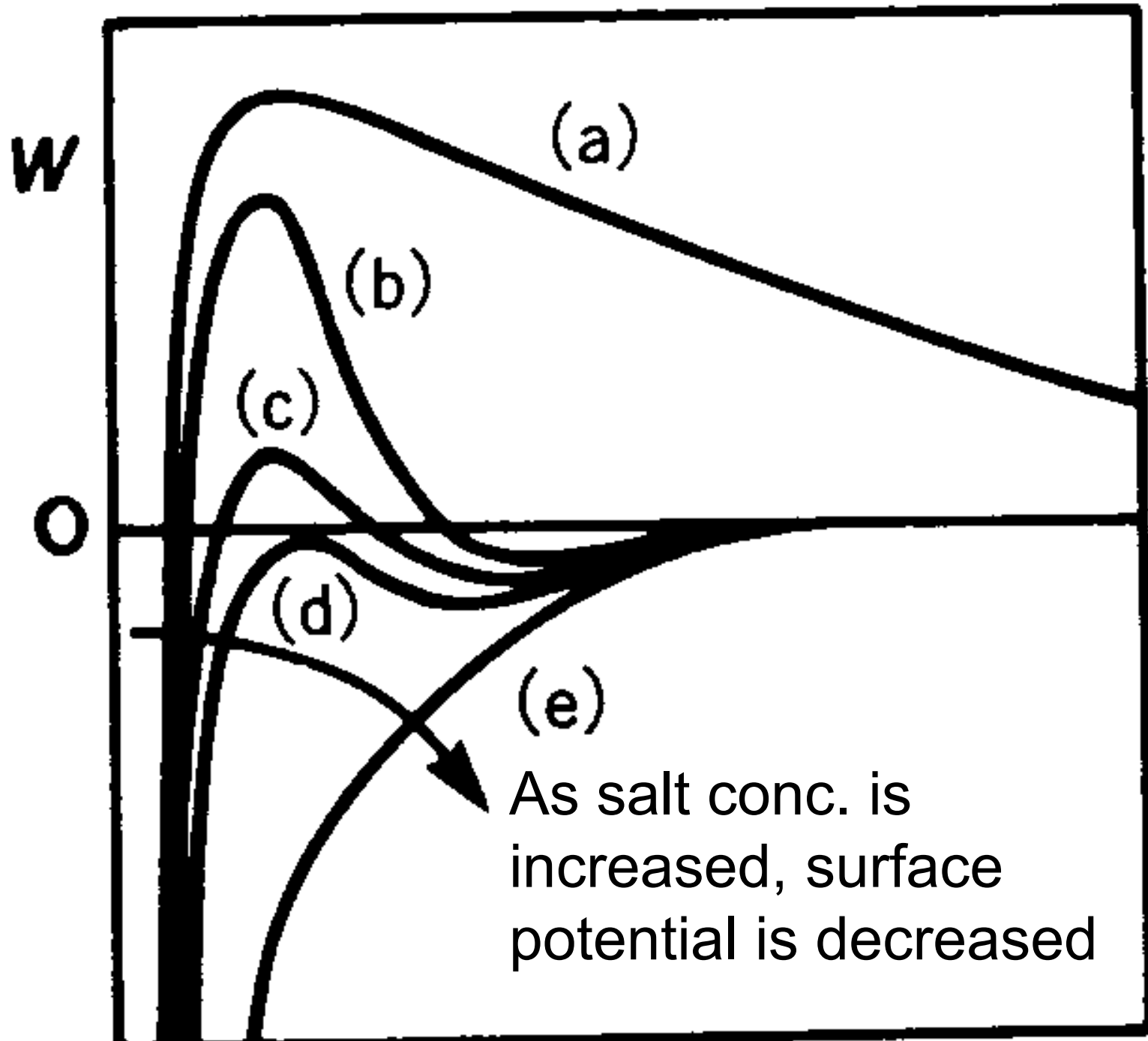


Repulsive energy

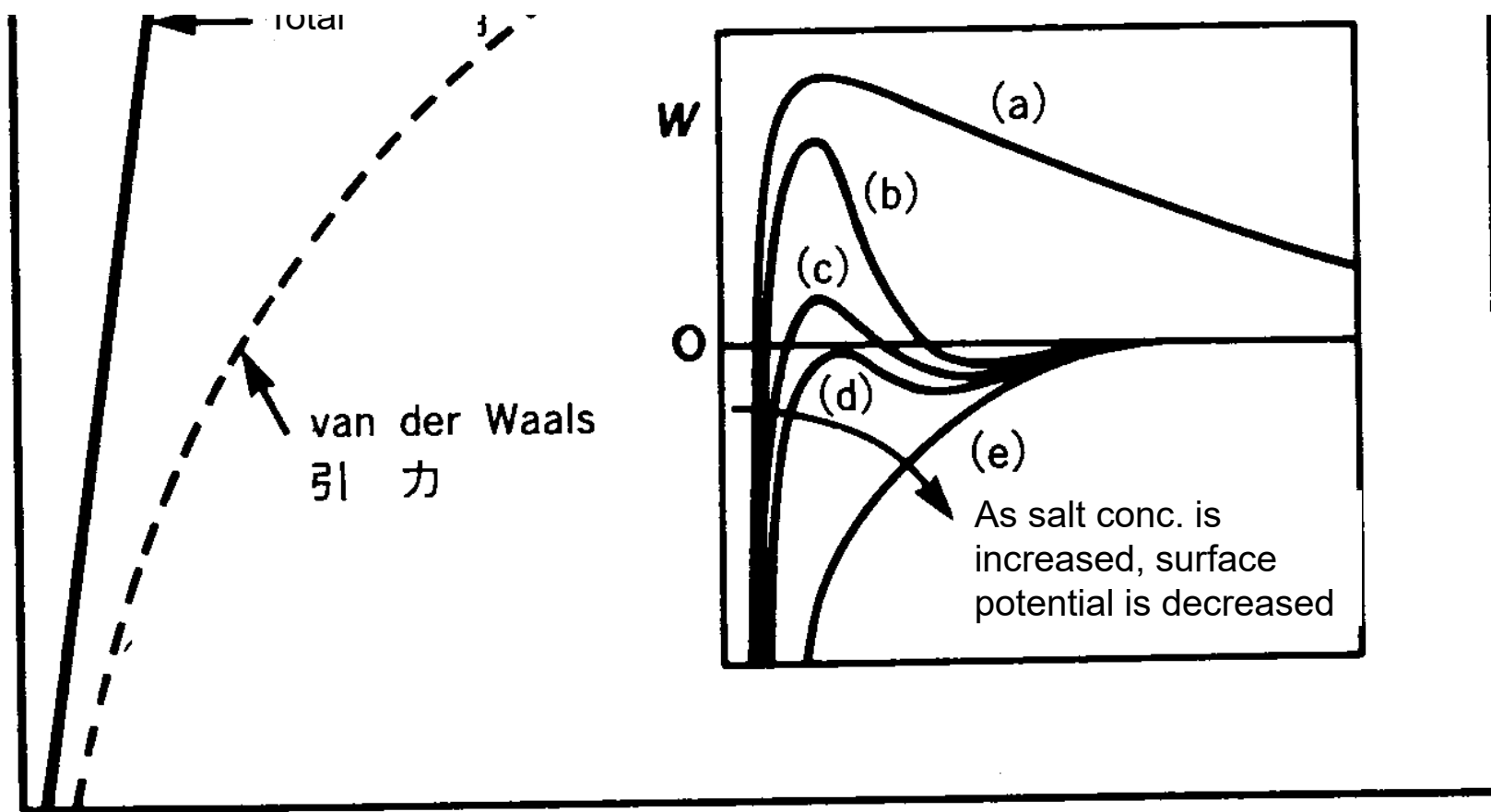
Total energy

van der Waals



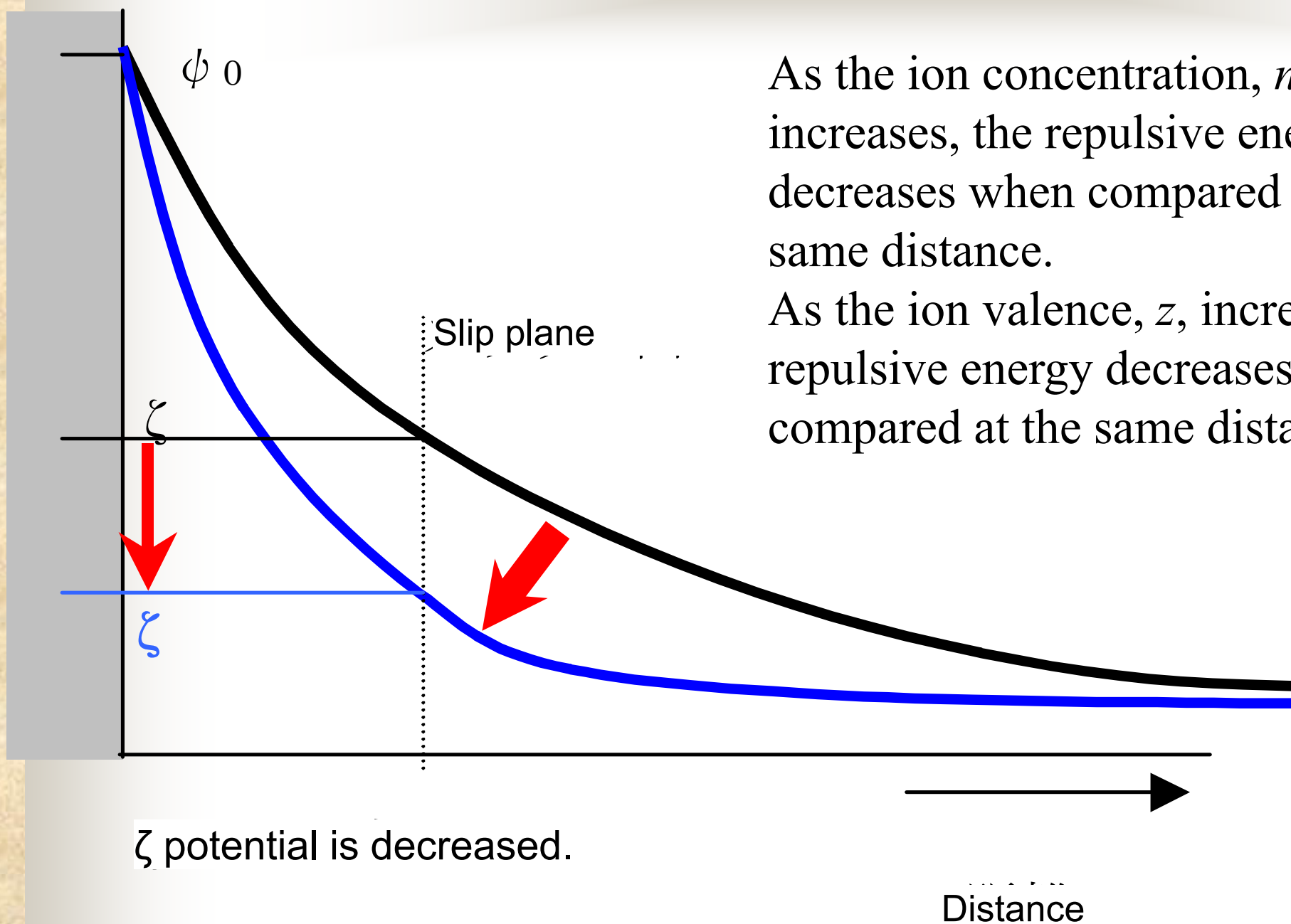


als



Schematic diagram of the energy versus distance profile of the DLVO interaction

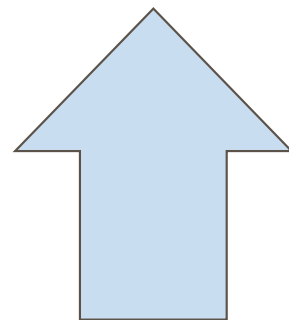
- (a) Colloidal particles are stable.
