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"?

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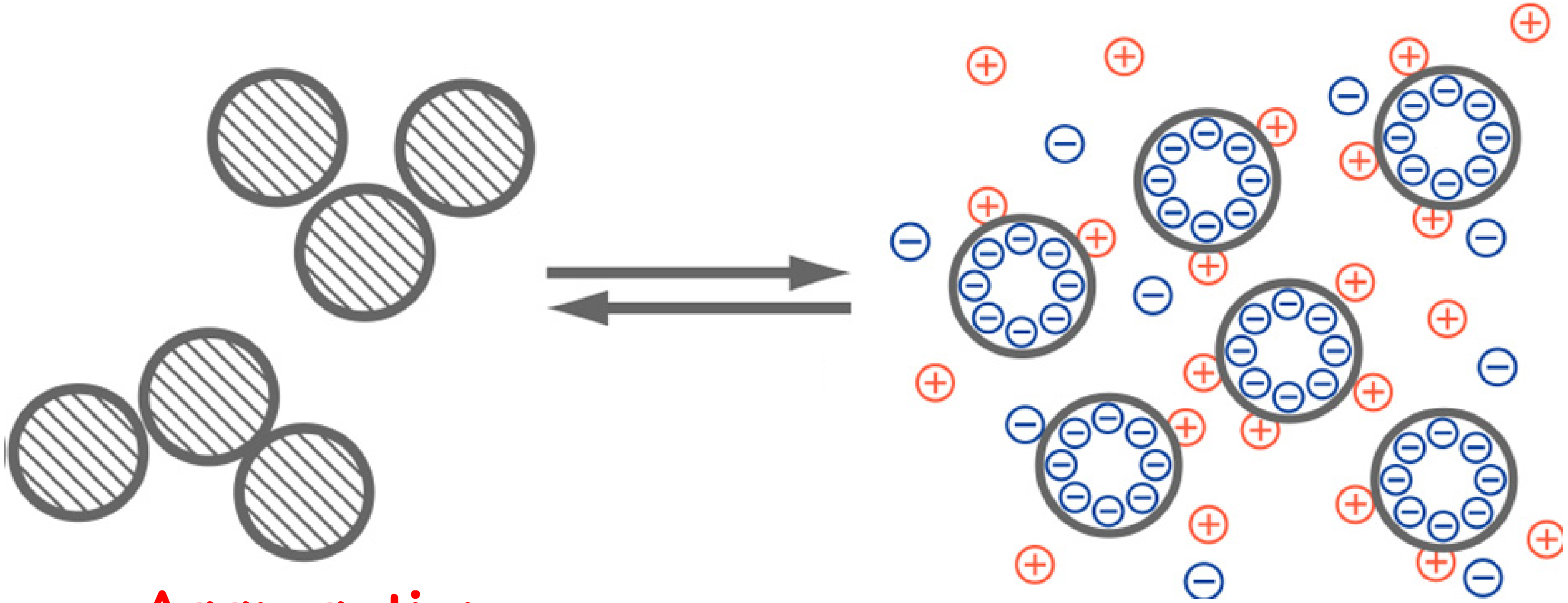
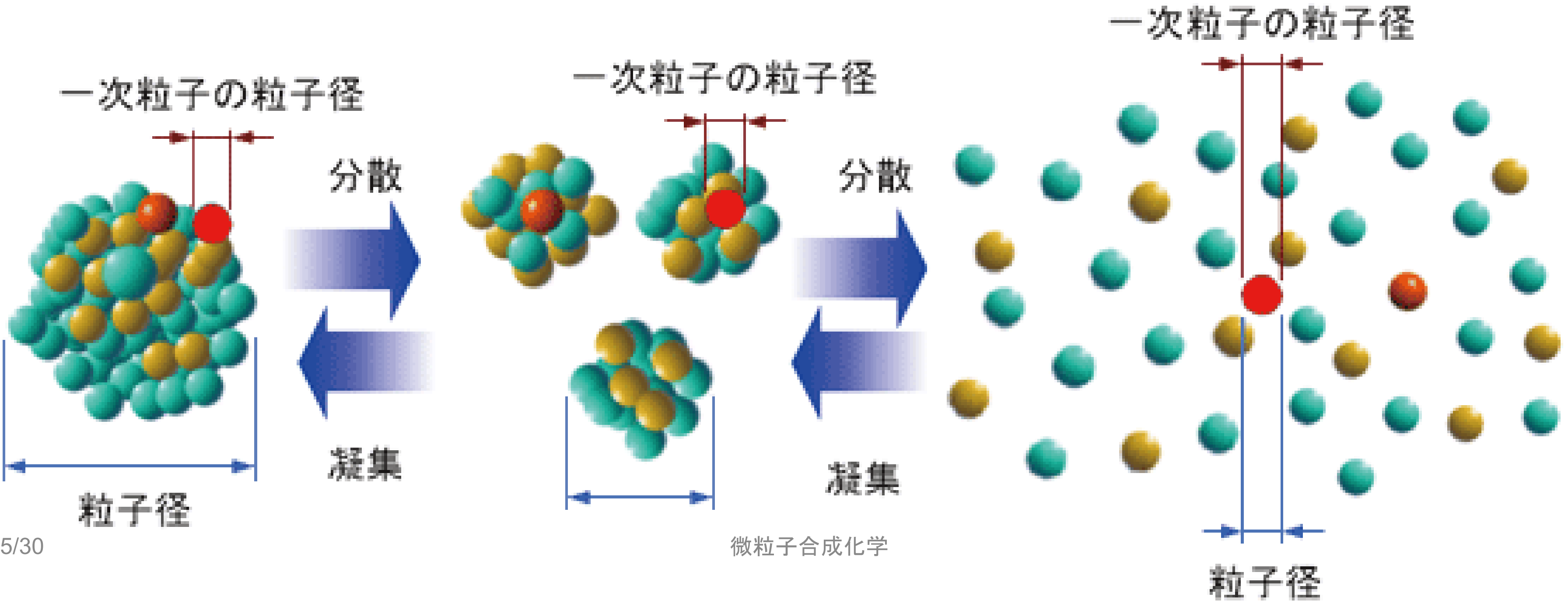
- **If "dispersion" and "aggregation" can be controlled, colloids can be manipulated freely.**



Aggregation

Colloidal dispersion



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

intermolecular force

van der waals force

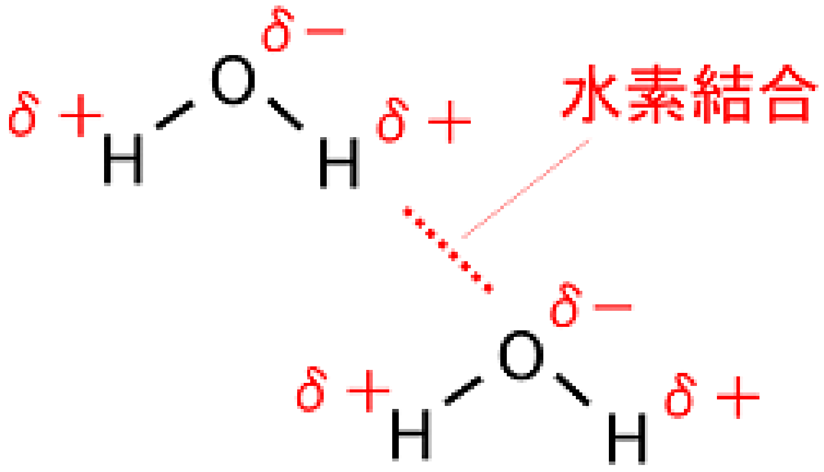
Attractive force acting between any molecule

(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.

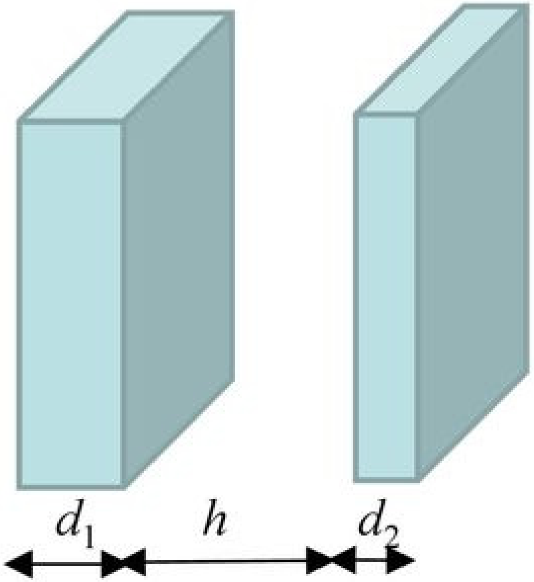
van der Waals force

- 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.

