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"?

↓

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

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

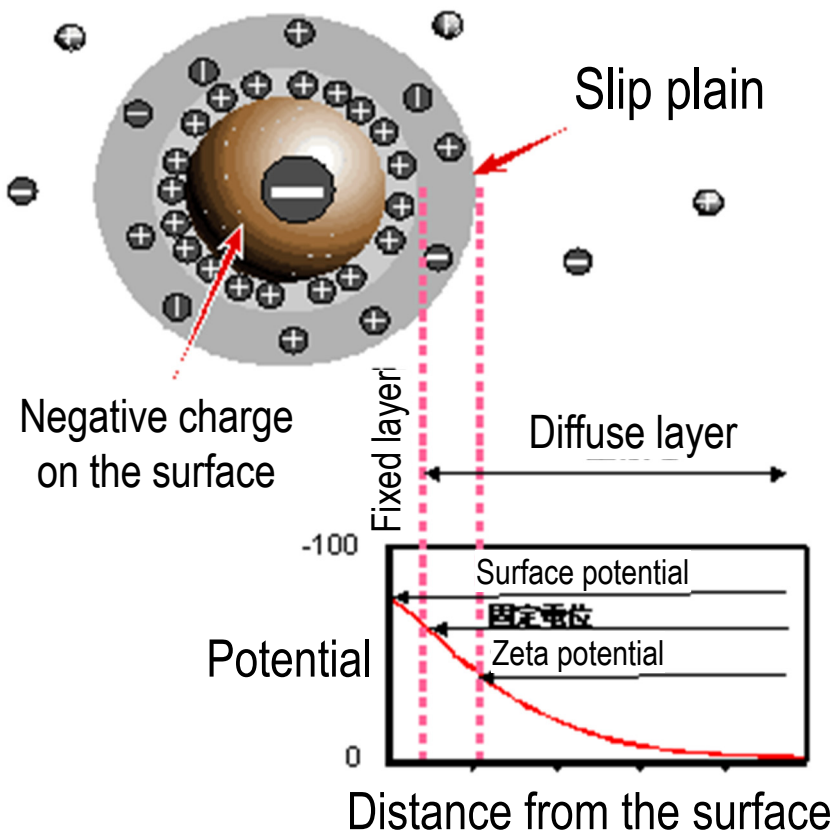### It's on your face, on your desk, on your foam, on everything!

What is the theory behind this?

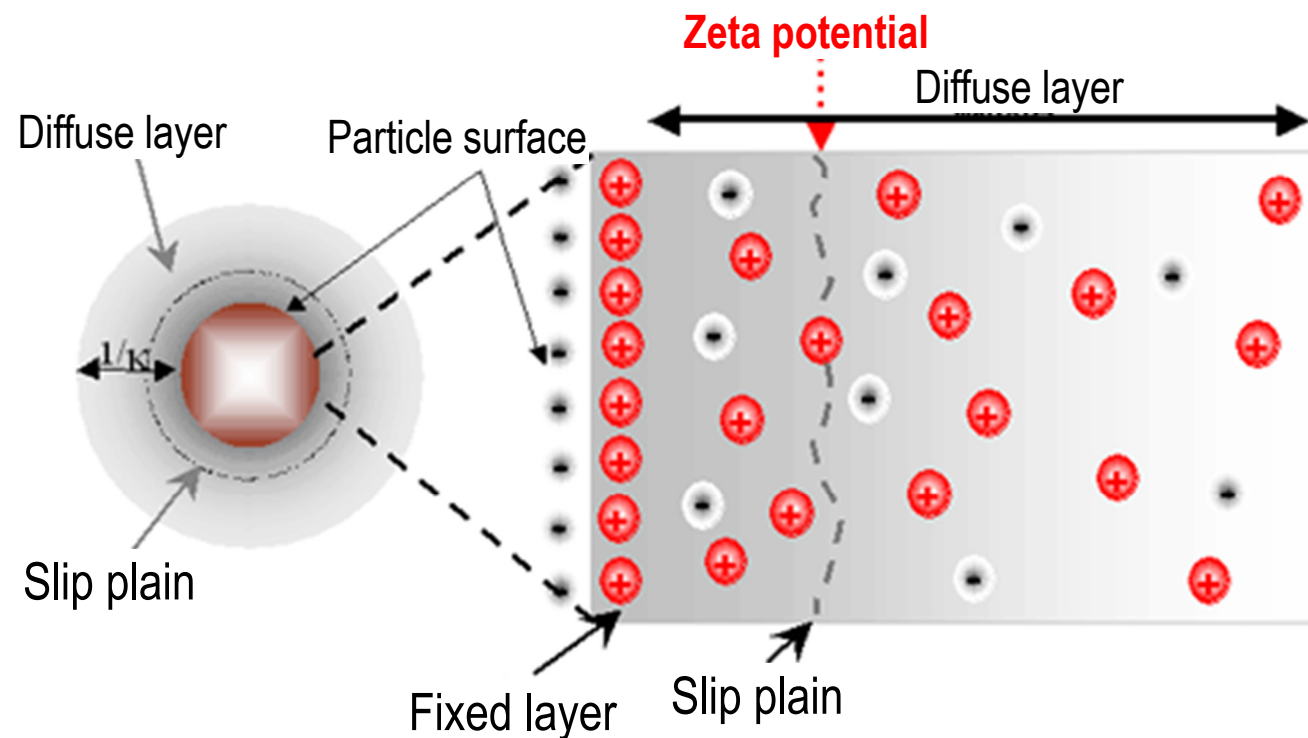What is the essence of particle dispersion and aggregation behavior?

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.

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Zeta potential

Slip plain

Negative charge
on the surface

Fixed layer

Diffuse layer

Potential

-100

Surface potential

固定電位

Zeta potential

0

Distance from the surface

Zeta potential at slip plane

Zeta potential

Diffuse layer

Diffuse layer

Particle surface

$1/\kappa$

Slip plain

Fixed layer

Slip plain
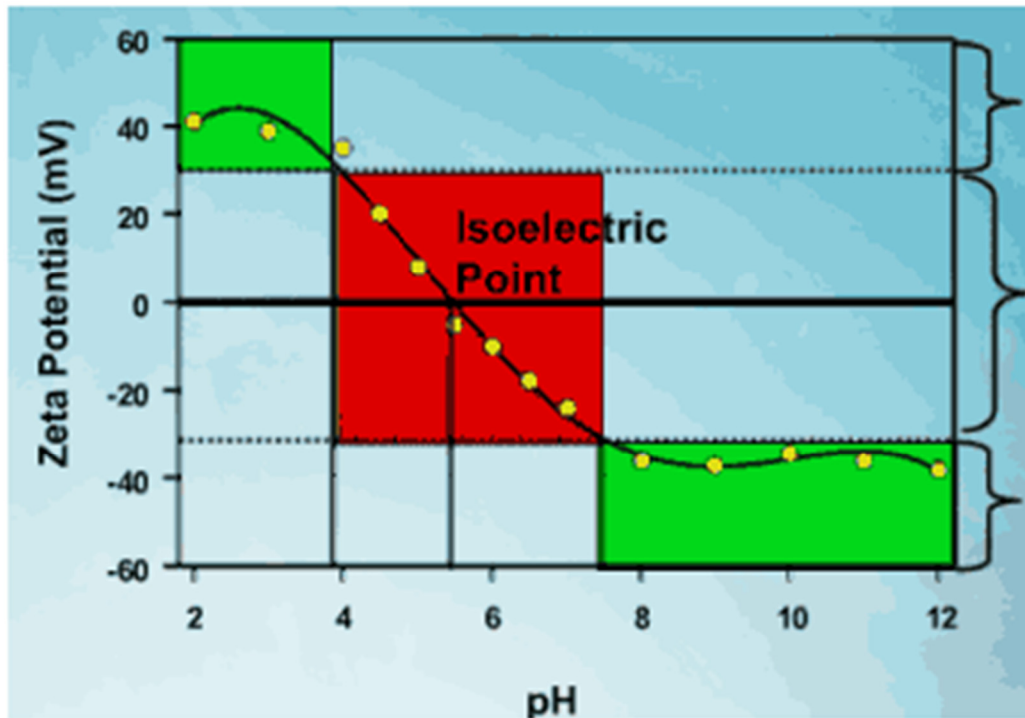
図 6　Electrophoresis

Negative electrode　　　　　　　　　　　　Positive electrode

Particles with the same negative charge are
moving to the positive electrode.
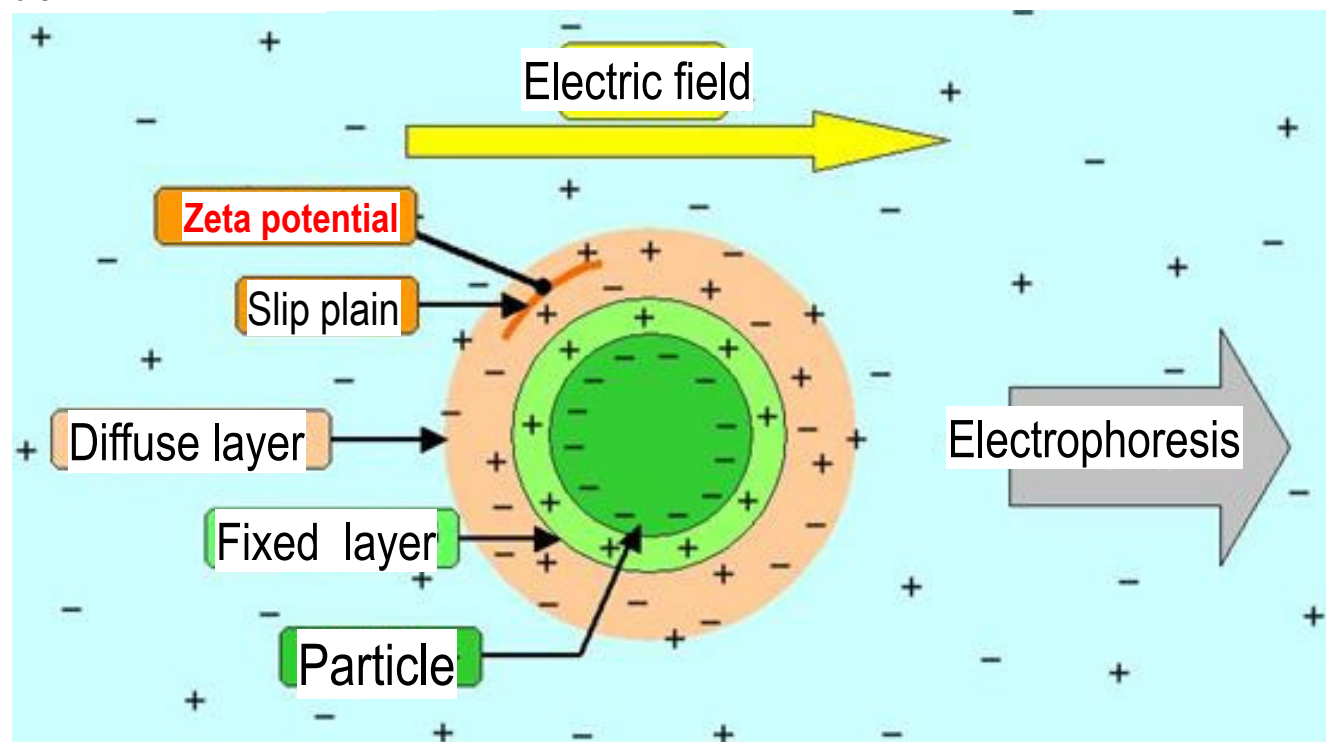
Zeta potential as a function of pH

Stable

Unstable
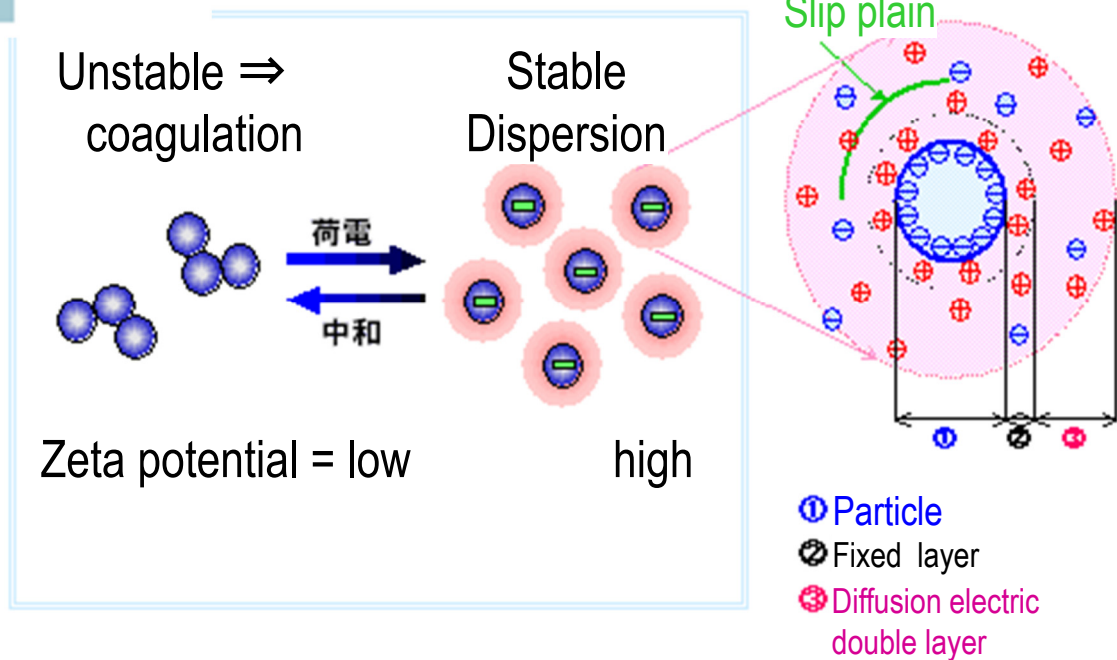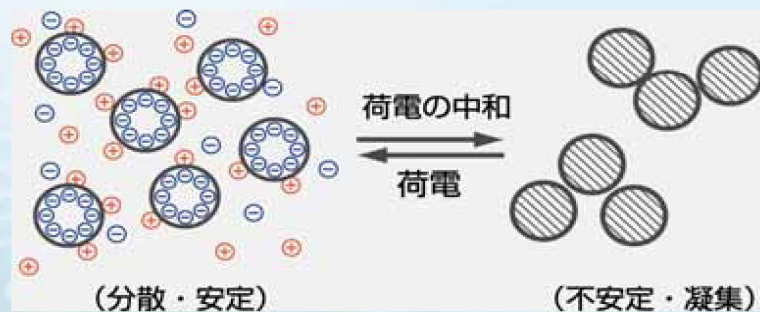
Stable