- (b) If the secondary minimum is deep enough, the colloidal particles are stable.
- (c) Colloids aggregate slowly
- (d) and (e) Colloids aggregate rapidly.



As the ion concentration, n , increases, the repulsive energy decreases when compared at the same distance.

As the ion valence, z , increases, the repulsive energy decreases when compared at the same distance.

Colloids precipitate,
when electrolytes, i.e. salts, are added



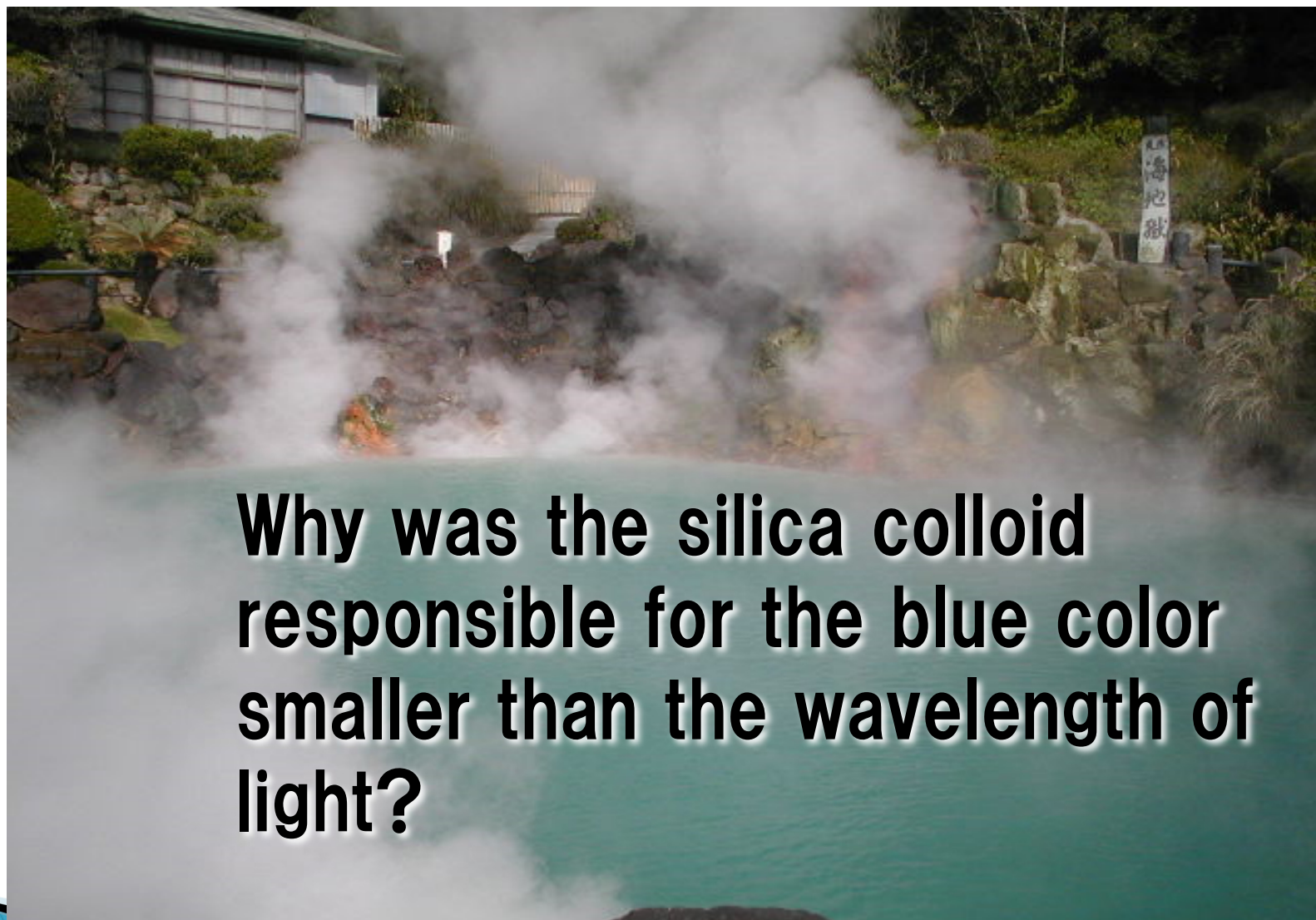
This phenomenon is proved by
the DLVO theory.

4. Concept of Rapid Aggregation Theory and Industrial Cases

2023/5/30

Use aggregation

Go back to Beppu sea hell



Why were the silica particles smaller than the wavelength?