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

(per unit area)

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

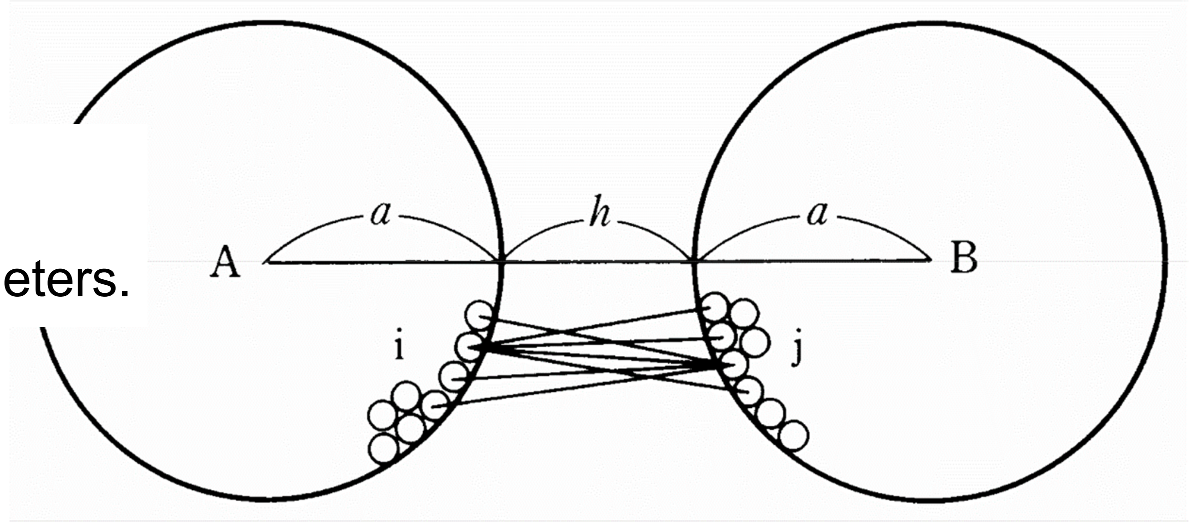
van der Waals forces between particles

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

S=2a+h

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

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



A: Hamaker constant

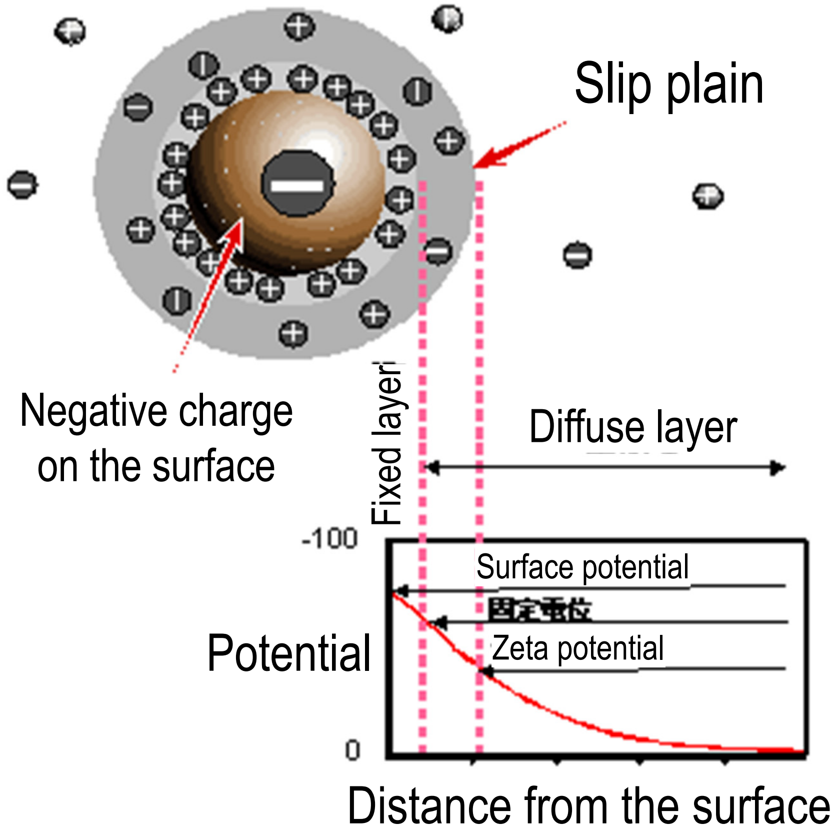
For particles with different diameters.

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

Between planes.

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

Zeta potential



Zeta potential at slip plane

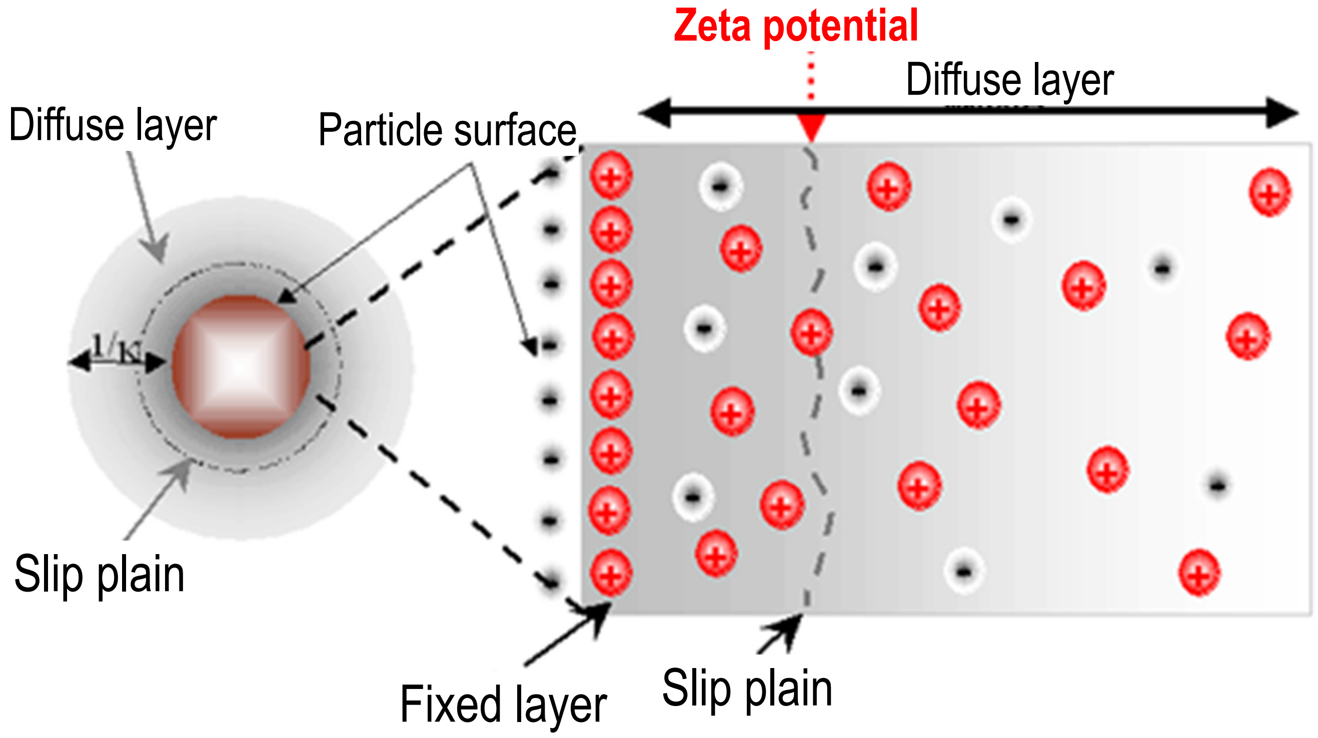
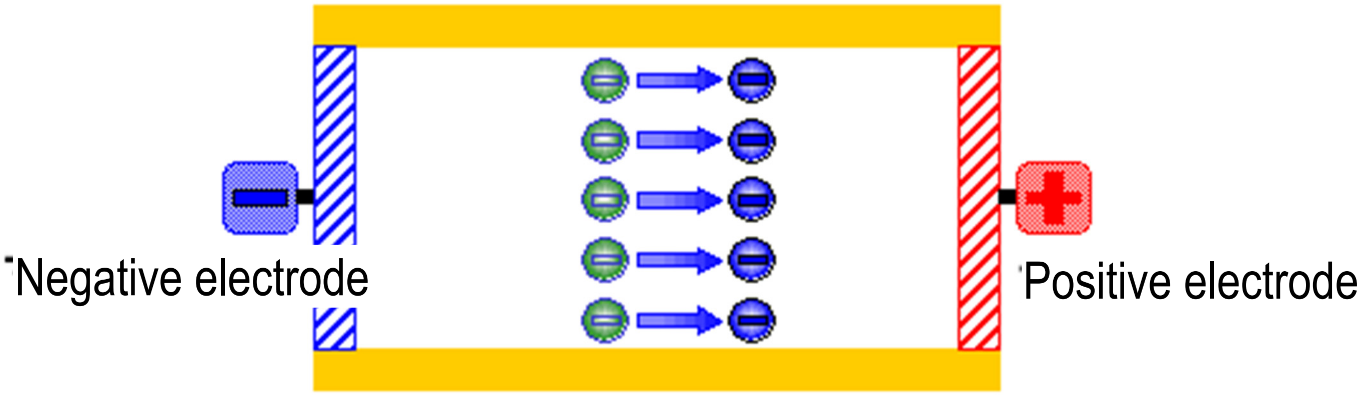
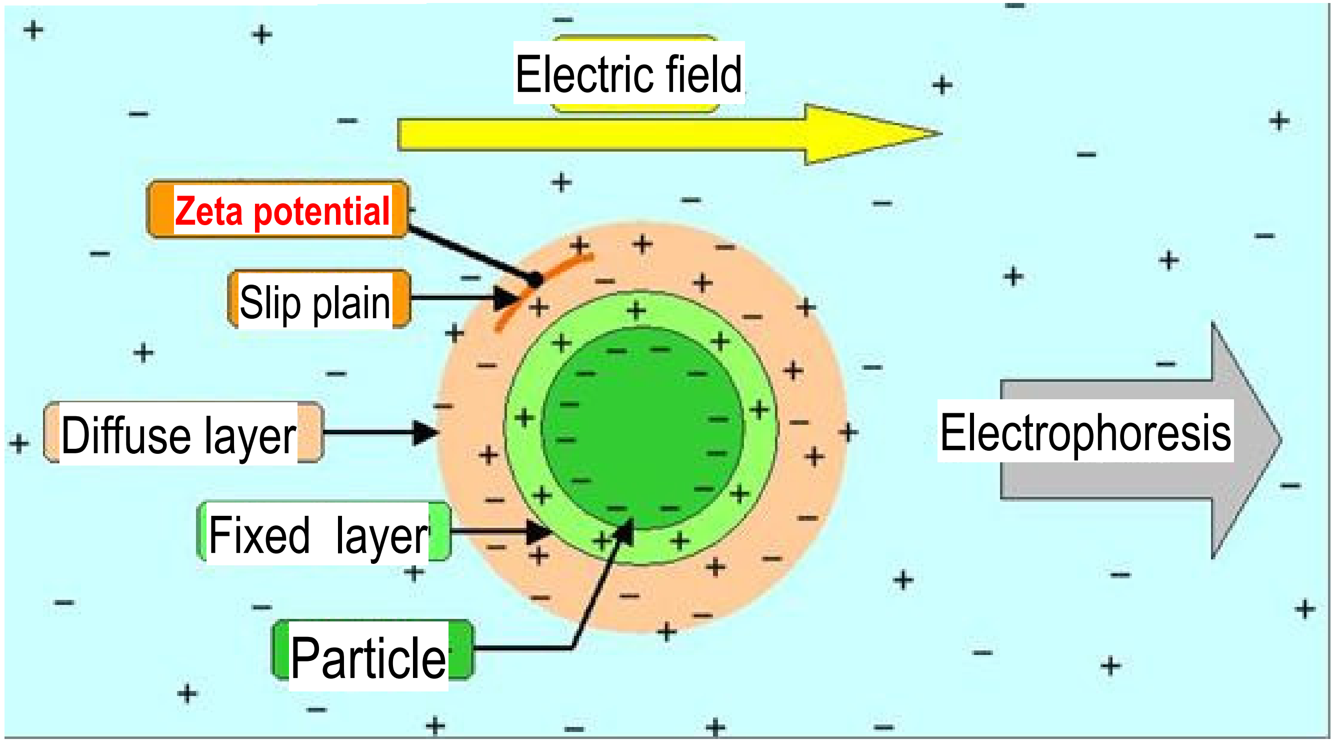