Zeta potential and dispersion

Unstable ⇒ coagulation

Stable Dispersion

荷電

中和

Zeta potential = low   high

Slip plain

① Particle
② Fixed layer
③ Diffusion electric double layer

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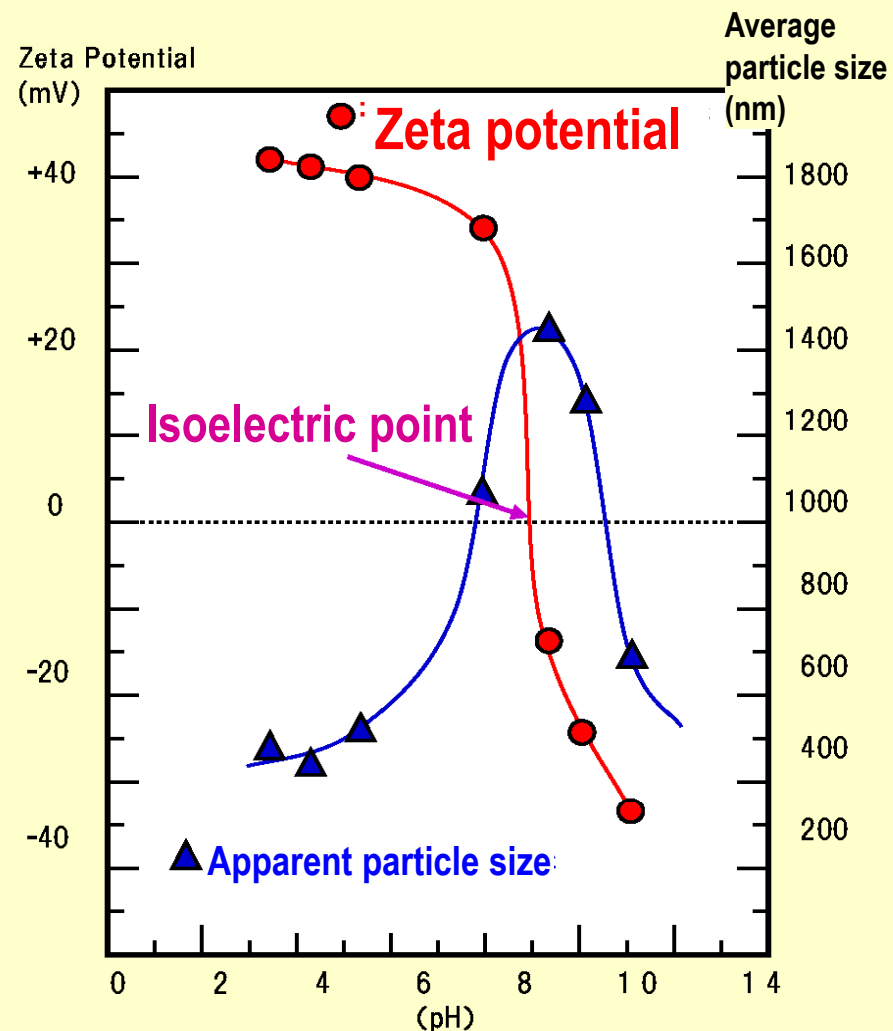
What can we learn from zeta potential?

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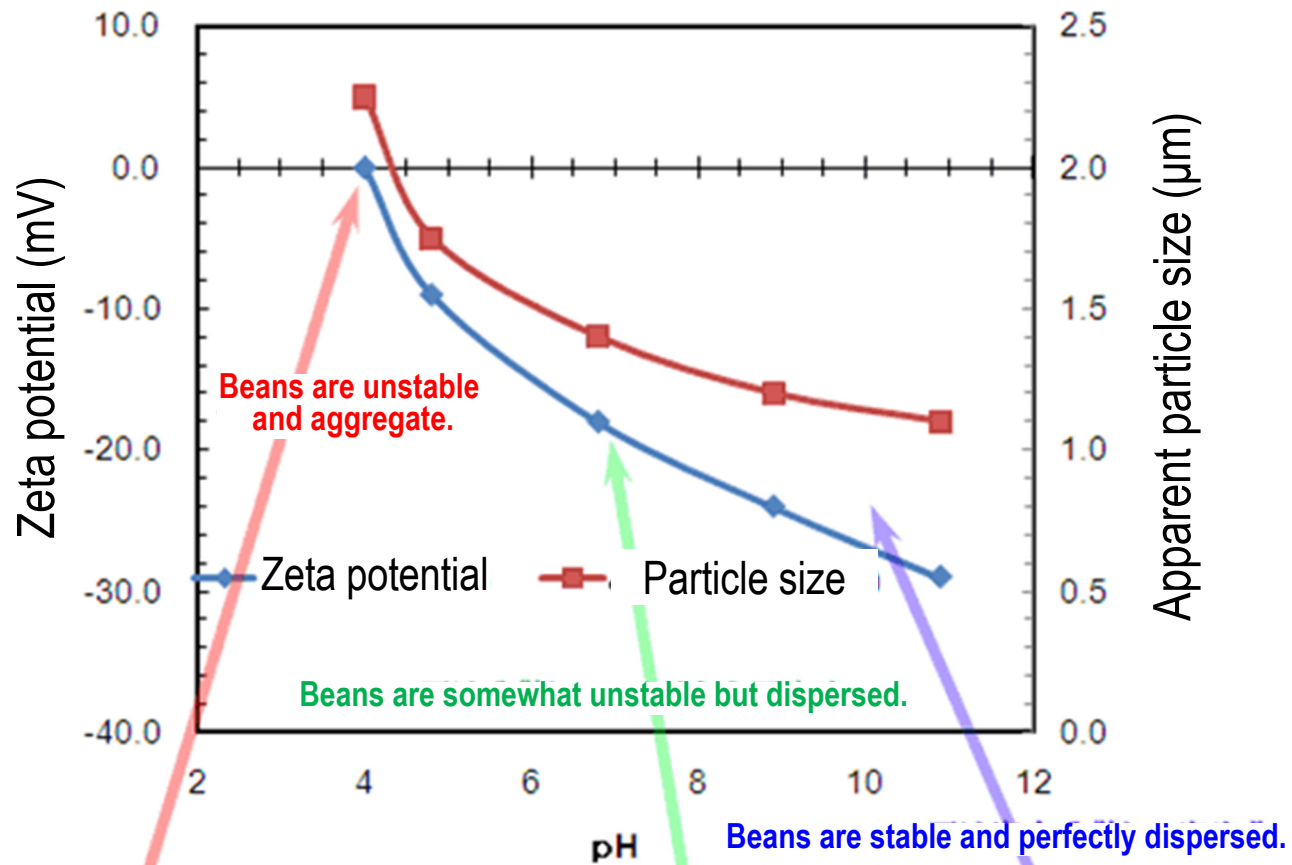
The average particle size is small in the pH region where the absolute value of the zeta potential is large. In the vicinity of the isoelectric point, they aggregate and have a large particle size.

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

Beans are unstable and aggregate.

Beans are somewhat unstable but dispersed.

Beans are stable and perfectly dispersed.

Zeta potential — Particle size

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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).
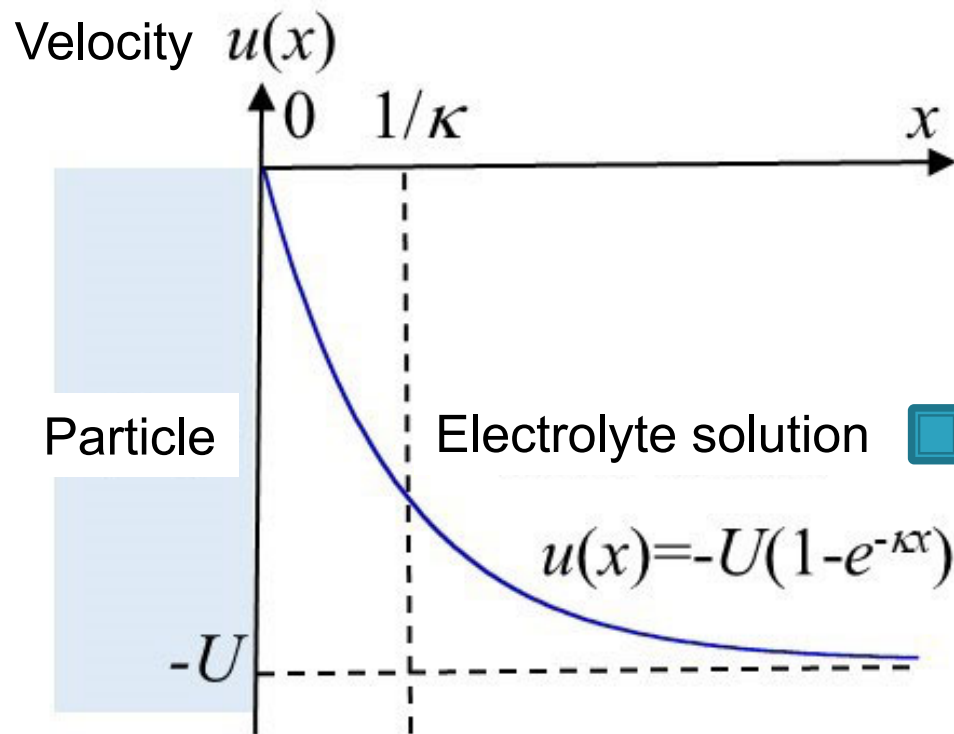The following electrokinetic phenomena are generally known.

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

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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).

$$\rho E = \eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

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Velocity $u(x)$

0    $1/\kappa$ x

Particle

Electrolyte solution

$u(x)=-U(1-e^{-\kappa x})$

$-U$

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.

Potential $\psi(x)$

Electric field E

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

Mobility U

ψ_o

Particle

Electrolyte solution

surface charge density, ρ

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

0    $1/\kappa$ x

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Electrokinetic Phenomenon ~Electrophoresis~

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$$\rho E = \eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

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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.

$$V = (\varepsilon_0 \varepsilon_r / \eta)\, \phi_0 E \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (7)$$

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

$$\Delta\psi = \mathrm{div}\,(\mathrm{grad}\,\psi) = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0}$$

ε_r: Dielectric constant of solution

ε_0: Dielectric constant in vacuum

ρ: Charge density

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Smoluchowski formula

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

$$u = (\varepsilon_0 \varepsilon_r / \eta) \zeta \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

▸ 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/*κ*) (*a* ≫ 1/*κ*, or *κa* ≫ 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℃ (ε_r = 78.5, η = 0.89mPa), it can be expressed as follows.　　　　　$\zeta = 12.8 \, u \, (\text{mV})$

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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.

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

- 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.

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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.

$$u = (\varepsilon_0 \varepsilon_{\mathrm{r}}/\eta)\, \zeta \cdot f(\kappa a) \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (12)$$

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Henry coefficient

▸ The function *f(κa)* is called Henry's coefficient and expresses the degree of distortion of the external electric field due to the presence of particles. Here, when $κa \to 0$, $f = 2/3$ and the Henry equation becomes the Hückel equation.

▸ Conversely, when $κa \to \infty$, $f = 1$ 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.
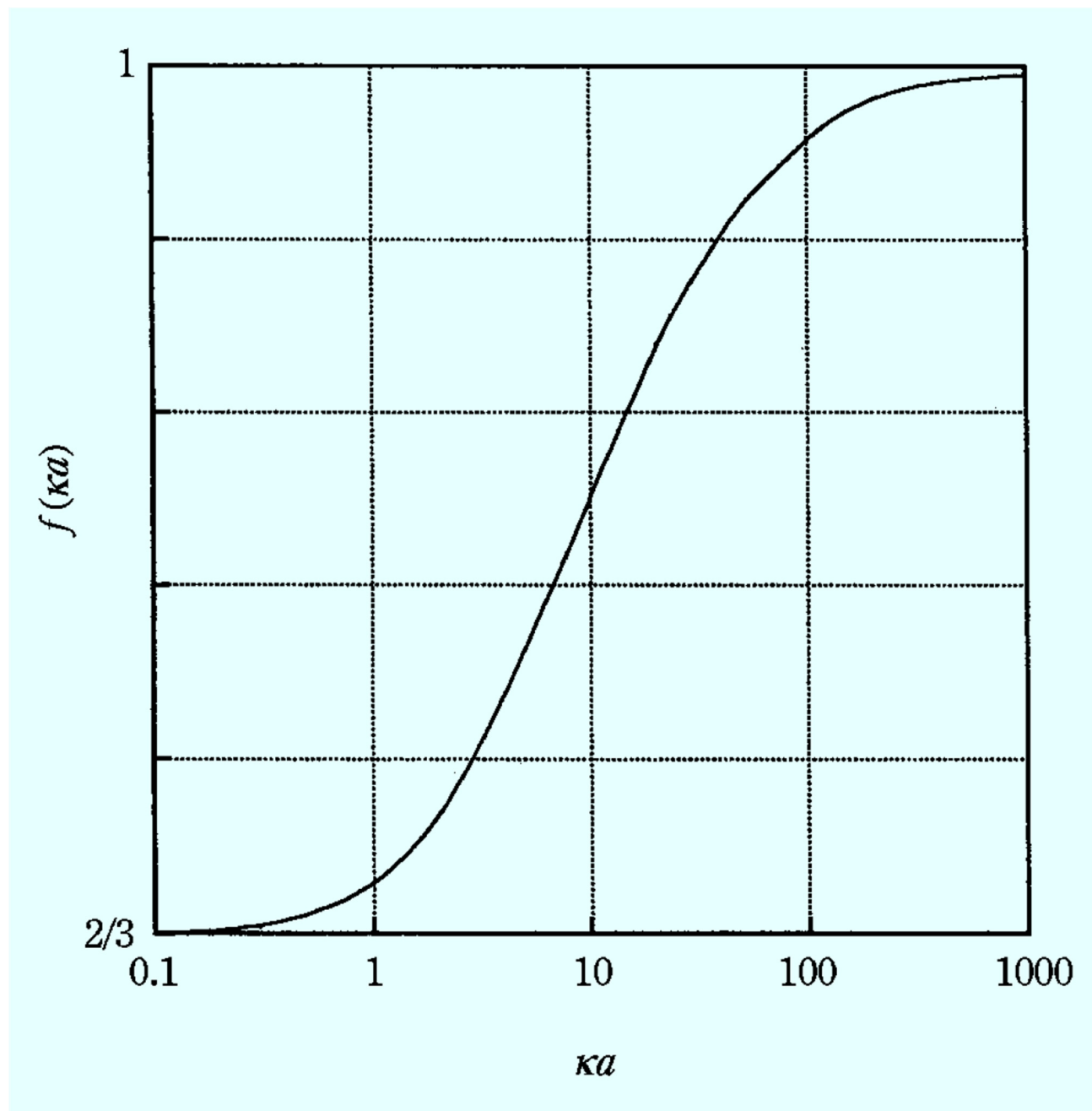
電気泳動移動度の式