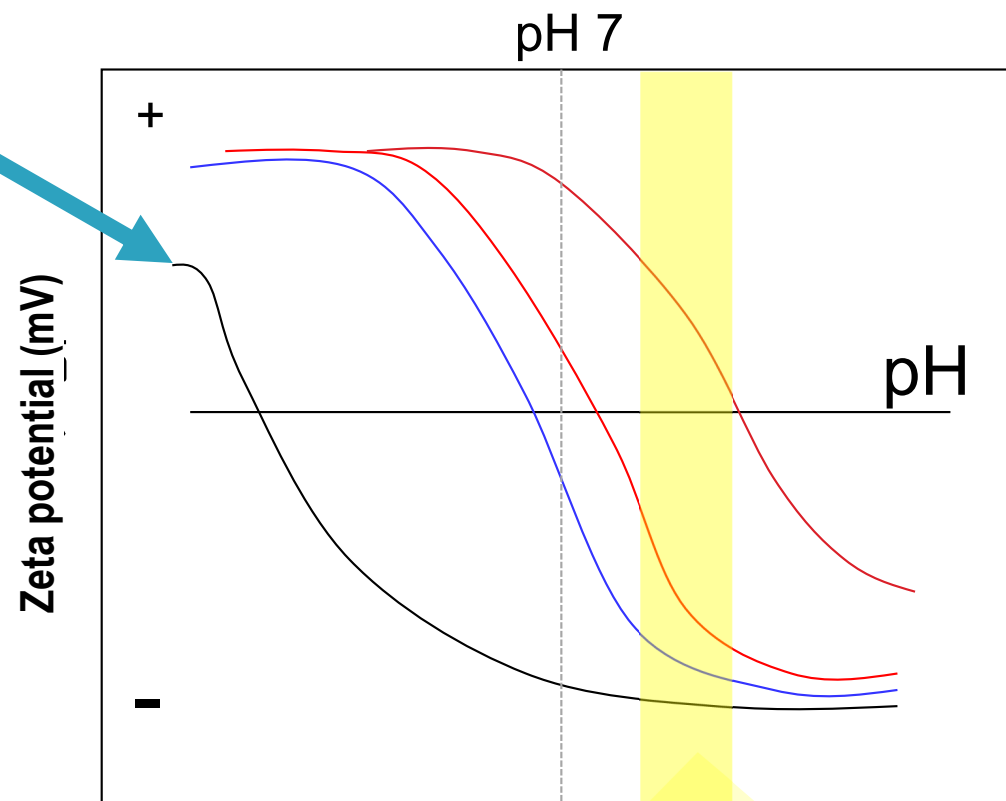
That's because it didn't aggregate and was stably dispersed in water!

Isoelectric point of oxides

depending on crystal plane, structure, etc.

The isoelectric point is the pH at which the zeta potential becomes 0 (zero).

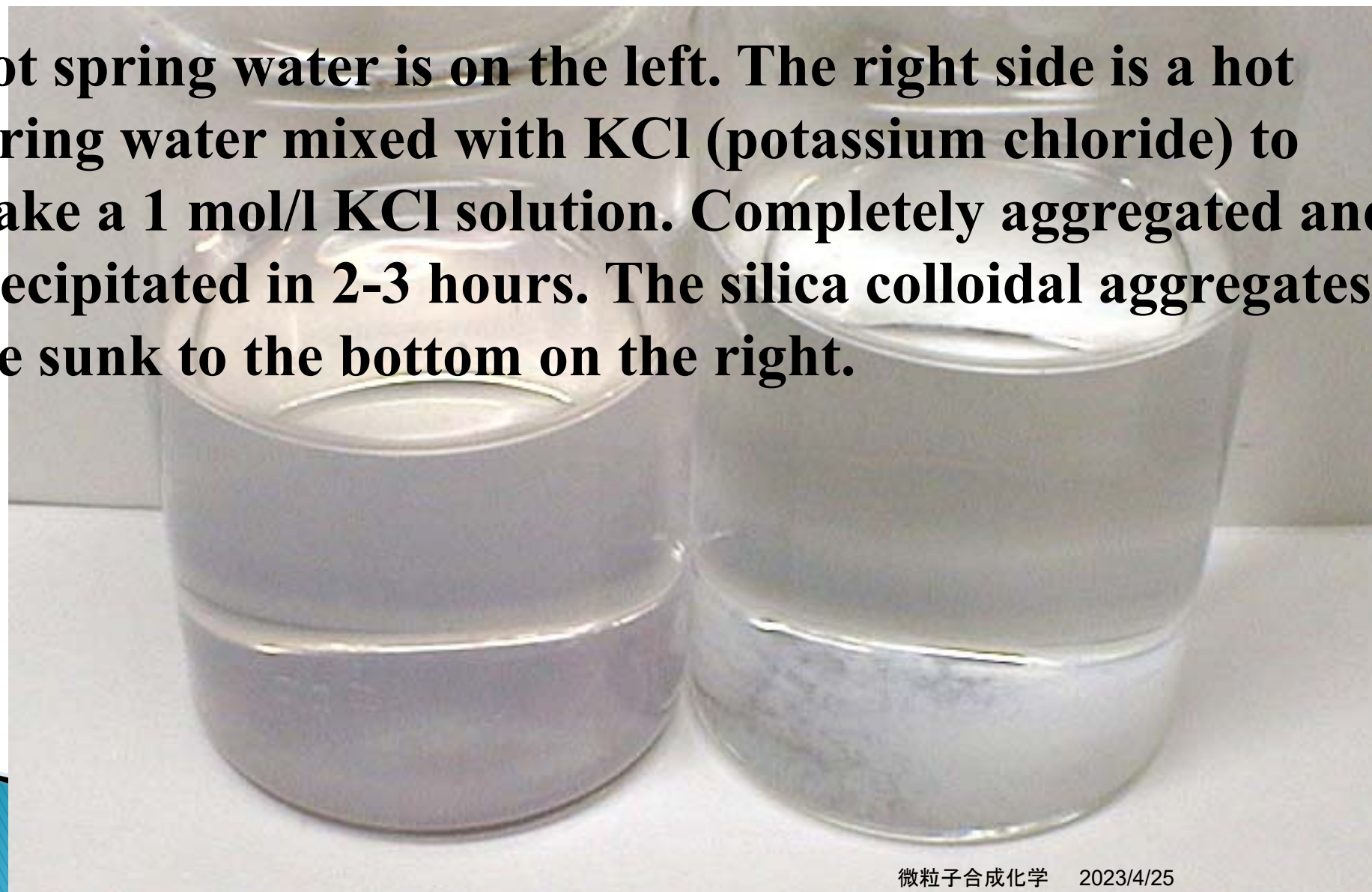
- ▶ SiO_2 2~3
- ▶ TiO_2 6~8
- ▶ Fe_2O_3 6~8
- ▶ ZrO_2 7~9
- ▶ Al_2O_3 7~9
- ▶ MgO 9~11