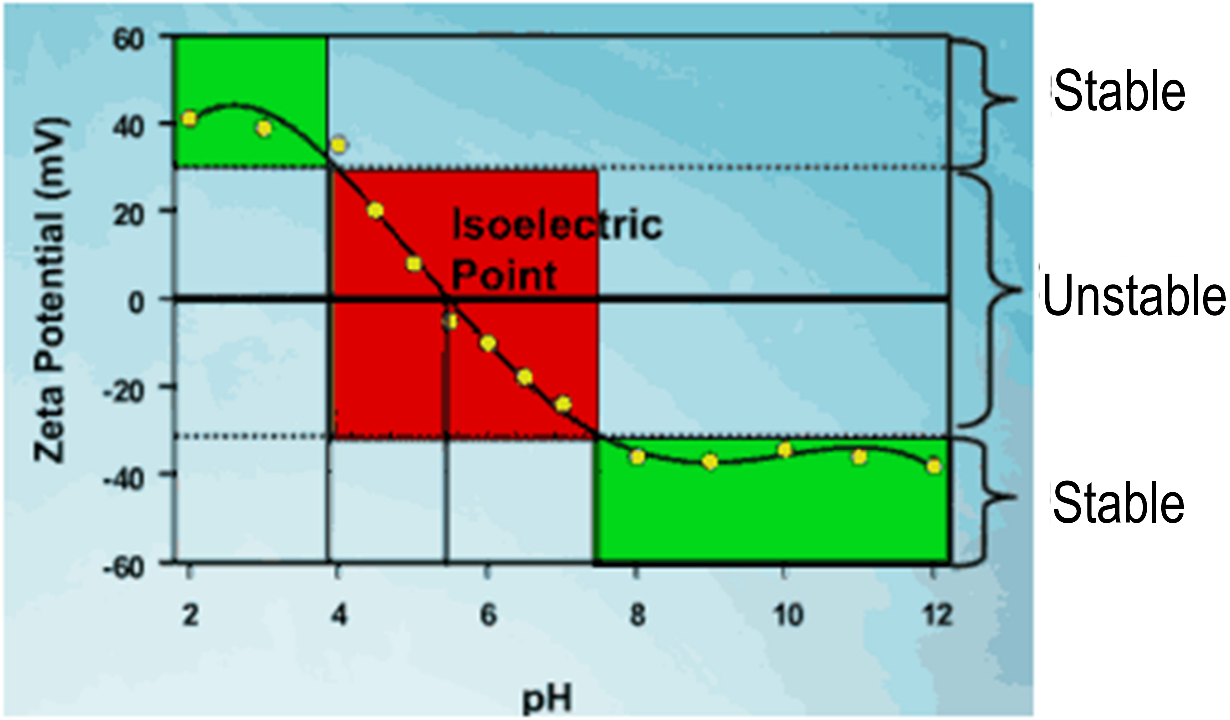
図６ Electrophoresis



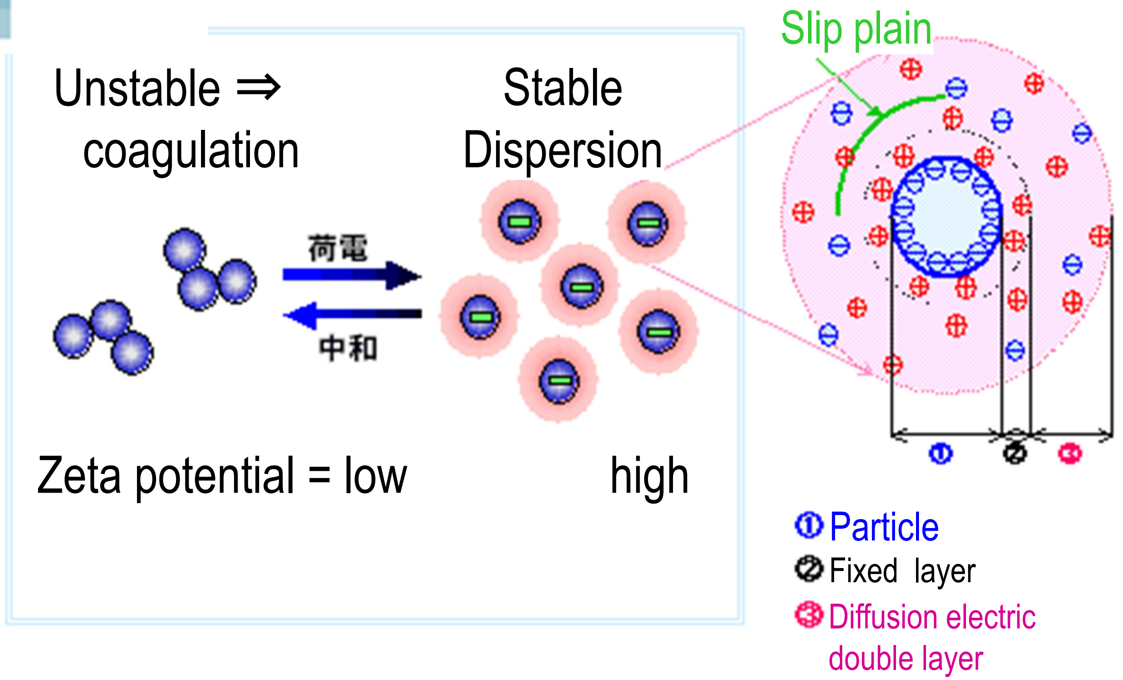
Particles with the same negative charge are 、
moving to the positive electrode.