$κa \ll 1$

$κa \gg 1$

$\mu = \dfrac{2\varepsilon_r\varepsilon_0}{3\eta}\zeta$

$\mu = \dfrac{\varepsilon_r\varepsilon_0}{\eta}\zeta$

Hückelの式

Smoluchowski の式

2/3の違い

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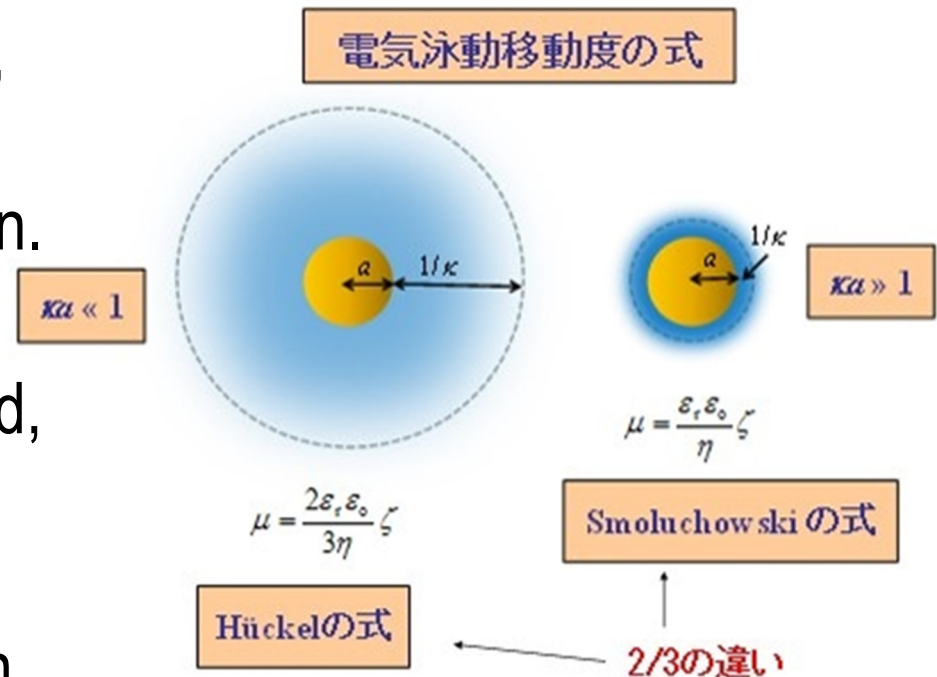
Relaxation effect

- 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.

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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.

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

▸ u_{app} varies parabolically with cell depth h and is given by the following equation when k = (cell width/cell depth)>>1.

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

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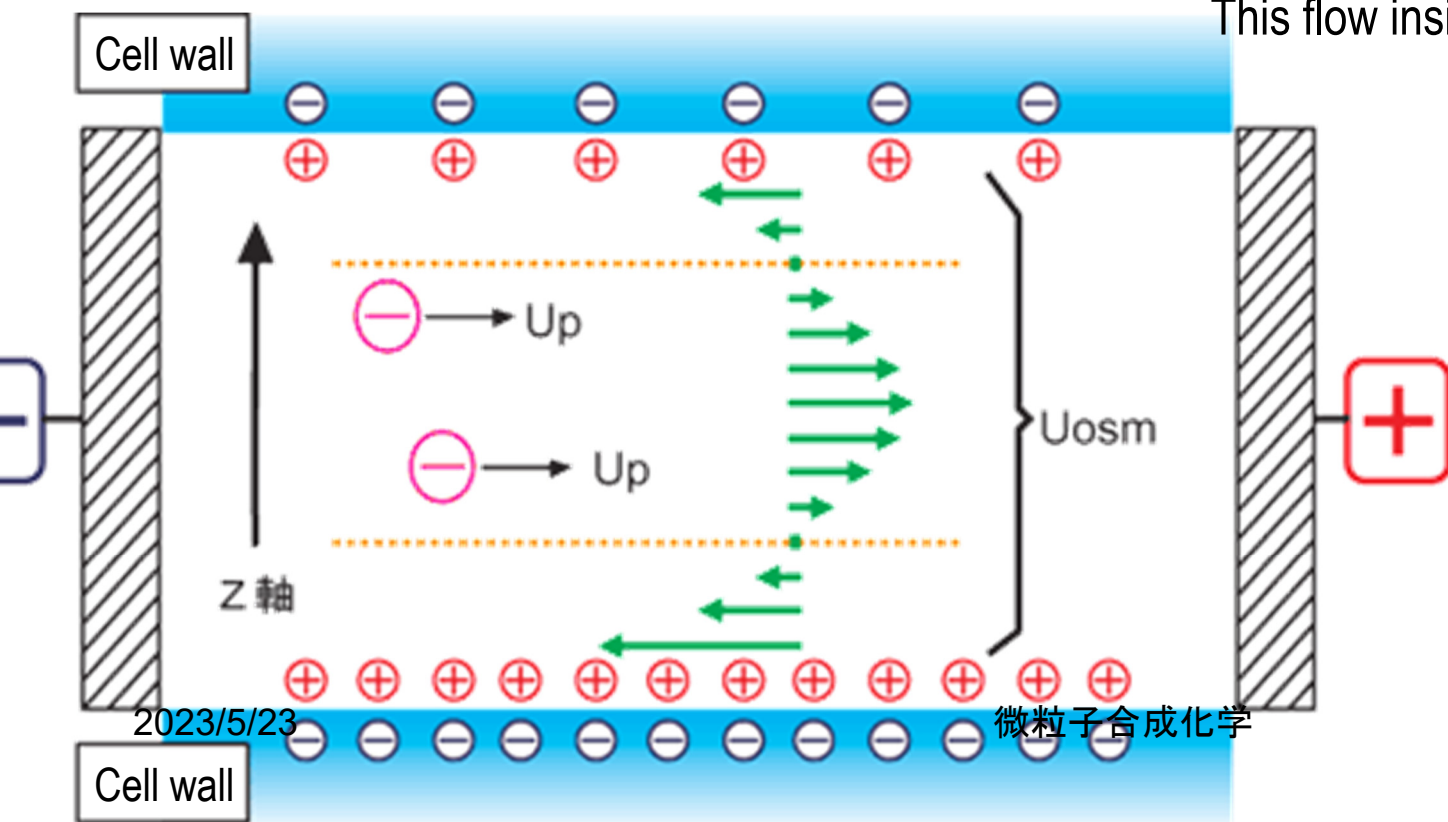
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Electroosmotic flow

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.

Electroosmotic flow curve

Negative charge inside the cell

Stationary level

Negative electrode

Positive electrode

Cell wall

Up

Up

Uosm

Z 軸

Cell wall

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Electrophoresis measurement

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

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Electrophoresis measurement

▶ u_{app} at level h_s, giving $u_{osm}=0$, gives the true electrophoretic mobility u. This h_s is called the stationary level and given by the following equation.
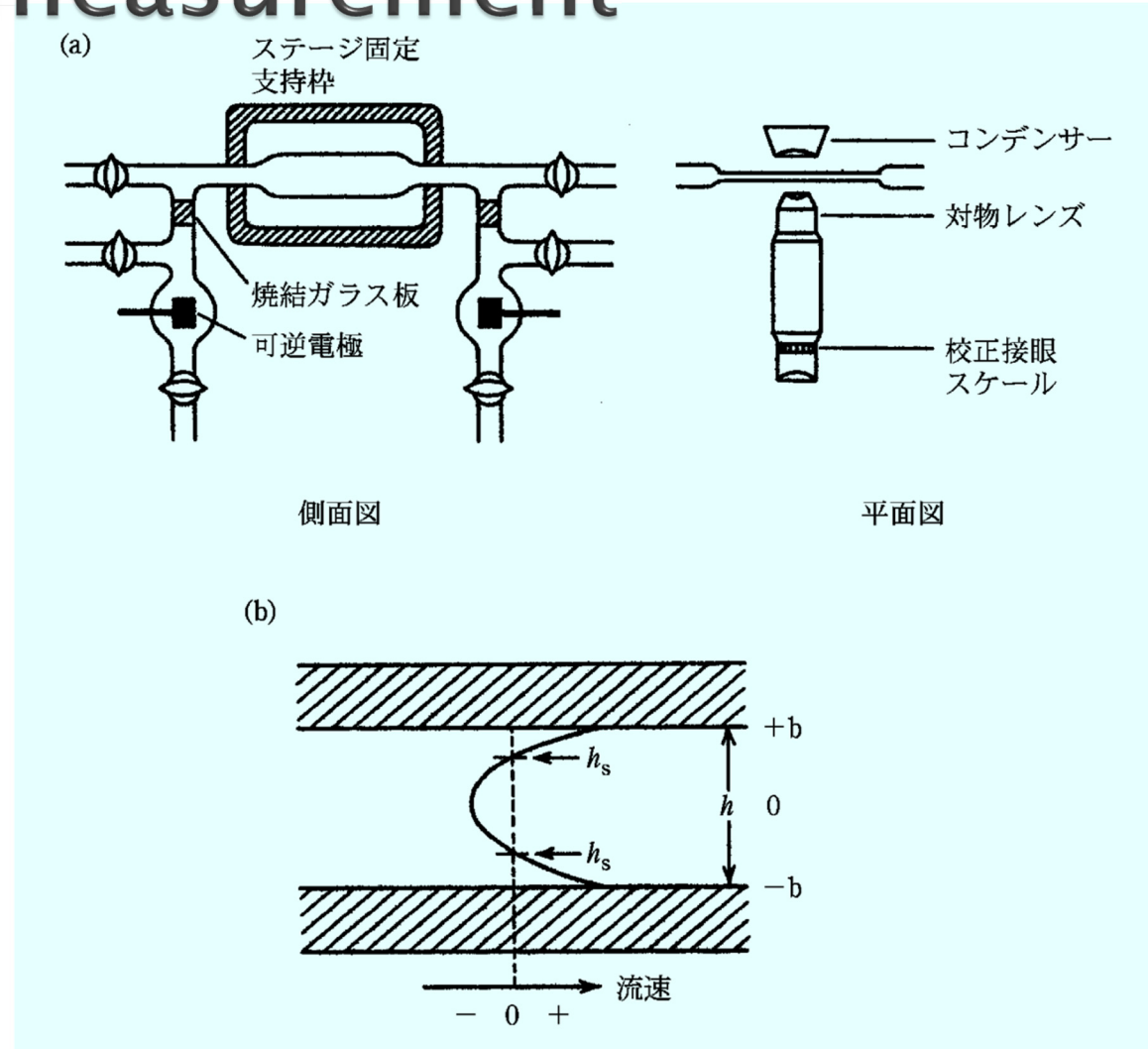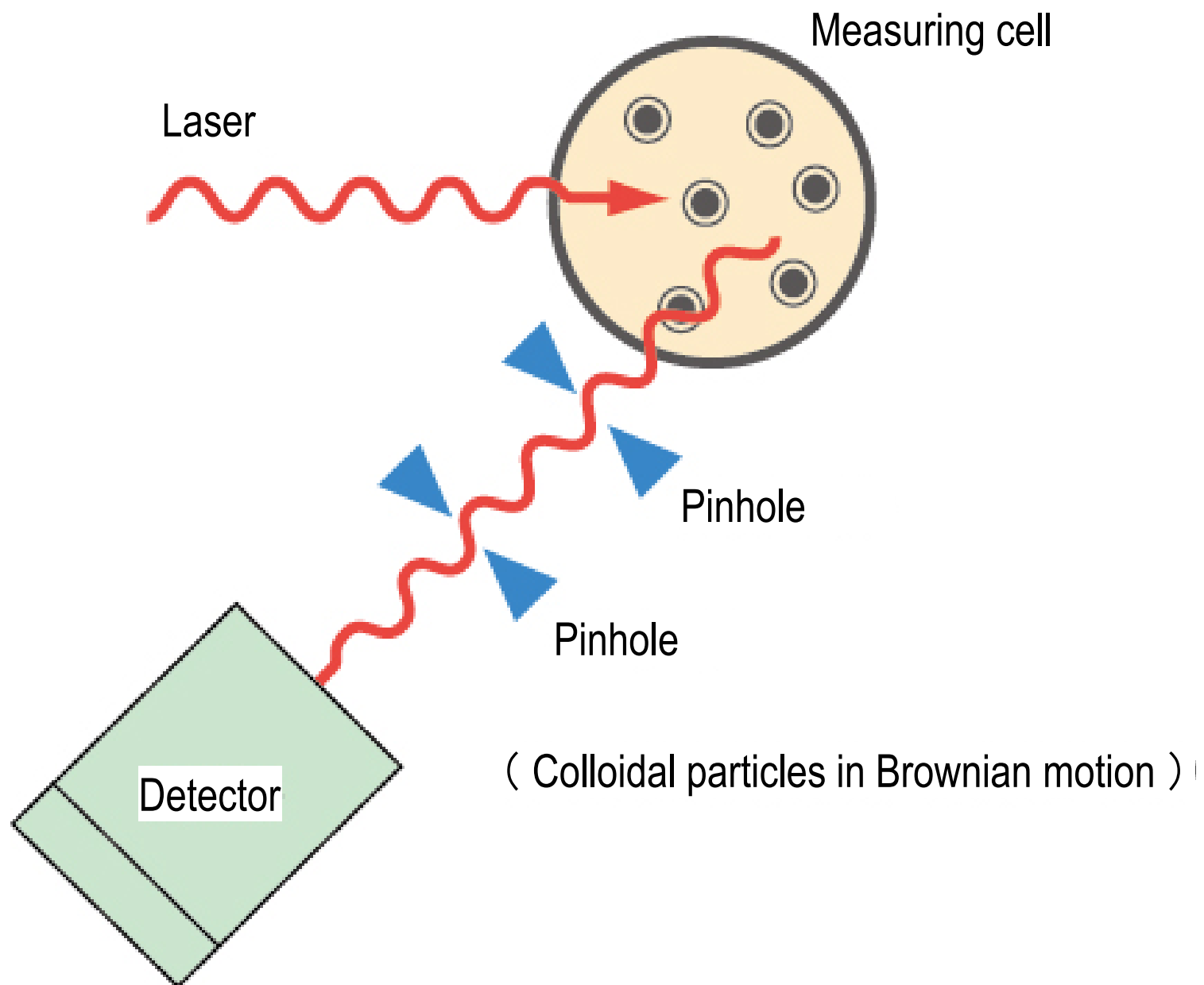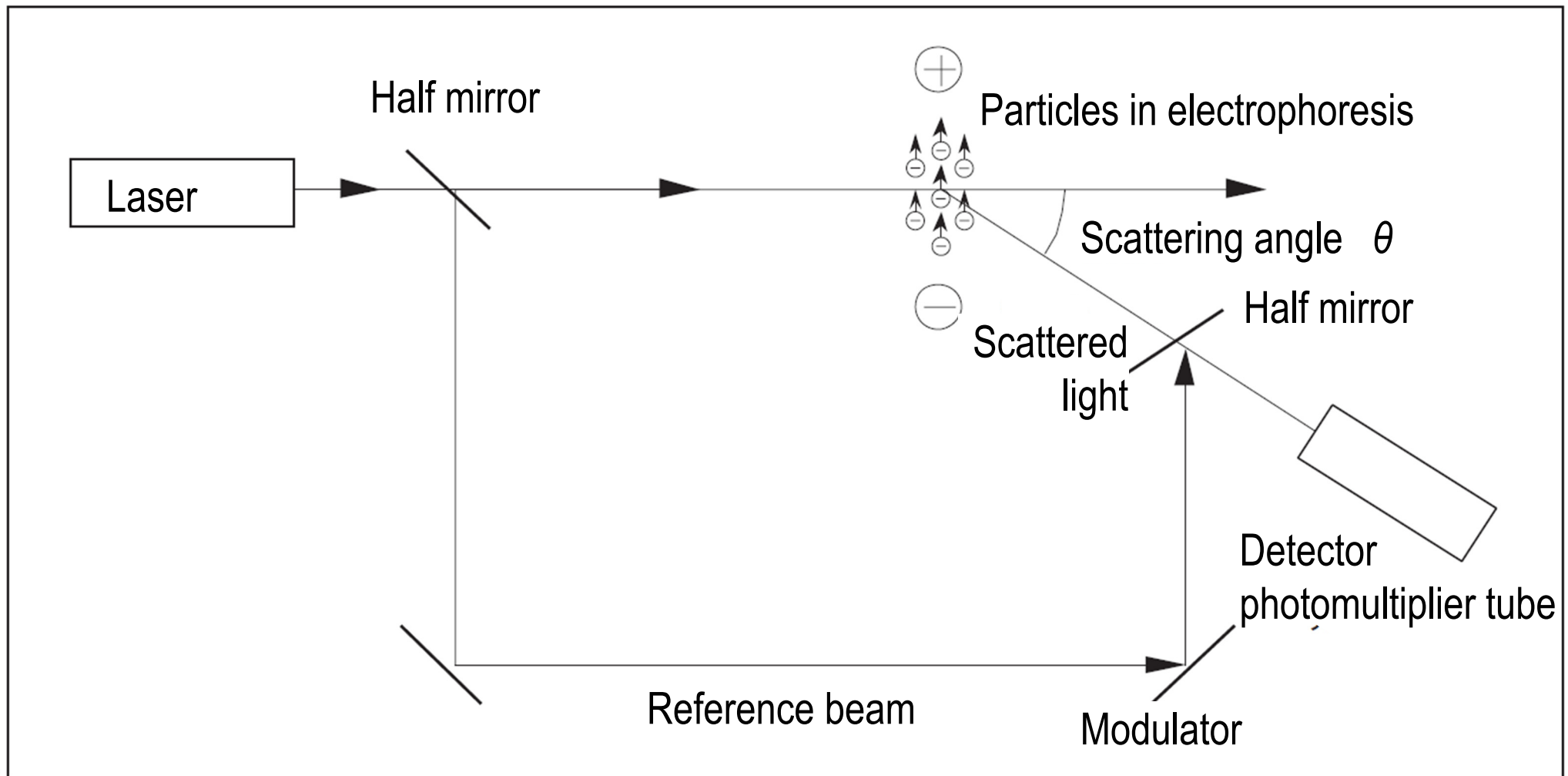
$$h_s = \pm \frac{b}{\sqrt{3}} = \pm 0.577b$$