pH of Umi Jigoku hot spring water : 8~9

Aggregation and precipitation of silica colloid

Hot spring water is on the left. The right side is a hot spring water mixed with KCl (potassium chloride) to make a 1 mol/l KCl solution. Completely aggregated and precipitated in 2-3 hours. The silica colloidal aggregates are sunk to the bottom on the right.



Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?
- ▶ Tofu is a typical example of a "aggregation" product!

Ureshino specialty! Hot spring tofu



The secret of Ureshino Onsen tofu

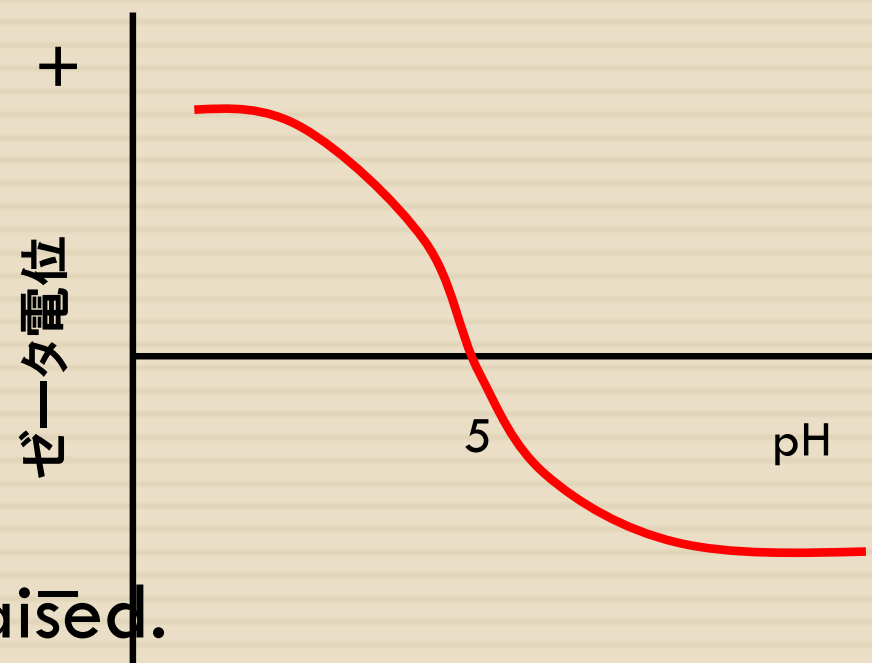
- ▣ The relationship between Ureshino Onsen and



Why does boiled tofu dissolved in Ureshino Onsen water?

Tofu

- The isoelectric point of normal soybean protein is about 4.5 to 5.0.
 - Over pH 5: —
 - Below pH 4.5 : +
- pH of household water
 - 5.0 ~ 6.0
- Homoaggregation near the isoelectric point
- They disperse when the pH is raised.



Tofu is a product of rapid aggregation.

- The main ingredient of nigari, which is used to harden tofu, is magnesium chloride with a small amount of magnesium sulfate.
- Magnesium and calcium dissolve as divalent cations.
- The sulfate ion of magnesium sulfate is a divalent anion.
- In general, when substances aggregate, there is a certain trigger. This is called rapid aggregation, and the trigger is electrolyte ions, that is, salts.
- When you make butter from milk, you use salt, and it's the same.

Tofu is a product of rapid aggregation.

- In aggregative sedimentation, divalent and trivalent ions are overwhelmingly more advantageous than monovalent ions for obtaining the same aggregates. The effect is inversely proportional to the sixth power of the ion valence.
- In other words, magnesium ions have the power to aggregate 6 times, that is, 64 times more than sodium ions even at the same concentration.