Zeta potential as a function of pH



Zeta potential and dispersion



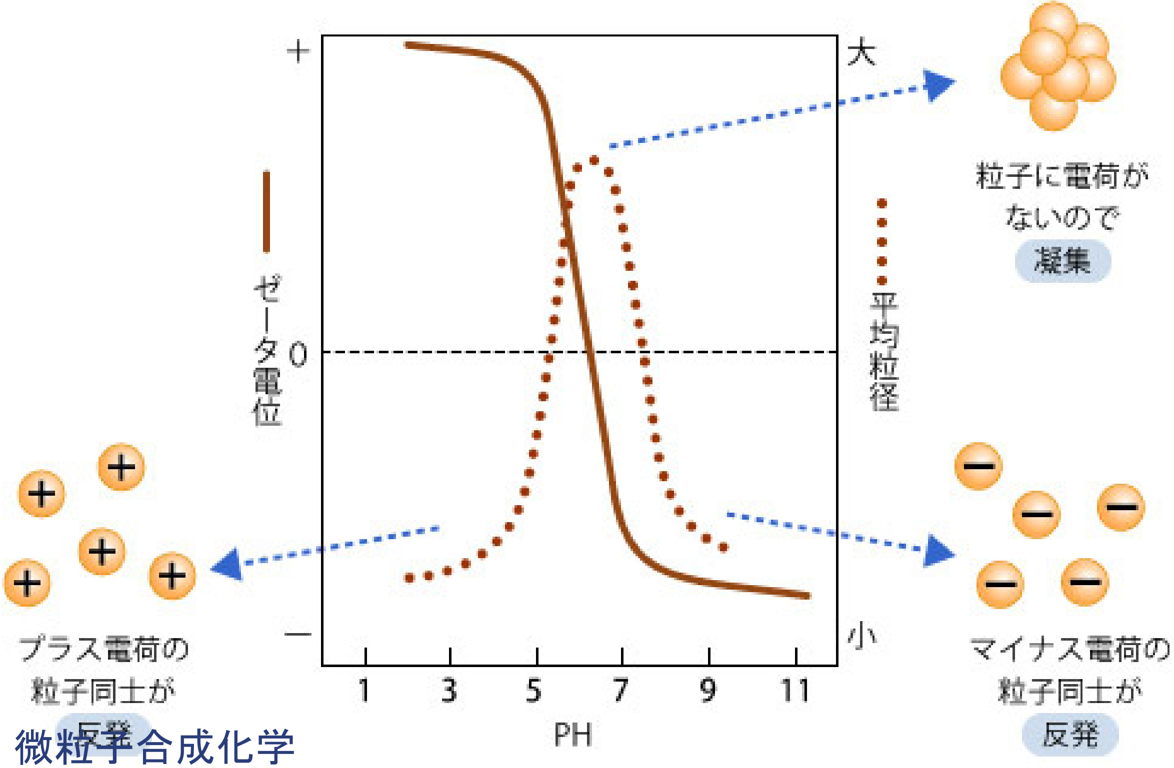
DLVO理論

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

↓

  - Repulsion due to surface potential

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

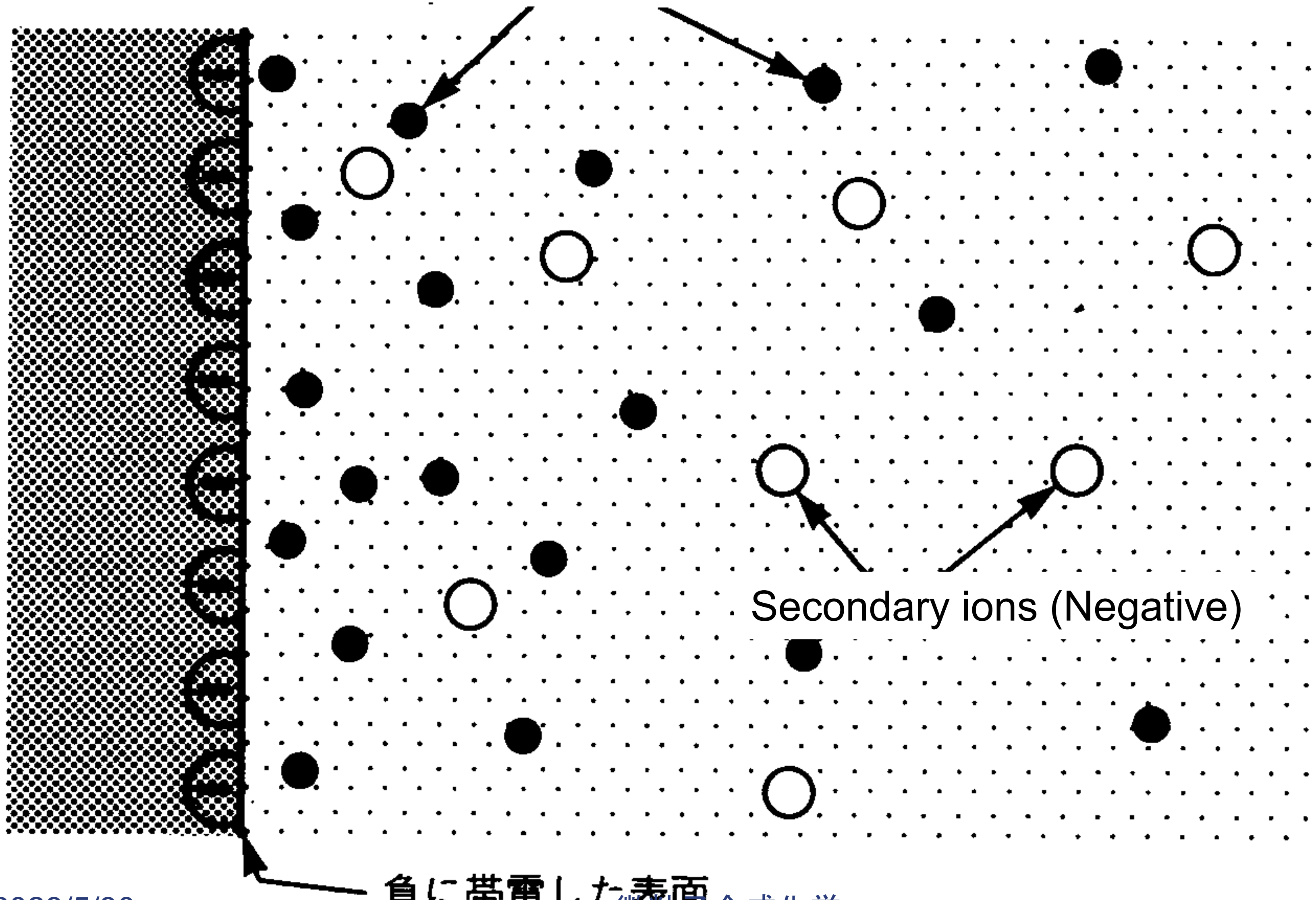
V_{total} Negative→Aggregation