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）

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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.

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Measuring cell

Laser

Pinhole

Pinhole

Detector

（Colloidal particles in Brownian motion）

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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

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Electrophoretic light scattering measurement method

▸ In general, particles migrate at a slow speed, so their Doppler shift amount (~100 Hz) is significantly smaller than the frequency of incident light (5 × 10 12 Hz). The Heterodyne method is a technique for detecting such small frequency differences. It mixes part of the incident light (reference light) and scattered light in the optical system. Doppler-shifted scattered light from migrating particles and reference light corresponding to non-migrating particles are simultaneously observed.). It is expressed as an autocorrelation function of scattering intensity by a photon correlator. Since the observed particles are in Brownian motion, this autocorrelation function becomes a decaying cosine wave. That frequency corresponds to the amount of Doppler shift.

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Electrophoretic light scattering measurement method

▸ By performing FFT analysis on the obtained autocorrelation function, the distribution of frequency components can be obtained. Furthermore, the distribution of electrophoretic mobility is required. Actually, a sample dispersed in a solvent with a refractive index (n) is irradiated with a laser beam of a wavelength (λ), and the mobility (U) and the Doppler shift (Δv) when detected at the scattering angle (θ) The relationship is expressed by the following equation.

$$\Delta v = \frac{2 V\, n \sin(\theta/2)}{\lambda}$$

$$U = V / E$$

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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.

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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.

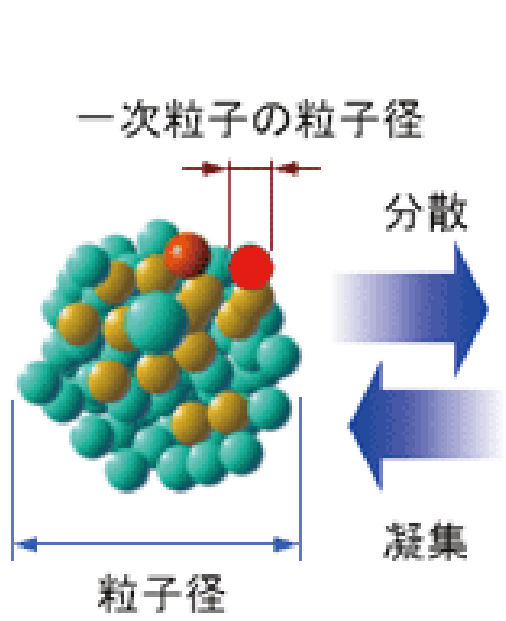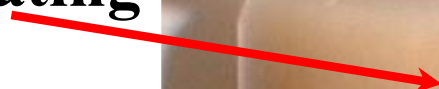微粒子合成化学   2023/5/23
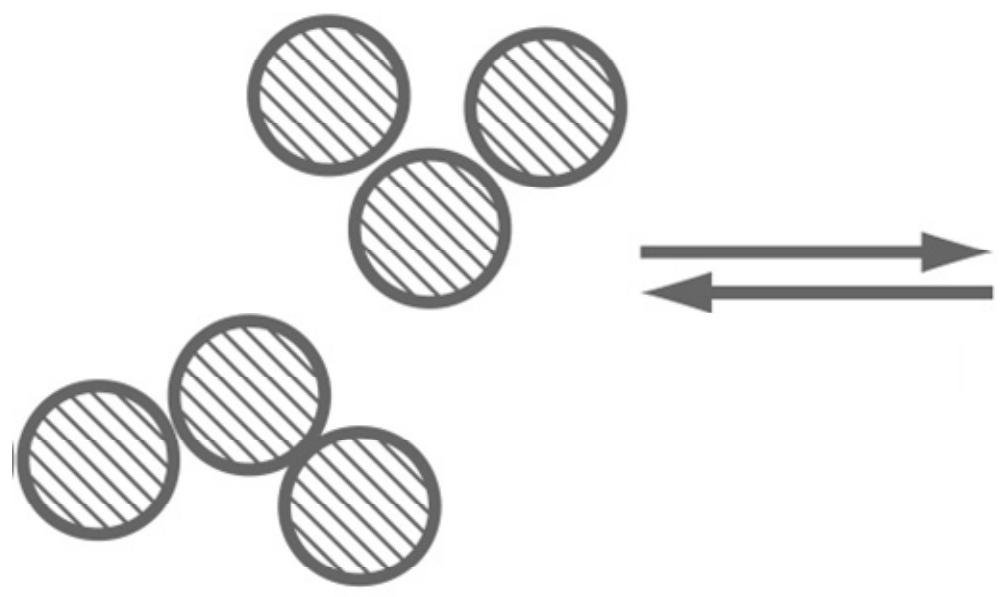
Aggregation

Colloidal dispersion

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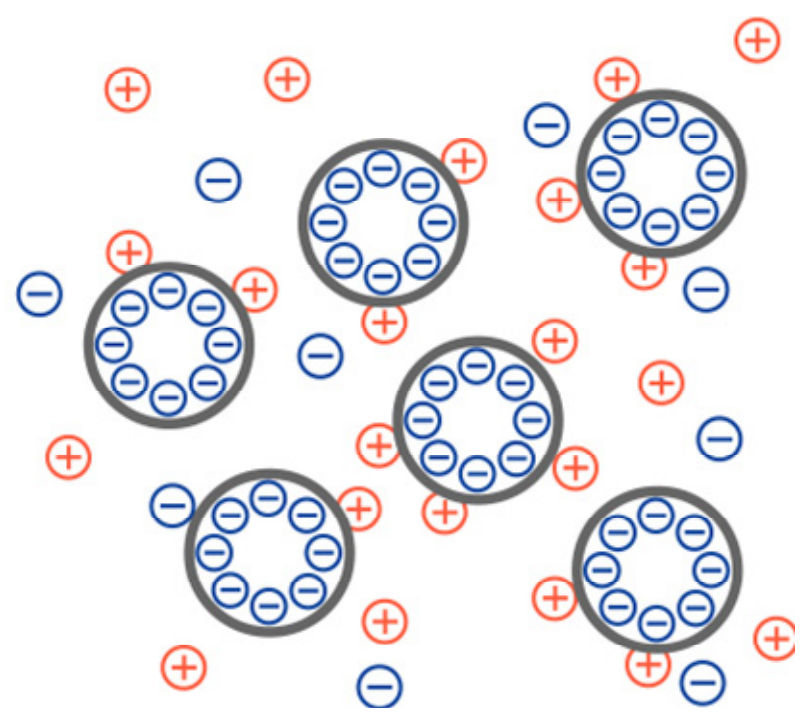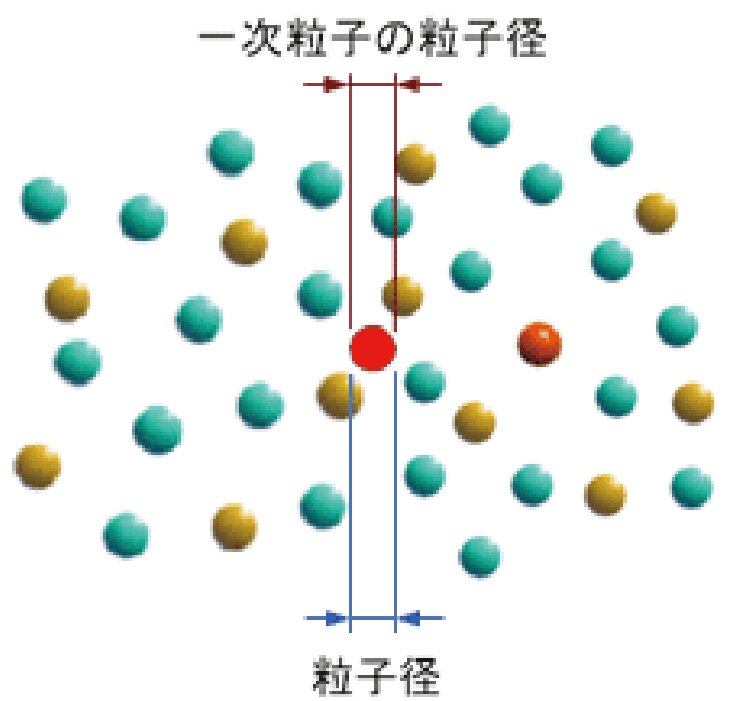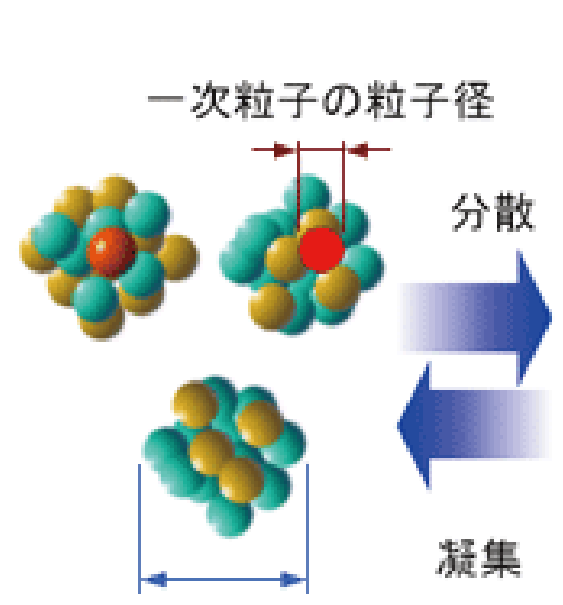
Add salt to coffee milk

Milk fat floating

1 mol/L KCl溶液

coffee milk only

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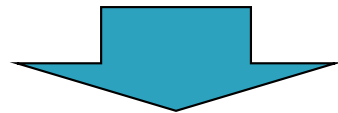
Why did milk fat in coffee surface?