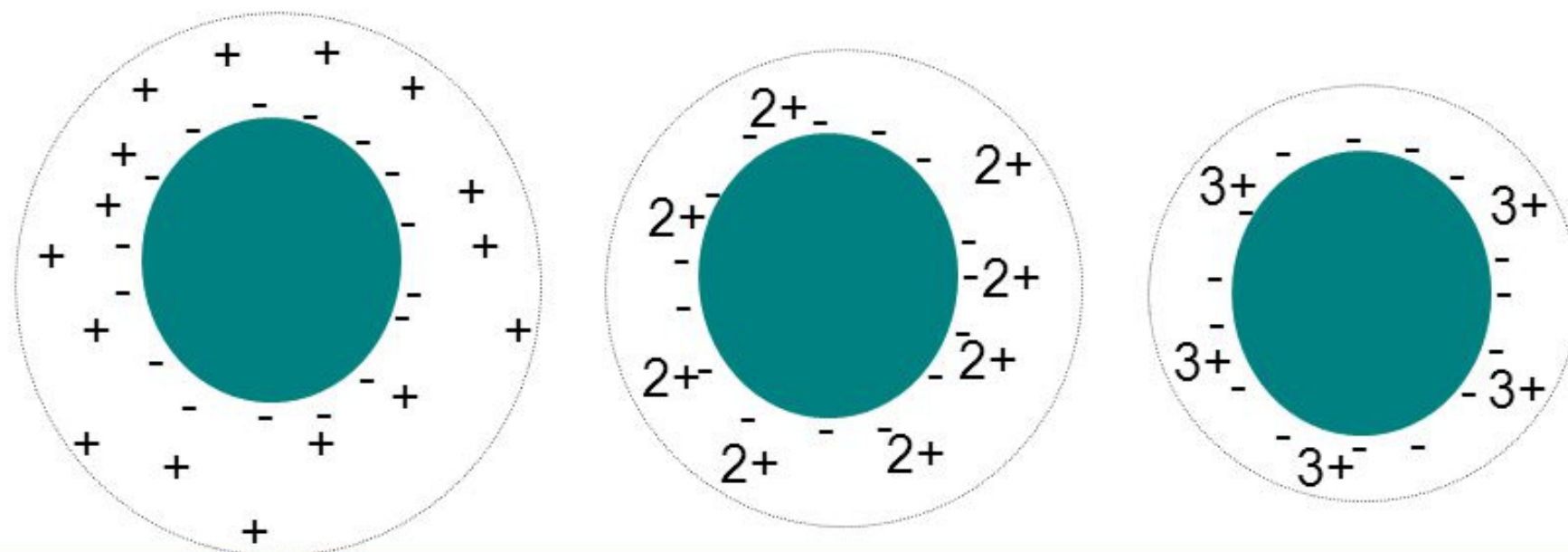
Ingredients of Ureshino Onsen

- Ureshino Onsen is a sodium-bicarbonate-chloride spring. It is a weakly alkaline spring (pH7.5-8.5), and the sodium ion content is about 400-500mg in 1kg of sample.
- Since the amount of calcium and magnesium that coagulates tofu is small, the tofu is dispersed due to the pH effect.
- This is not the decomposition of proteins, as is generally said, but a physicochemical phenomenon called "dispersion".



Hardy-Schulze Rule

- Flocculation is controlled by the valency of the counter-ion (added electrolyte with charge opposite that of the particle surface)
- Fewer 3+ ions than 2+ than 1+ ions are needed to cancel out colloid charge on negatively charged colloid → *more compact* counter-ion cloud (the critical coagulation concentration is lower for 3+ than 2+)



Rapid coagulation

- Colloidal particles in water are dispersed by the electrostatic repulsion between the particle surfaces, and the surface potential of the particles is gradually neutralized by adding oppositely charged electrolyte ions to the solution. The attractive force between the particles becomes strong, finally causing coagulation and then sedimentation. If C_1 , C_2 , and C_3 are the minimum concentrations of monovalent, divalent, and trivalent counterions necessary to cause coagulation and sedimentation within a certain period of time, the ratio of the reciprocals of the minimum concentrations is $1/C_1 : 1/C_2 : 1/C_3 = 100 : 1.6 : 0.13$, which indicates that the critical aggregation concentration of the colloidal system is inversely proportional to the sixth power of the counter ion valence used.
- This type of aggregation is called Schultz-Hardy aggregation.

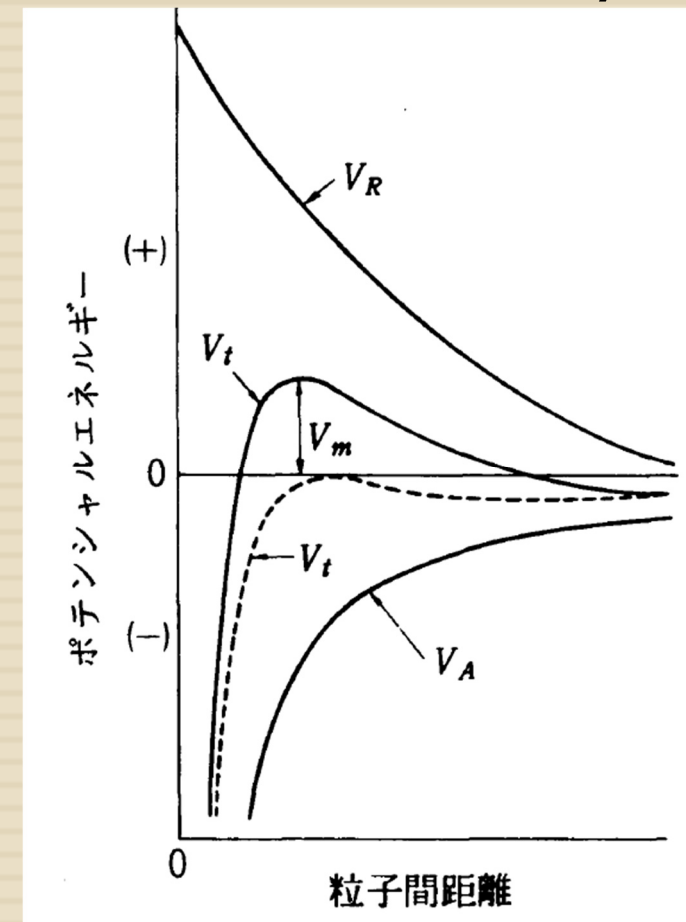
Schulze-Hardy rule

- This rule is given a theoretical basis from the DLVO theory.