Electrostatic repulsion

Electrostatic repulsion

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

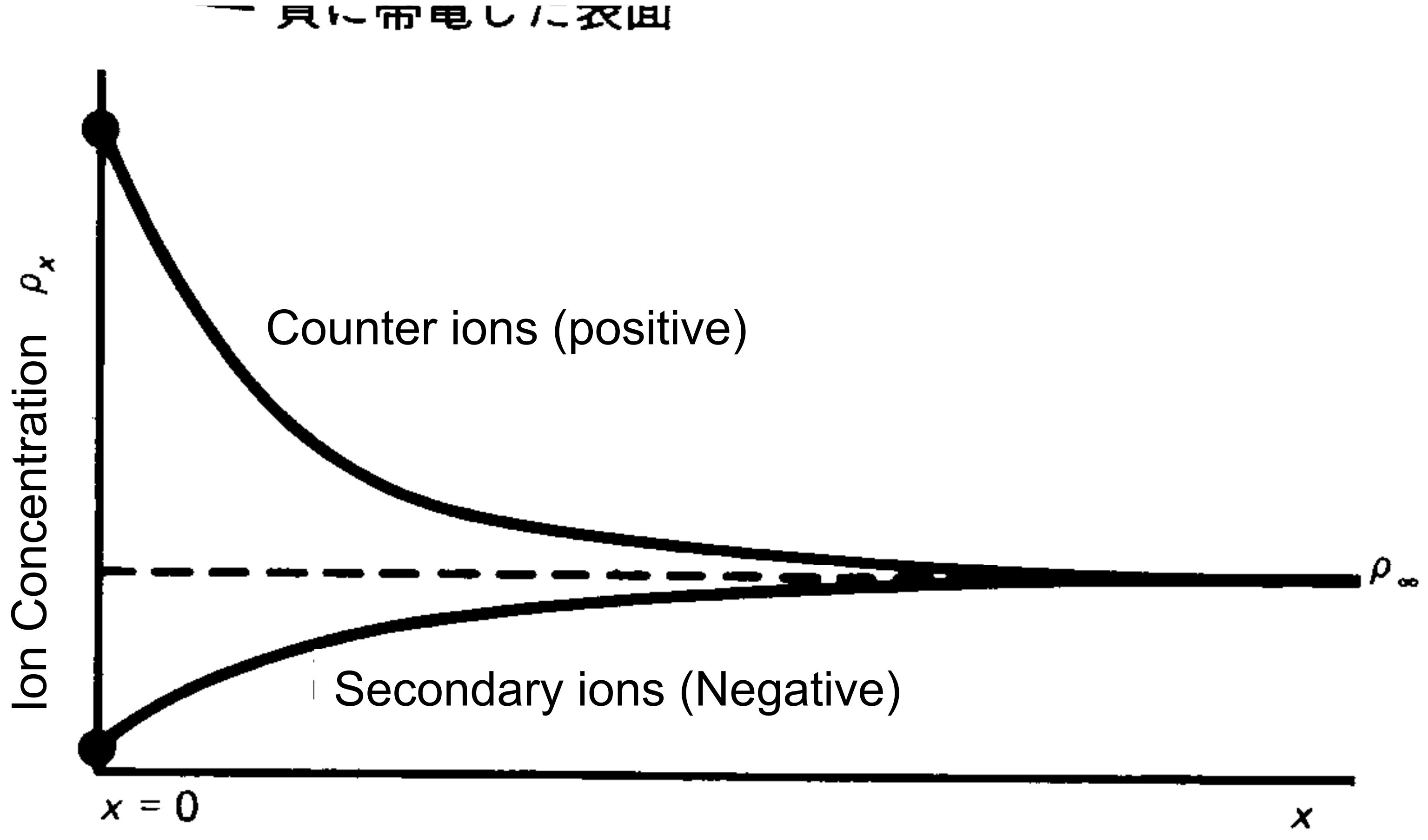
- Start here



Counter ions (positive)

Secondary ions (Negative)

負に帯電した表面



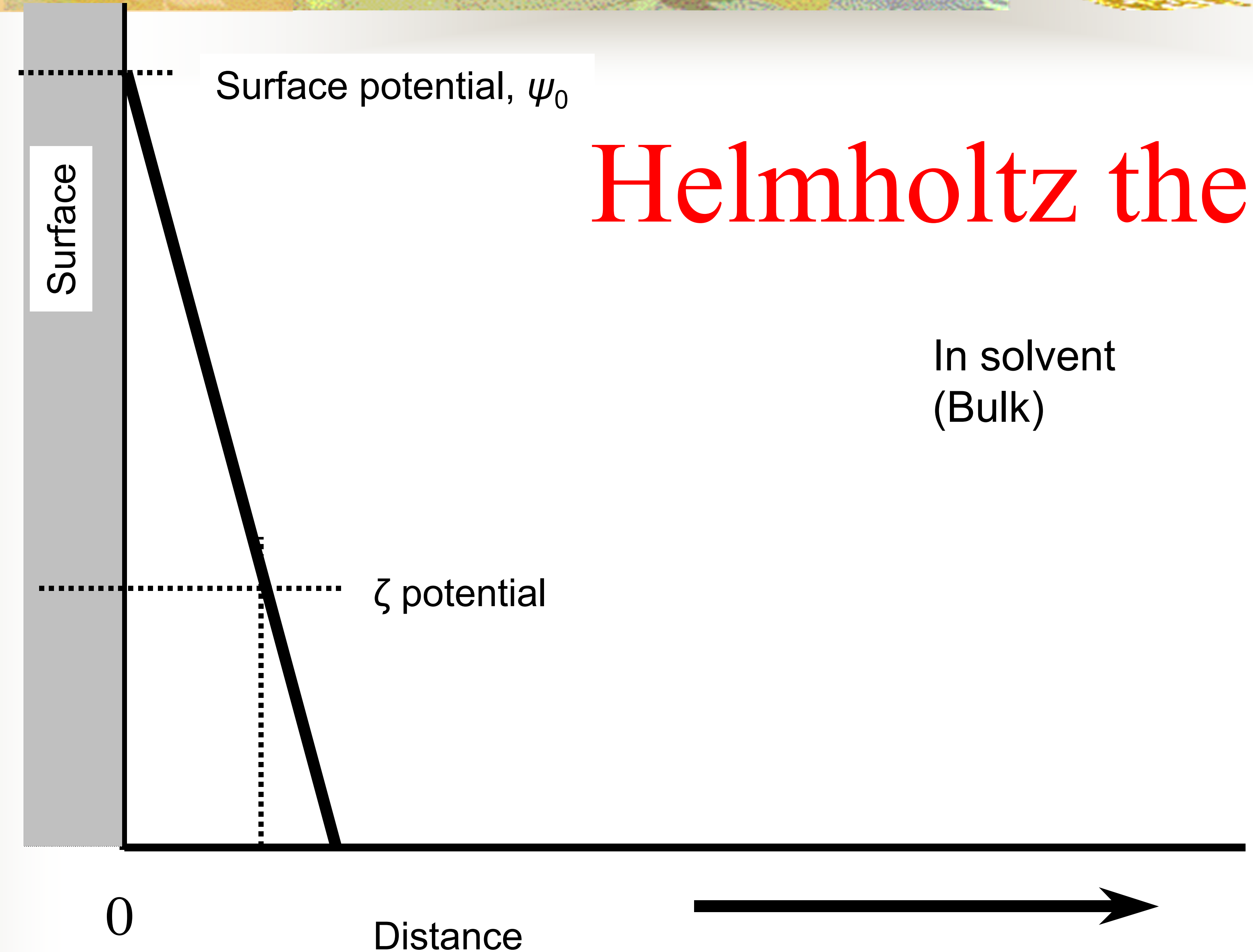
図

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.