▸ Milk fat is lighter than water.
▸ Milk is a dispersion of milk fat.

▸ By adding salt, it "agglomerated" and surfaced.
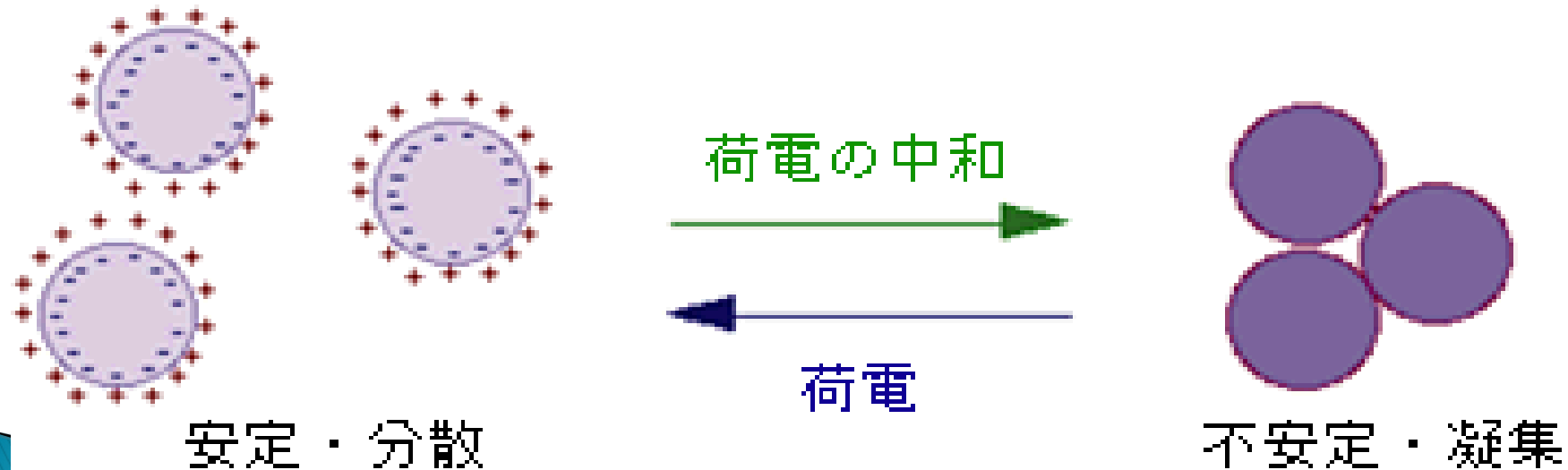
荷電の中和

荷電

安定・分散　　　　　　　　　　　　　不安定・凝集

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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

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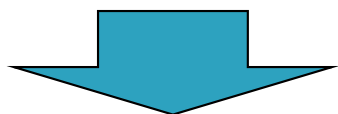# Dispersion and aggregation (Equilibrium consideration)

- ▸ Aggregation
  - ◦ van der Waals interaction

凝集

- ▸ Dispersion
  - ◦ Electrostatic repulsion

分散

  - ◦ Repulsion due to surface potential

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Dispersion and aggregation (kinetic consideration)

- ▸ In order to disperse
  - ◦ be in a condition of dispersion in equilibrium
  - ◦ be kinetically dispersive

- ▸ Brownian motion

  (thermal motion)

分散

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Kinetics: Brownian Motion

▶ In the equilibrium, theoretical interpretation of dispersion is electrostatic repulsion, while as to the motion of colloidal particles floating in water and dispersed in air, the kinetic interpretation is Brownian motion.

X

分散
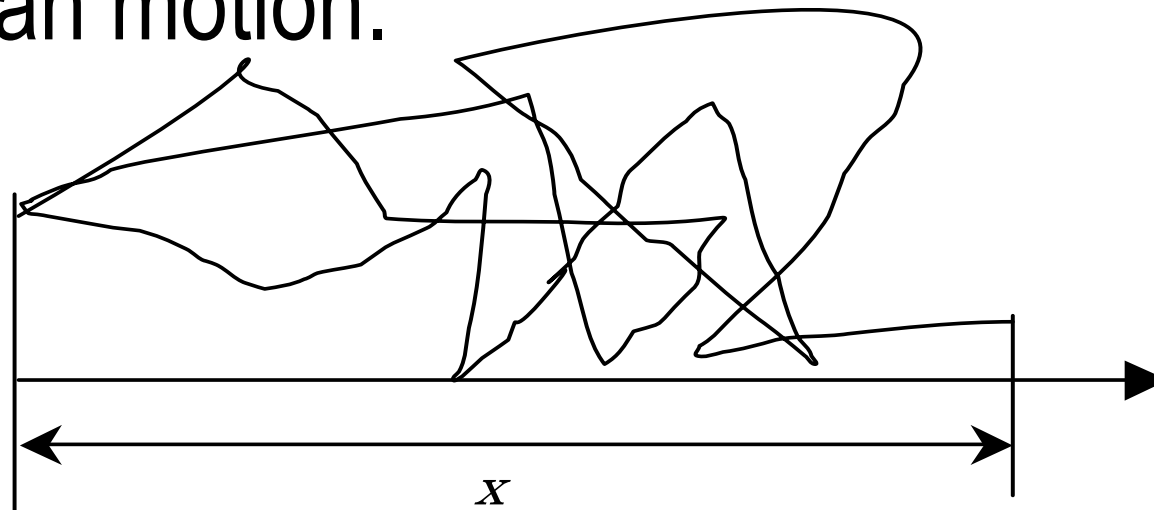
Kinetics: Brownian Motion

▸ If the particles are in Brownian motion (irregular motion), the Brownian motion is the thermal motion of the particles, so each particle has an energy of kT.

▸ Assuming that this is converted to kinetic energy, it is expressed by the following equation.

$$kT = 1/2\ mv^2$$

分散

Kinetics: Brownian Motion

▸ According to Einstein's statistical calculation, the average distance x that one particle moves in the x direction in time t due to Brownian motion is

$$x = \sqrt{sDt}$$

▸ D is the diffusion constant of the particle. Einstein also provided an equation for the diffusion constant,

$$D = \frac{kT}{f}$$

▸ where f is the so-called coefficient of friction. Stoks' law holds true when the particles are very large compared to the molecules of the medium.

分散

Kinetics: Brownian Motion

$$f = 6\pi\eta a$$

▶ where η is the viscosity of the substance and a is the particle radius.

$$x = \sqrt{\dfrac{RTt}{3\pi\eta a N_A}}$$

▶ R is the gas constant, N_A is Avogadro's number.

分散

Kinetics: Brownian Motion

▸ For example, the displacement x of the particles after 1 second in distilled water at 20℃ is calculated as follows.

▸ Particle radius   Displacement after 1 second （μm）

▸   1 nm   20.7

▸   10 nm   6.56

▸   100 nm   2.07

▸   1μm   0.656

分散

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Dispersion or Aggregation?

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

What is electrostatic repulsion?

▶ The source of the force is the surface potential of the particles.

▶ The phenomena related to the surface potential are as follows.
  ◦ electrophoresis
  ◦ electroosmosis
  ◦ sedimentation potential

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Electrophoresis

▸ Electrophoresis is a phenomenon in which electrically charged molecules (ions) move when an electric field is applied.
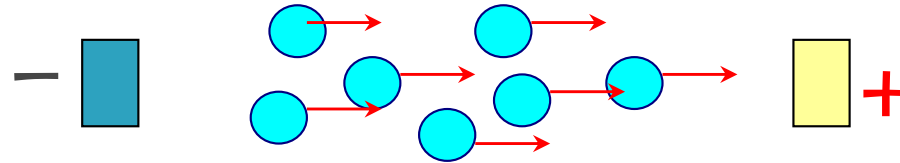
▸ Positively charged molecules are attracted to negative electrodes, and negatively charged molecules are attracted to positive electrodes.

▸ The same is true for colloids.

▸ In a place where a voltage is applied (an electric field), the colloid as a whole moves toward the electrode of the opposite sign of charge.

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Theory of dispersion & aggregation, and evaluation of dispersion stability

2023/5/23

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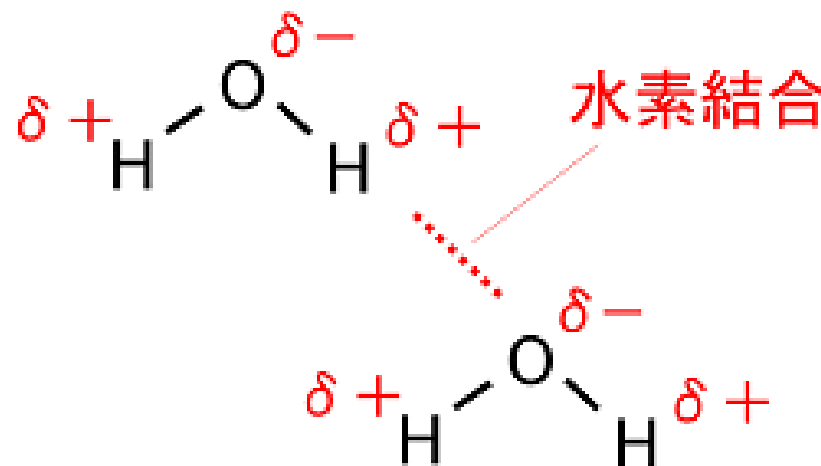(Molecular melting point and boiling point increase in proportion to molecular weight.)

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)

$\delta-$
$\delta+$ H — O
H $\delta+$ 水素結合
$\delta+$ H — O $\delta-$
H $\delta+$

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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.


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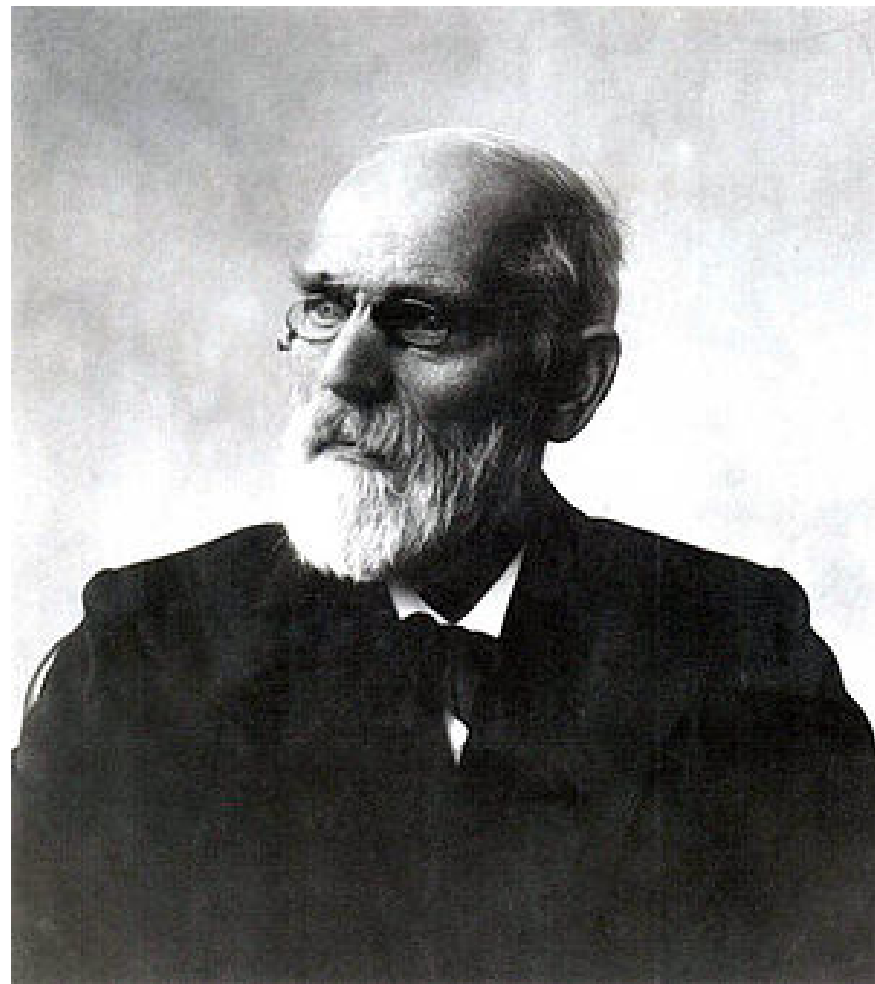
van der Waals force

- 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.

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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.

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van der Waals interaction energy between plates
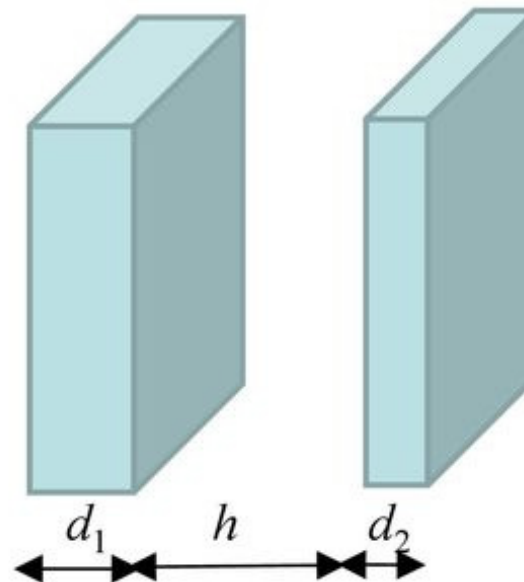
The Hamaker constant is named after the German scientist H. C. Hamaker. His 1937 paper is famous.