$$V_T(H) = 2\pi a \varepsilon_r \varepsilon_0 \psi_0^2 \exp(-\kappa h) - \frac{aA}{12H}$$

- As the electrolyte concentration is increased, a point corresponding to V_m appears in the figure.
- This is the critical coagulation Concentration (C_c), which is expressed by the following equation. ■

$$c_c = 8 \times 10^{-22} \frac{r^4}{A^2 v^6}$$



The reciprocal of the valence, v , to the 6th power proved this rule.

Colloids in life

□ Udon

The concept of colloidal surface chemistry is also included in "Udon"!

The amount of salt used for Sanuki udon is 3% or more of the flour.



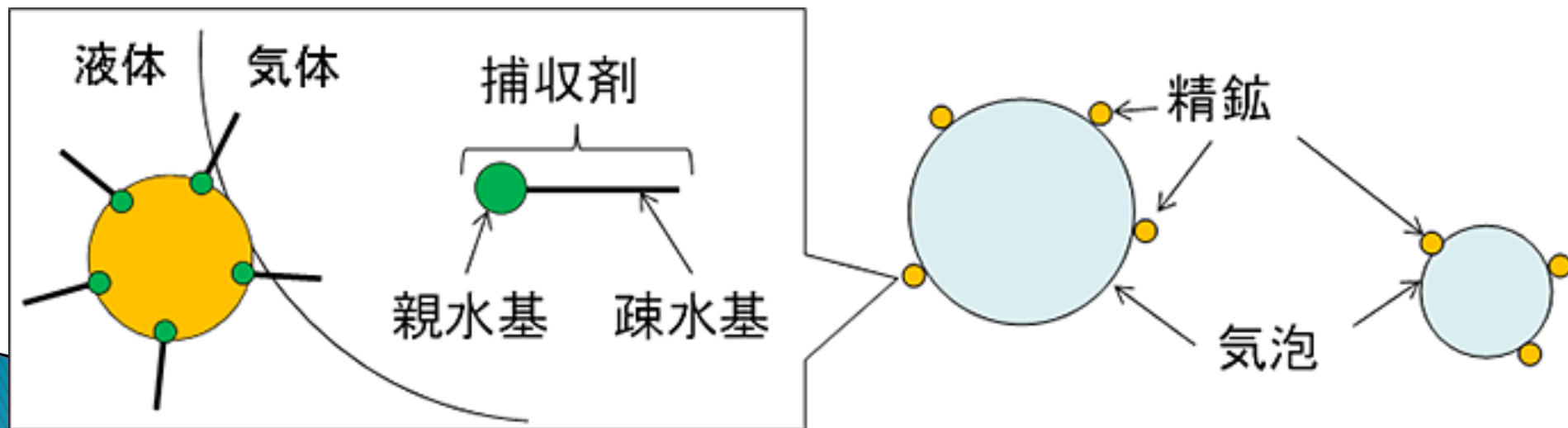
Sanuki Udon

The fabric is stable and does not sag too much.

- Wheat flour can be kneaded in fresh water to form gluten, but salt water produces stronger gluten.
- This is called the astringent effect of salt, and it becomes the base of the udon noodles.
- The salt helps keep the dough from getting mushy if it's ripened for the right amount of time.