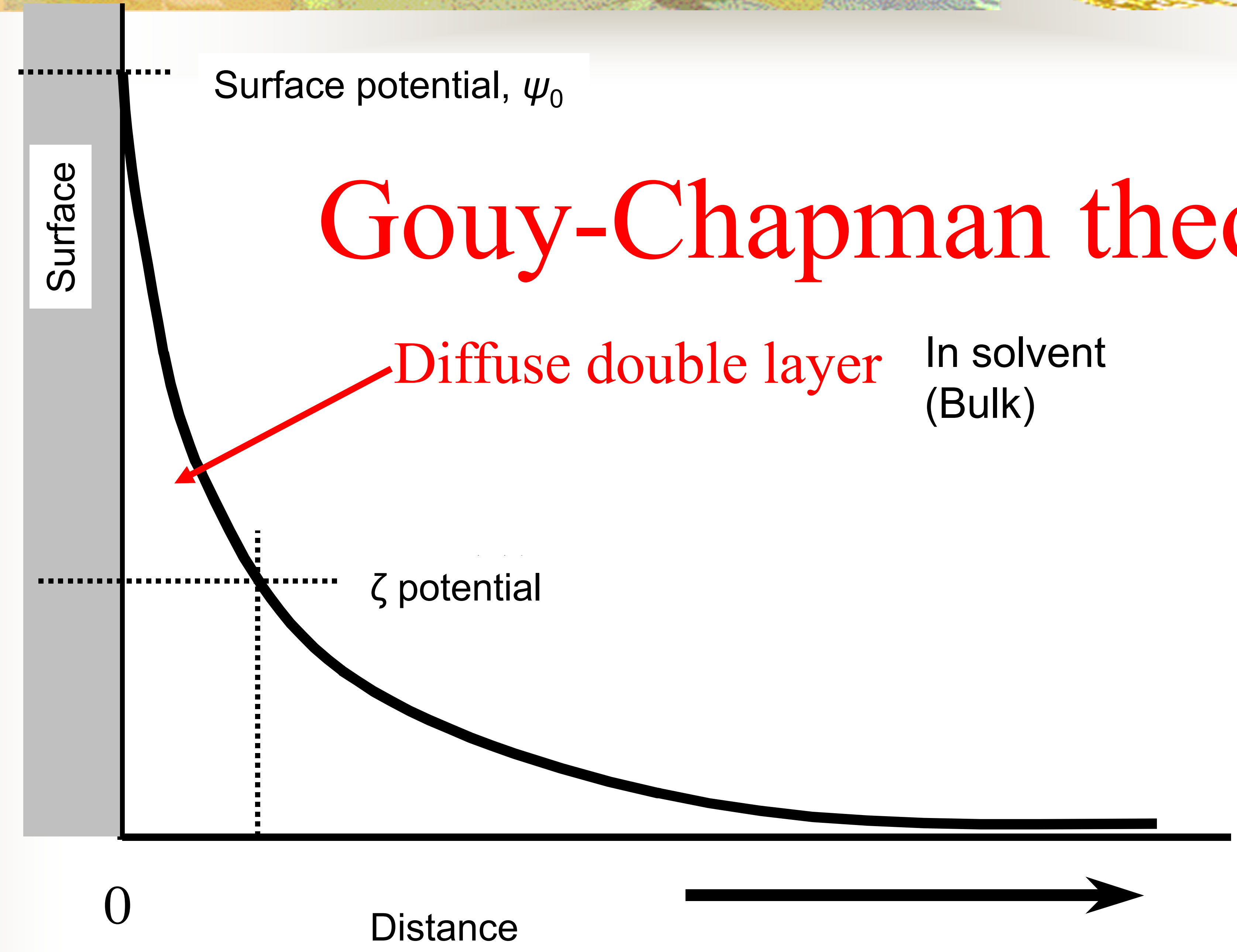
Potential drops with distance

- Helmholtz theory
- Gouy-Chapman theory
- Stern theory

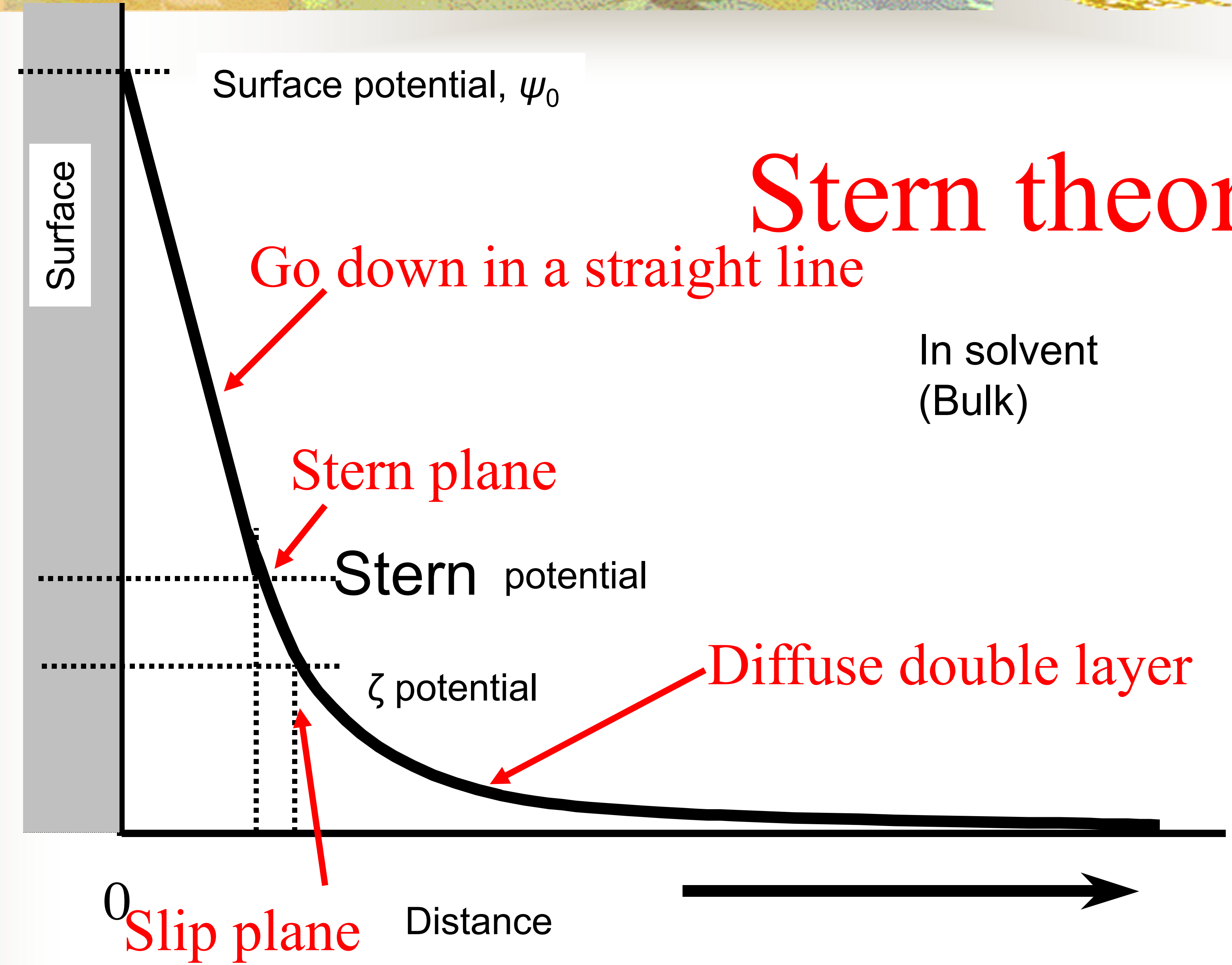
Helmholtz theory



Gouy-Chapman theory



Stern theory



Surface potential, ψ_0

Surface

Go down in a straight line

In solvent
(Bulk)