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

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

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

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

$$S=2a+h$$

If h is significantly smaller than a, the potential energy is
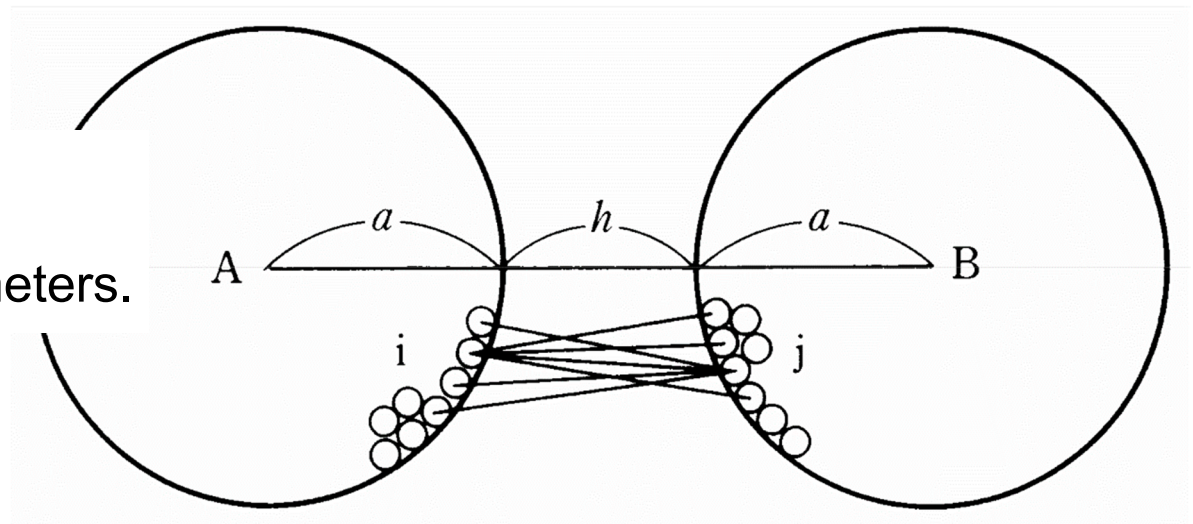
$$V_{vdw} = -\frac{Aa}{12h}$$

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.

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ハーマーカー定数（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, A11 and A33 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.
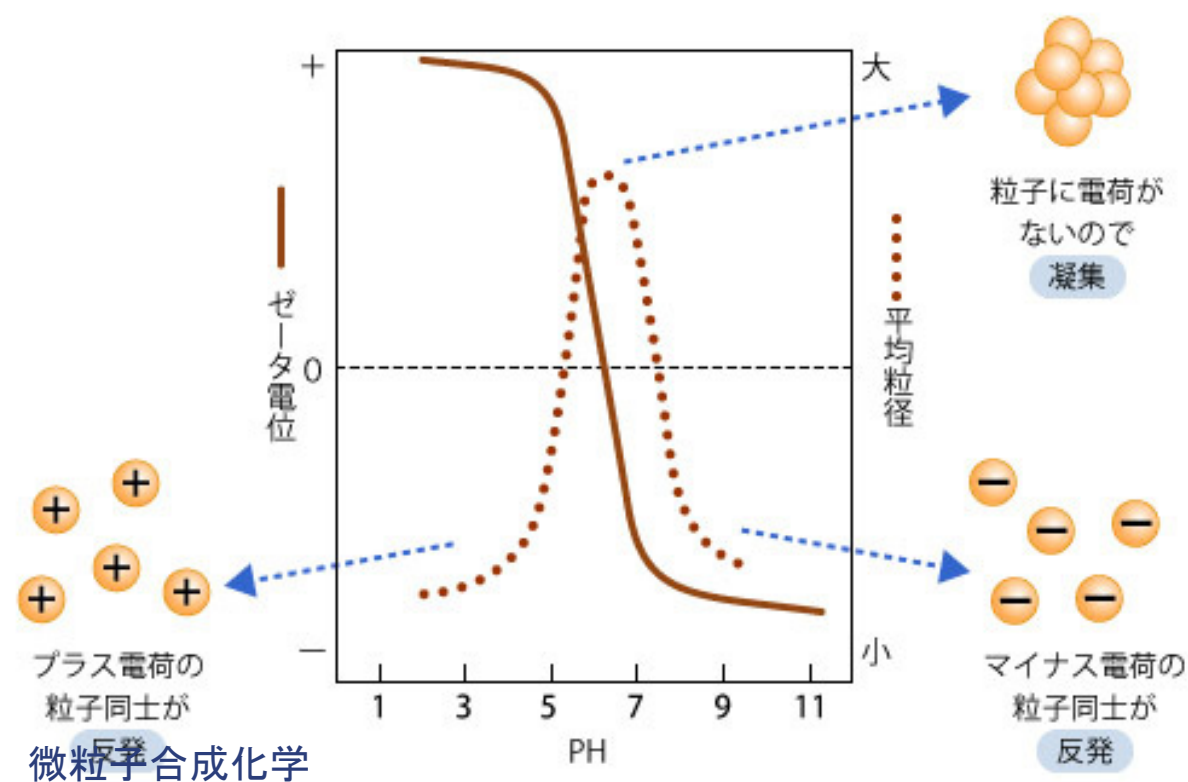
（古澤）

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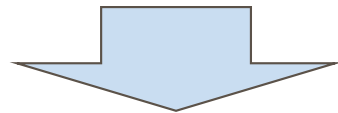
DLVO theory

Dispersion and Aggregation

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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
    $$\rightarrow \text{van der Waals force}$$

Dispersion and aggregation （Equilibrium consideration）
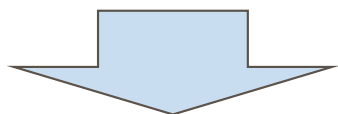
- ■ Aggregation

  - ■ van der Waals interaction

- ■ Dispersion

  - ■ Electrostatic repulsion

    ⬇

  - ■ Repulsion due to surface potential

凝集

分散

Way to think

Dispersion and aggregation

- Interaction due to van der Waals forces
- electrostatic repulsion

$$V_{total} = V_H + V_{el}$$

V_H : interaction energy due to van der Waals force

V_{el} : interaction energy due to electrostatic repulsion

Way to think

Dispersion and aggregation

$$V_{total} = V_H + V_{el}$$

V_H ： interaction energy due to van der Waals force

V_{el} ： interaction energy due to electrostatic repulsion
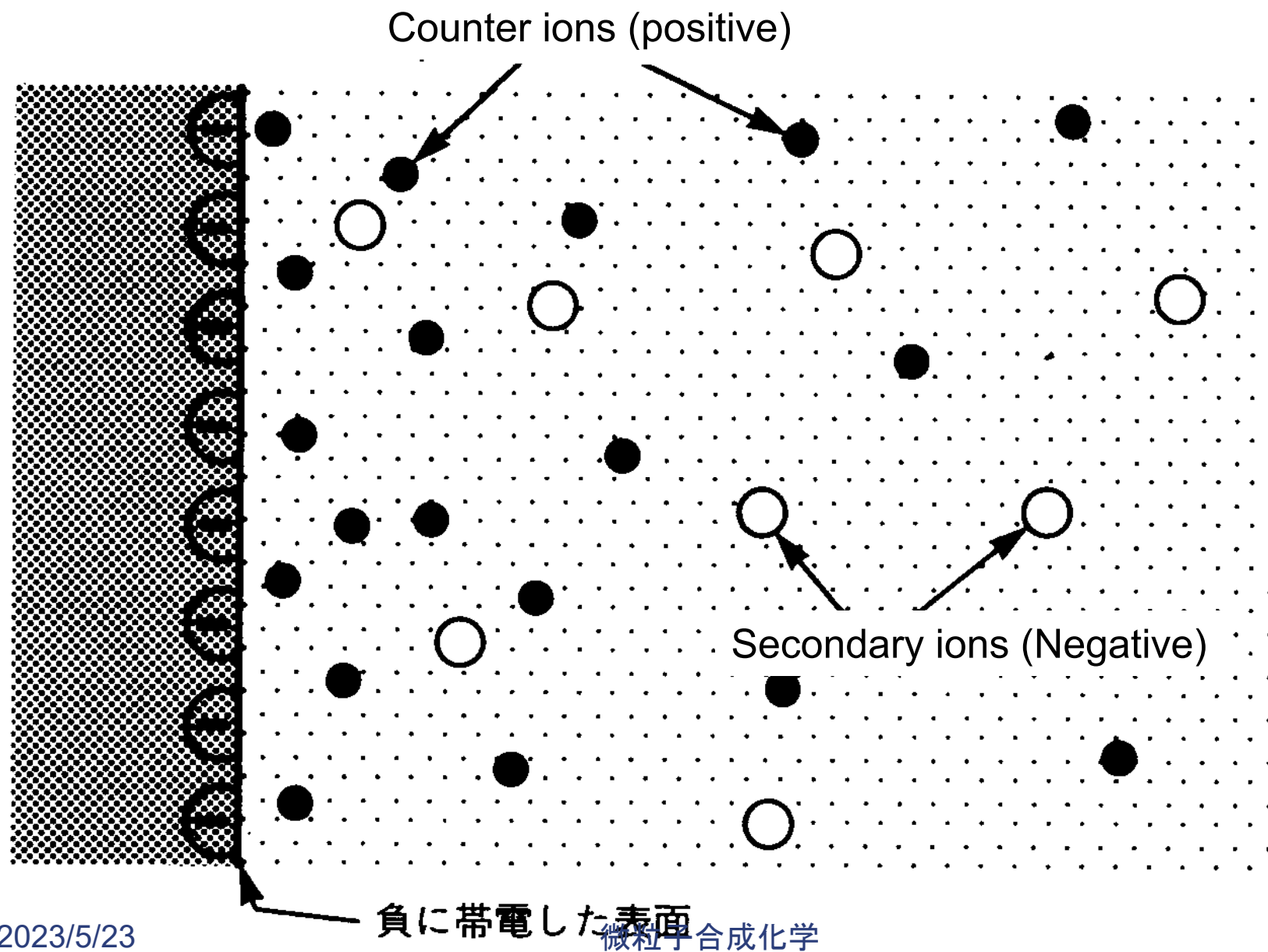
V_{total} Positive→ Dispersion

V_{total} Negative→Aggregation

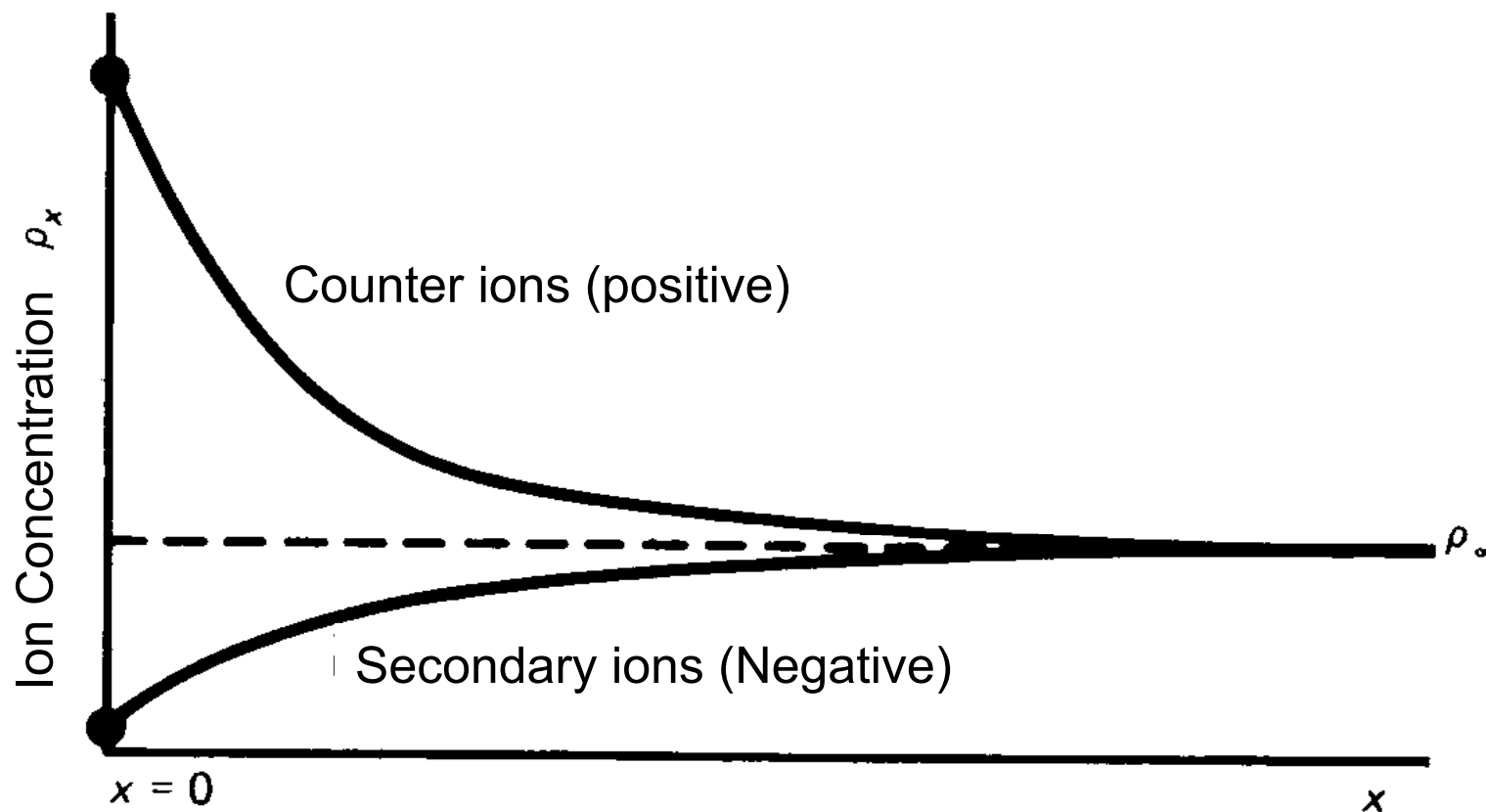微粒子合成化学

Electrostatic repulsion

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Electrostatic repulsion

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

- Start here

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Counter ions (positive)