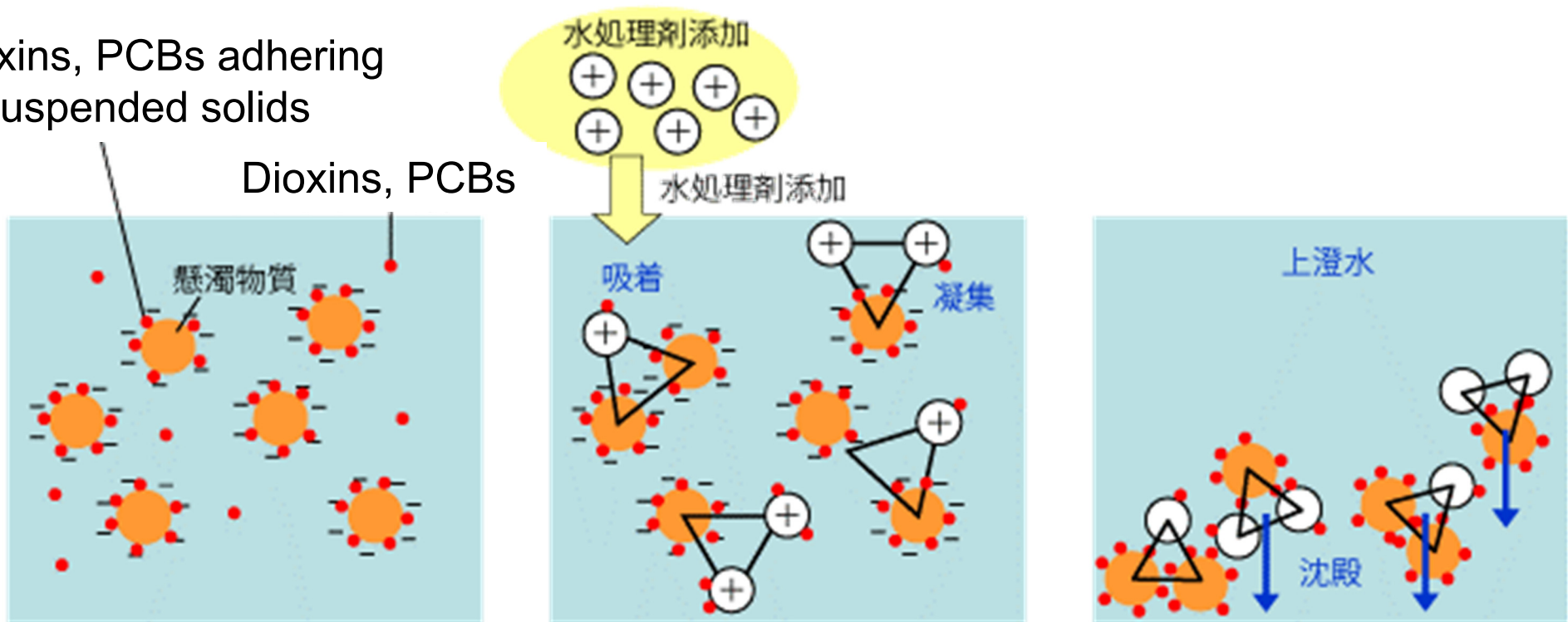
Flotation

- ▶ In flotation, after finely ground ore is suspended in water, fine air bubbles are generated in the water. Hydrophobic minerals adhere to the bubbles. Then, the minerals are recovered along with the floating bubbles. Flotation agents such as collectors are used to create differences in wettability between minerals.



Removal of Dioxin and PCB

Dioxins, PCBs adhering to suspended solids

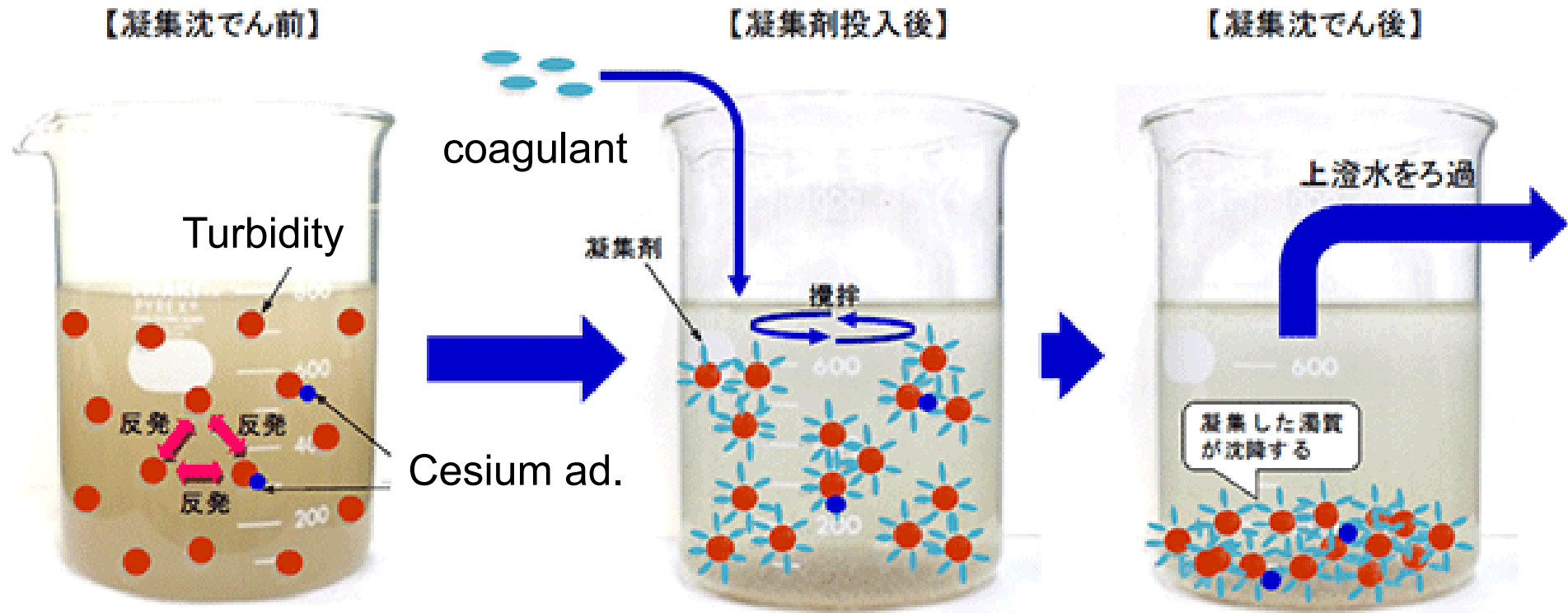


Dioxins, PCBs in water

Adsorption then aggregation

Removal by sedimentation

Removal of radioactive cesium by coagulation sedimentation treatment



Turbidity repels each other and disperses.

The coagulant eliminates the repulsive force.

Turbidity aggregates and precipitates.

東京都水道局から

Development of dispersion/aggregation control

- ▶ protective colloid
 - Polymer systems, biological systems, soft materials...
- ▶ Nanoink coating technology
 - Metal nanoink, Conductive oxide nanoink, Nanocarbon material ink
- ▶ slurry
 - metal slurry, ceramic slurry

Controlling dispersion and aggregation is very important in practical processes in many heterogeneous systems (solid-liquid, liquid-solid, etc.).

Basically, we can discuss only van der Waals and electrostatic repulsive forces, but there are cases where hydrophobic interactions (outside the purpose of today's lecture) should be taken into consideration.