Stern plane

Stern potential

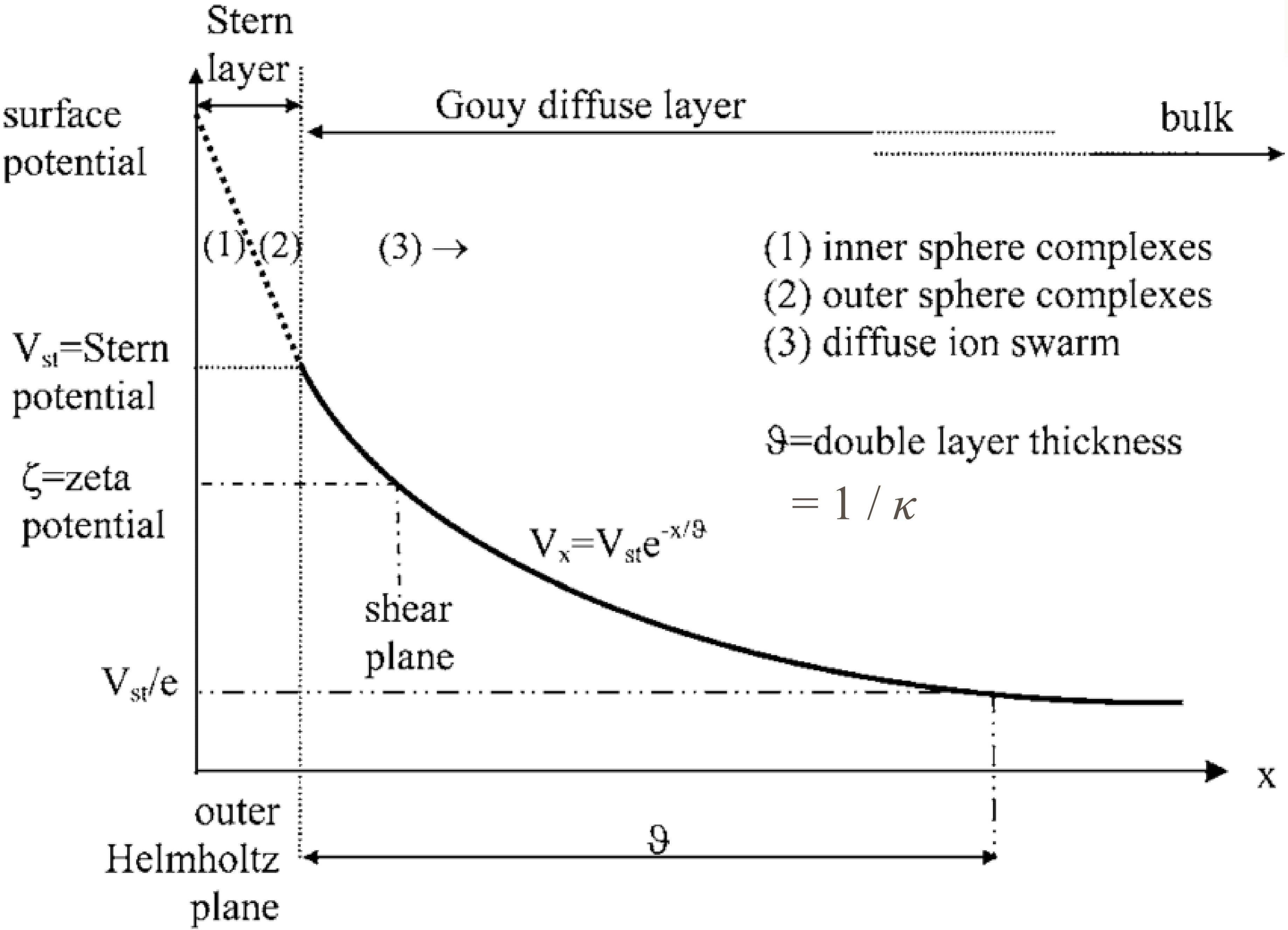
ζ potential

Diffuse double layer

0

Slip plane

Distance



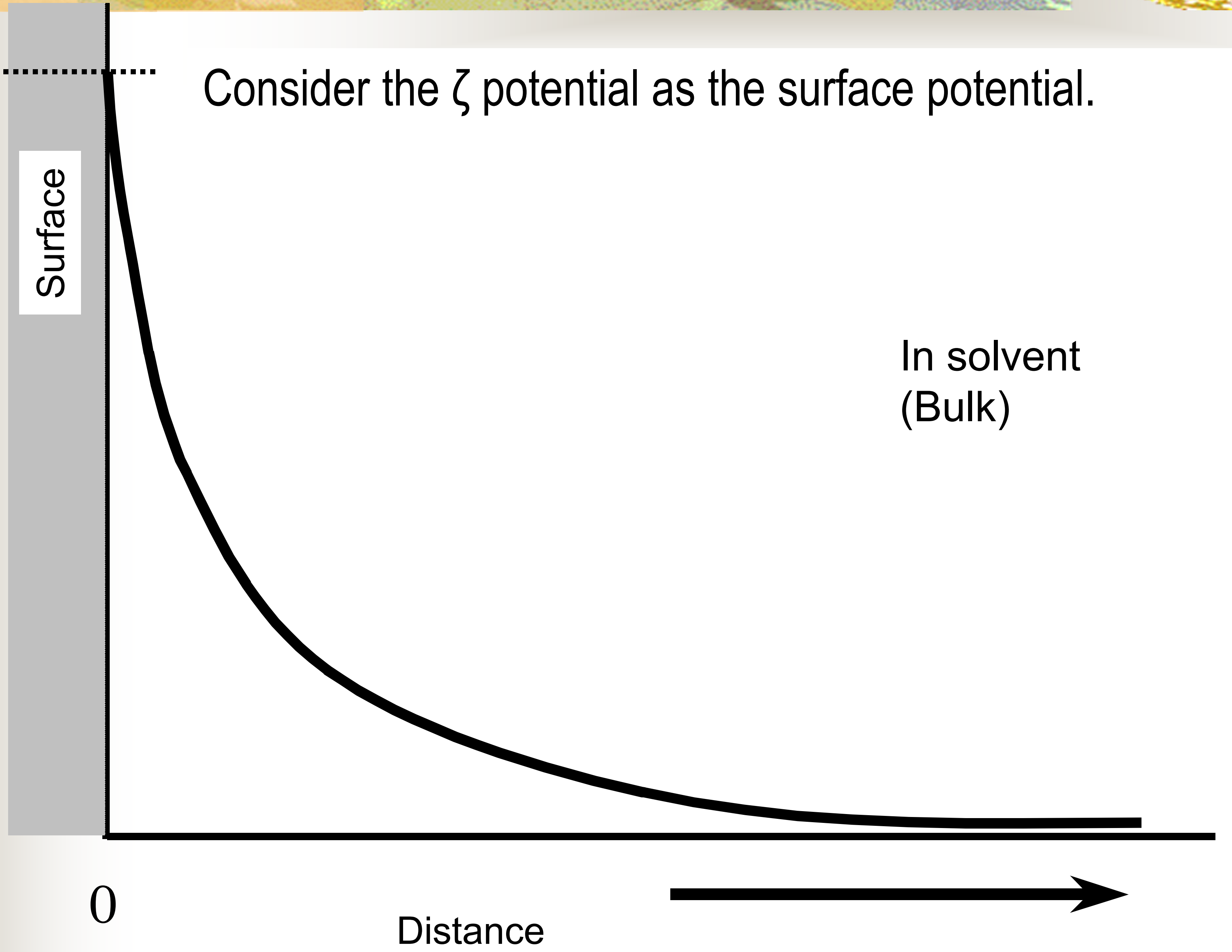
(1) inner sphere complexes
(2) outer sphere complexes
(3) diffuse ion swarm

ϑ=double layer thickness $= 1/\kappa$

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.

Consider the ζ potential as the surface potential.



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

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

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

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:

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

R: Gas constant

c_0: c at $\psi_0 = 0$

Potential in diffuse layer is defined as Poisson equation:

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

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.

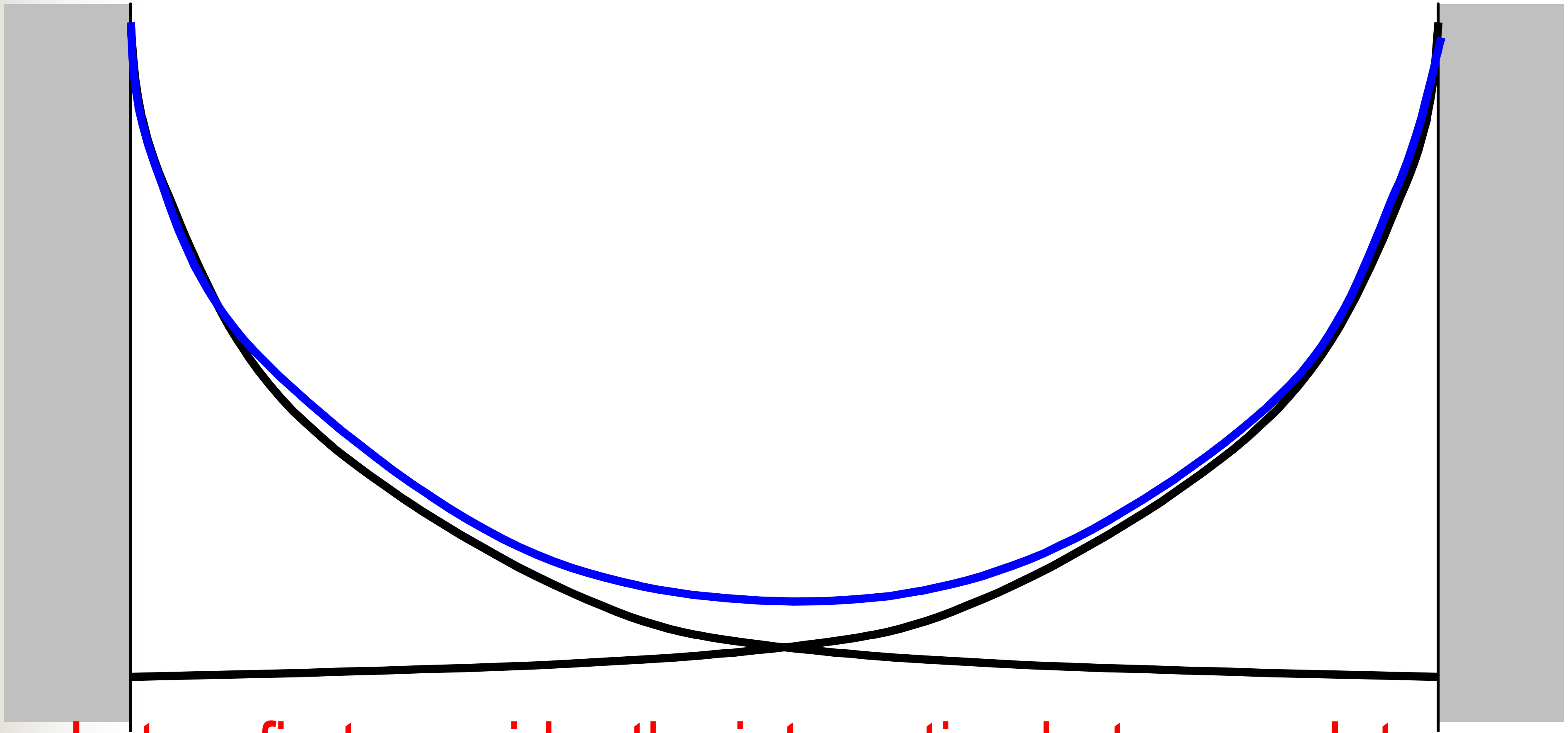
$$\kappa = 3.3\times10^9 z\sqrt{c} \qquad (9)$$

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

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.

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

(This approximation holds when Ψ<20mV, as will be described later.)

Eq. (6) is transformed as follows.

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

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

Eq. (17) is transformed as follows.