Secondary ions (Negative)
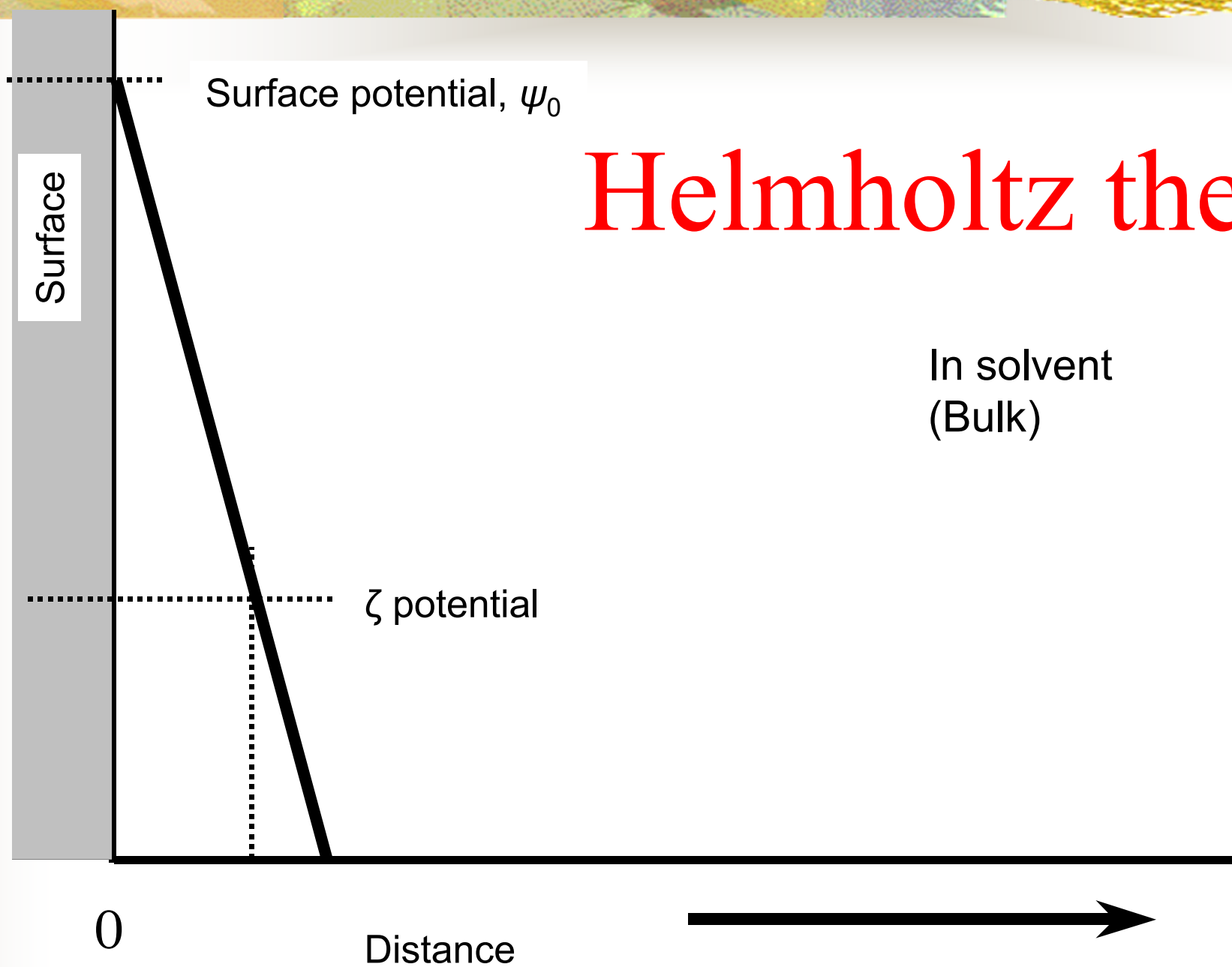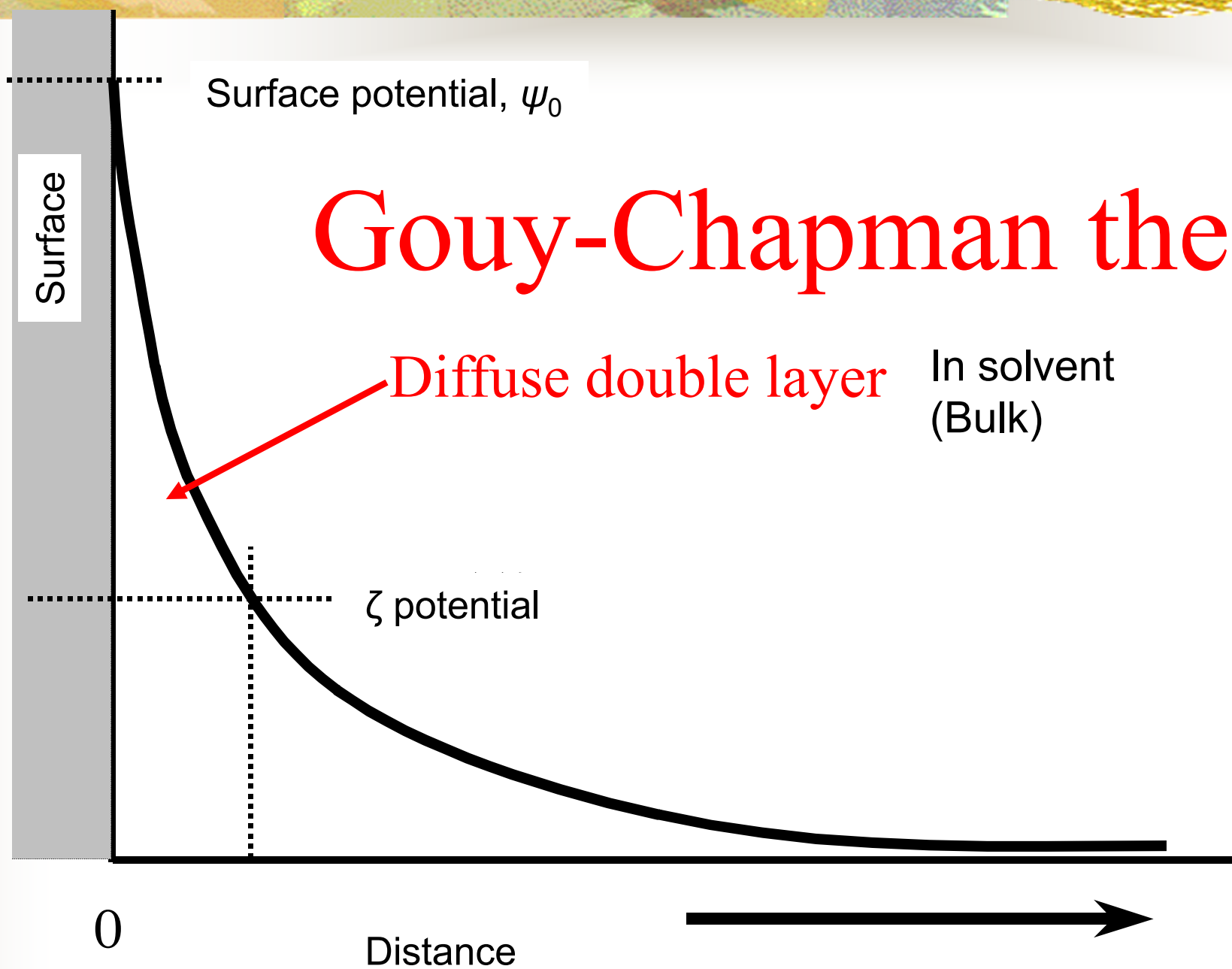
負に帯電した表面

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一 様に帯電した表面

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.
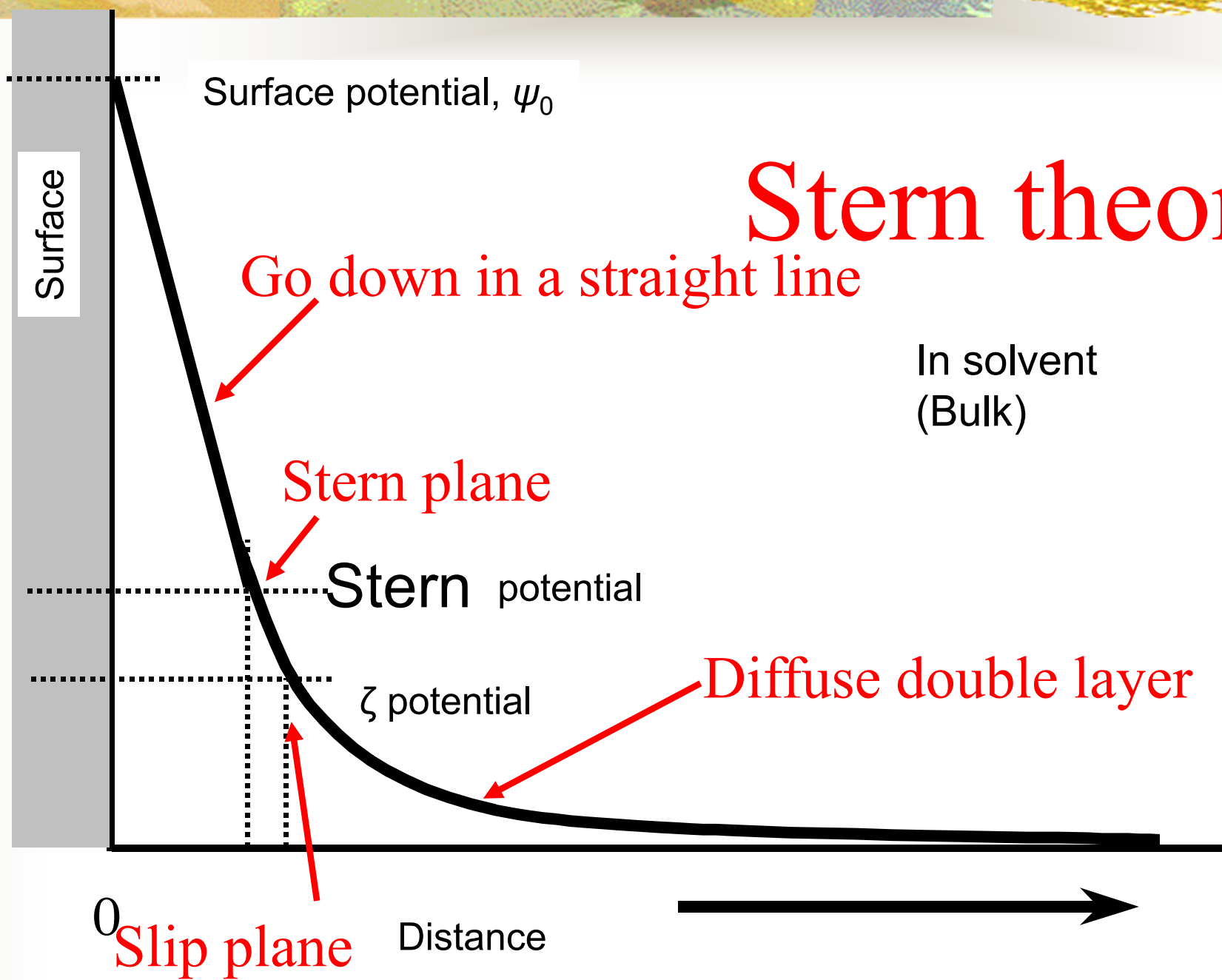
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Potential drops with distance

- ◼ Helmholtz theory

- ◼ Gouy-Chapman theory

- ◼ Stern theory

Helmholtz theory

Surface potential, ψ_0

Surface

ζ potential

In solvent (Bulk)

0

Distance

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Surface potential, ψ_0

Gouy-Chapman theory

Diffuse double layer

In solvent
(Bulk)

Surface

ζ potential

0

Distance

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Stern theory

Surface potential, ψ_0

Surface

Go down in a straight line

In solvent
(Bulk)

Stern plane

Stern potential

ζ potential

Diffuse double layer

0

Slip plane

Distance

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Stern layer

surface potential

Gouy diffuse layer

bulk

(1) (2)   (3) →

(1) inner sphere complexes
(2) outer sphere complexes
(3) diffuse ion swarm

V_{st}=Stern potential

ζ=zeta potential

ϑ=double layer thickness

$$= 1 / \kappa$$

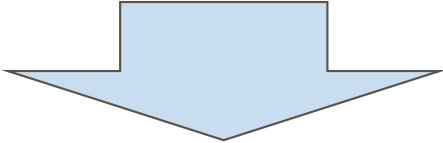$V_x = V_{st} e^{-x/\vartheta}$

shear plane

V_{st}/e

x

outer Helmholtz plane

ϑ

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.

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Consider the ζ potential as the surface potential.

Surface

In solvent
(Bulk)

0

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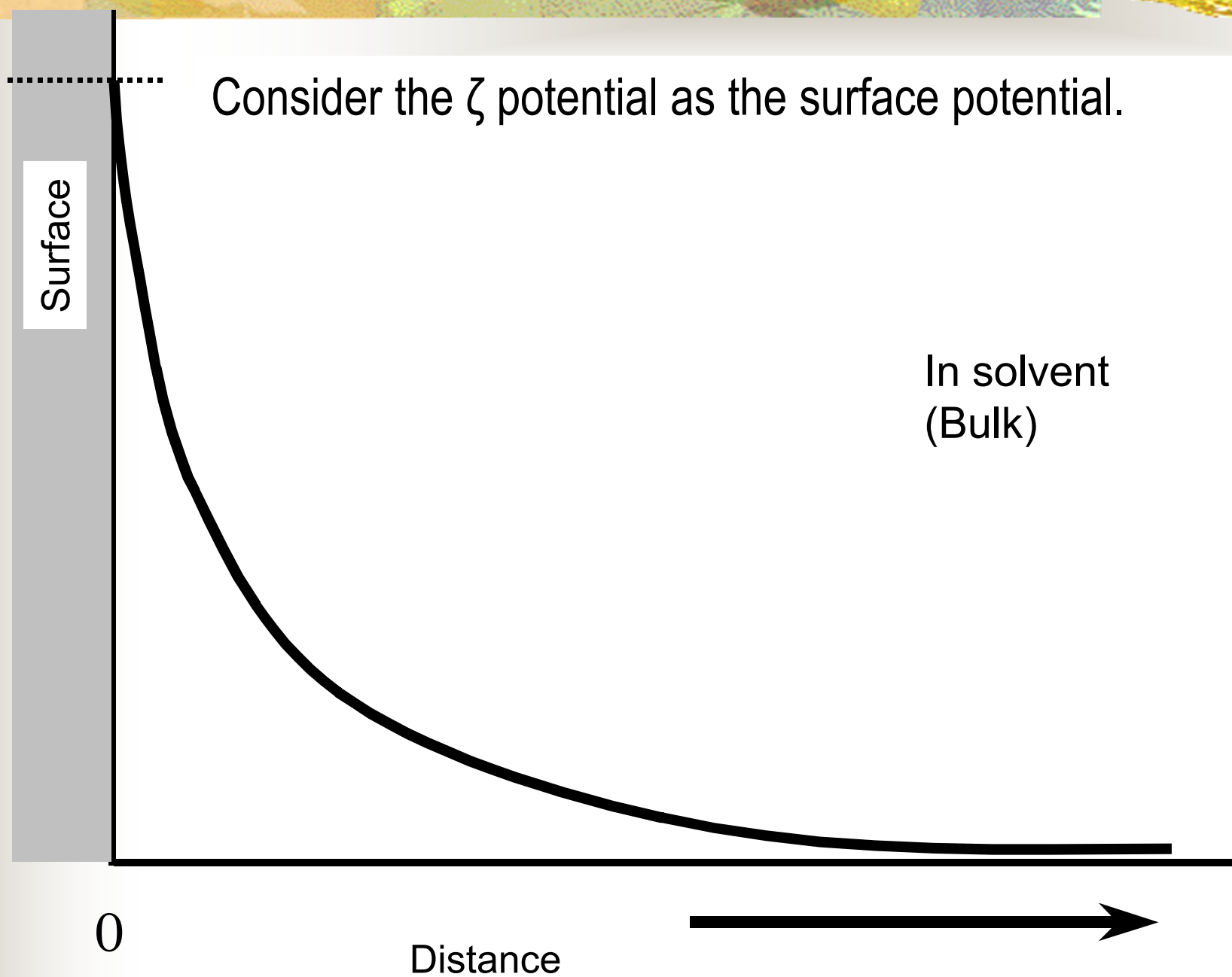
1. The ion concentration in the diffuse layer follows the Boltzmann distribution.

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

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

(1)

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:

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

R: Gas constant

c_0: c at $\psi_0 = 0$

Potential in diffuse layer is defined as Poisson equation:

$$\Delta\psi = \text{div }(\text{grad }\psi) = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\rho}{\varepsilon_r\varepsilon_0} \qquad (3)$$

ε_r: Dielectric constant of solution

ε_0: Dielectric constant in vacuum

ρ: Charge density

ρ: Charge density is defined by

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

$$\rho = ze(n_+ - n_-)$$

$$= nze \left\{ \exp\left(-\frac{ze\psi}{kT} \right) - \exp\left(\frac{ze\psi}{kT} \right) \right\}$$

$$= -2nze \sinh\left(\frac{ze\psi}{kT} \right) \qquad (4)$$

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

$$\frac{d^2\psi}{dx^2} = \frac{2nze}{\varepsilon_r \varepsilon_0} \sinh \frac{ze\psi}{kT} \qquad (5)$$

It is obtained by integrating Eq. (5).

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

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

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

where

$$\kappa^2 = \frac{2nz^2e^2}{\varepsilon_r\varepsilon_0 kT} \qquad (8)$$

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

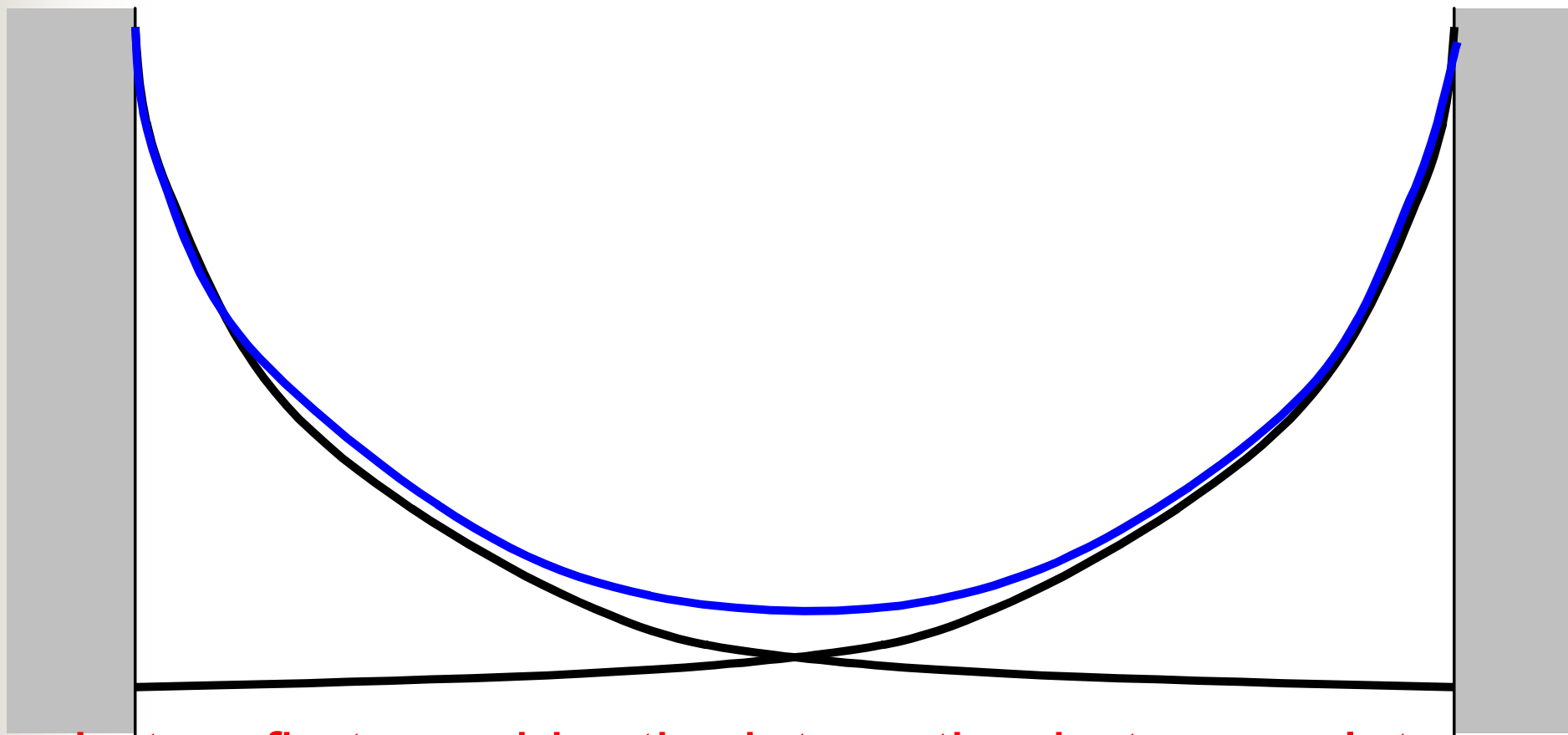$$\kappa = 3.3\times10^9 z\sqrt{c} \qquad (9)$$

Solving equation (7) yields the following.

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

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

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

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

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.

$$P_E = -\frac{\varepsilon_r \varepsilon_0}{2}\left(\frac{d\psi}{dx}\right)^2$$

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

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.

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

$\psi_{2/h}$: 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.

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

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

Eq. (6) is transformed as follows.

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

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

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Eq. (17) is transformed as follows.

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

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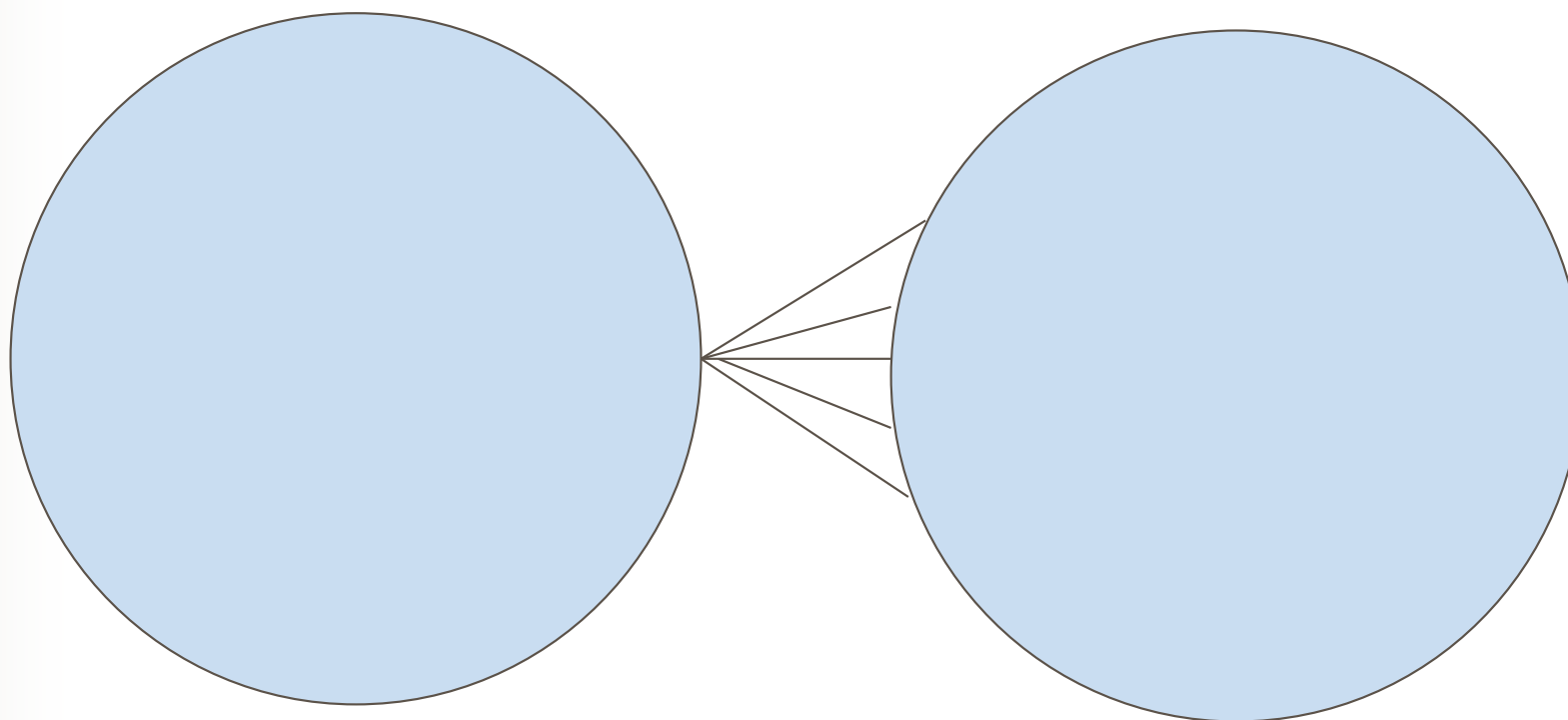For approximation, cosh $y = 1 + y^2$ was used.)

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

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

$$V_R(h) = -\int_{\infty}^{h} P_R(h)\,dh = \frac{64nkT}{\kappa}\gamma^2 \exp(-\kappa h) \qquad (21)$$
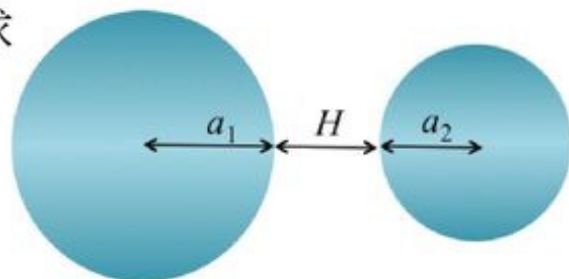
Next, consider the interaction between spherical particles

Next, let us consider the interaction between spherical particles.
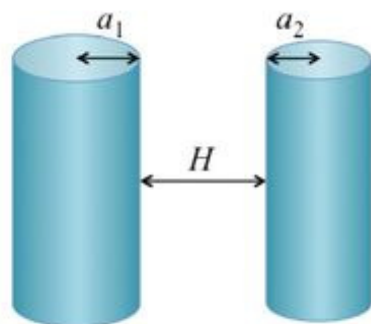
Derjaguin approximation

2球

Sphere 1　　　Sphere 2

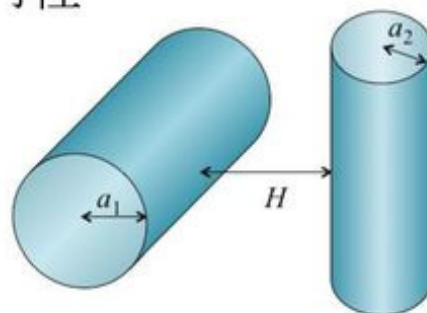$$V_{sp}(H) = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_H^\infty V_{pl}(h)\, dh$$

平行2円柱

Cylinder 1　　　Cylinder 2

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

(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:

$(H<<a_1,a_2)$

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

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

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

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

$$V_R(H) = -\int_\infty^H P_R(H)\,dH$$

$$= \frac{64\pi a n k T}{\kappa^2}\gamma^2 \exp(-\kappa h) \qquad (24)$$