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

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

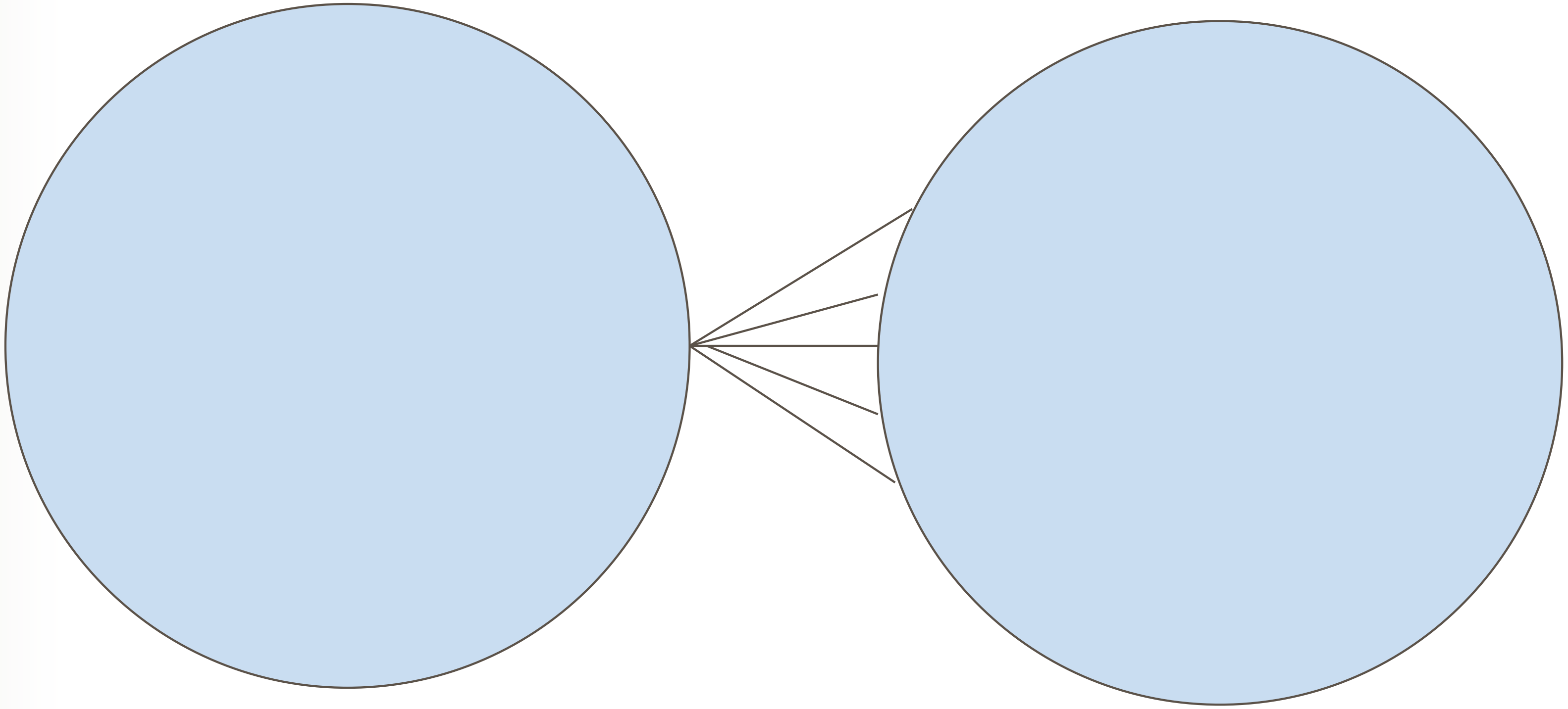
(This approximation holds when *κh*>1, that is, when h is larger than the thickness of the electric double layer.
For approximation, cosh *y* = 1+*y*² was used.)

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

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

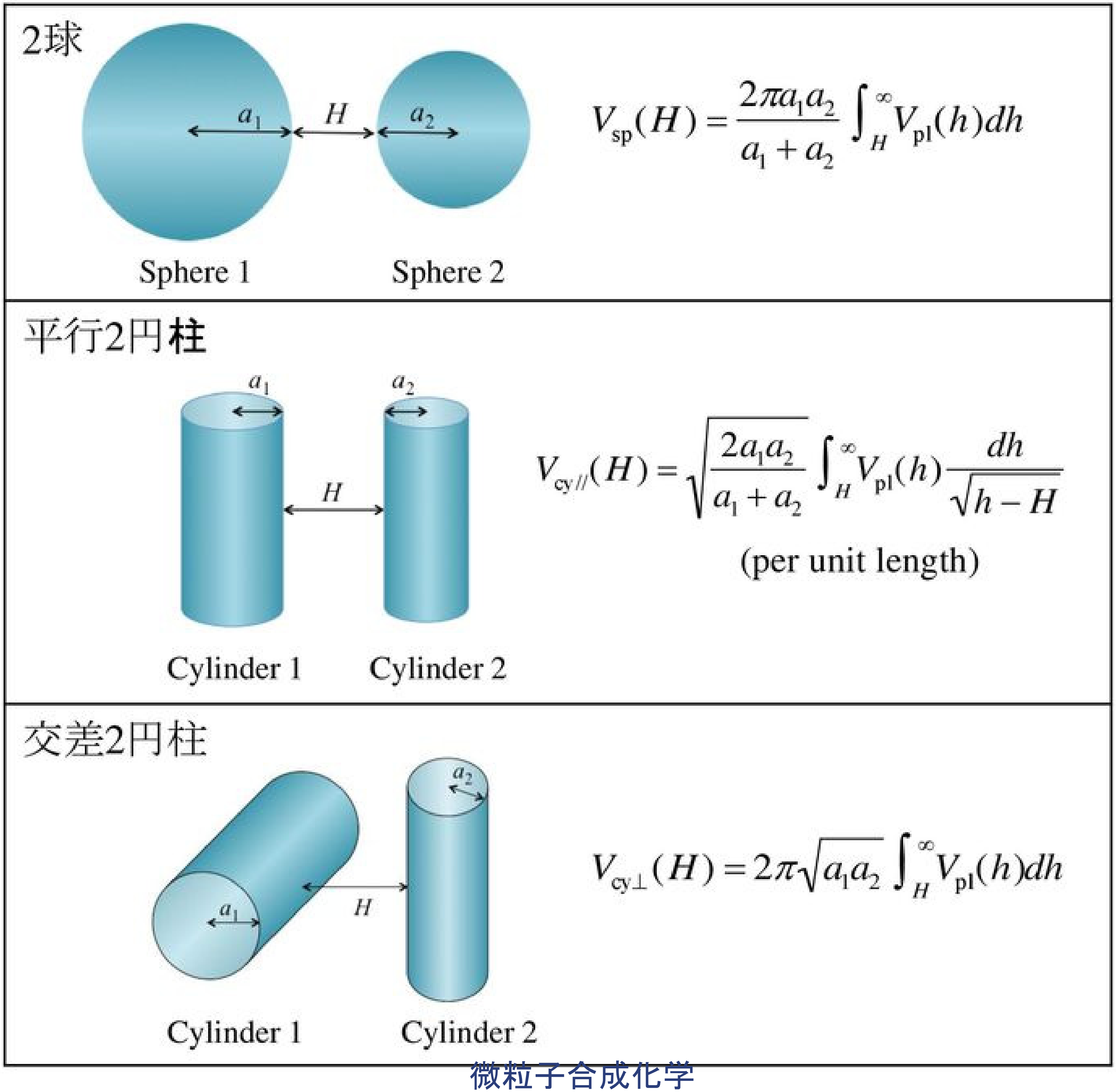
$$\boxed{V_R(h) = -\int_{\infty}^{h} P_R(h)\,dh = \frac{64nkT}{\kappa}\gamma^2 \exp(-\kappa h)} \qquad (21)$$

Next, consider the interaction between spherical particles



Next, let us consider the interaction between spherical particles.

Derjaguin approximation



2球

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

平行2円柱

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

(per unit length)

交差2円柱

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

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:

$(H \ll a_1, a_2)$

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

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.

$$\begin{aligned} V_R(H) &= -\int_\infty^H P_R(H)\,dH \\ &= \frac{64\pi ankT}{\kappa^2}\gamma^2 \exp(-\kappa h) \qquad (24) \end{aligned}$$

Derivation of approximation formula.

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

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

($ze\psi_0 = 4kT$ then

$\psi_0 = 103$ mV at 25℃ 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.)

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

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

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

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

Using Eq. (13),

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

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

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

Aggregation

van der Waals Interaction

van der Waals force and energy are

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

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

A is Hamaker constant.

The total energy is given below.

$$P_T(H) = \frac{2\pi a\sigma^2}{\kappa\varepsilon_r\varepsilon_0}\exp(-\kappa H) - \frac{aA}{12H^2} \qquad (31)$$

$$V_T(H) = \frac{2\pi a\sigma^2}{\kappa^2\varepsilon_r\varepsilon_0}\exp(-\kappa H) - \frac{aA}{12H} \qquad (32)$$

Or

$$\boxed{V_T(H) = 2\pi a\varepsilon_r\varepsilon_0\psi_0{}^2\exp(-\kappa h) - \frac{aA}{12H}} \qquad (33)$$

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 .

$$\kappa^2 = \frac{2nz^2e^2}{\varepsilon_r\varepsilon_0 kT}$$

e elementary charge. $\varepsilon_r\varepsilon_0$ 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

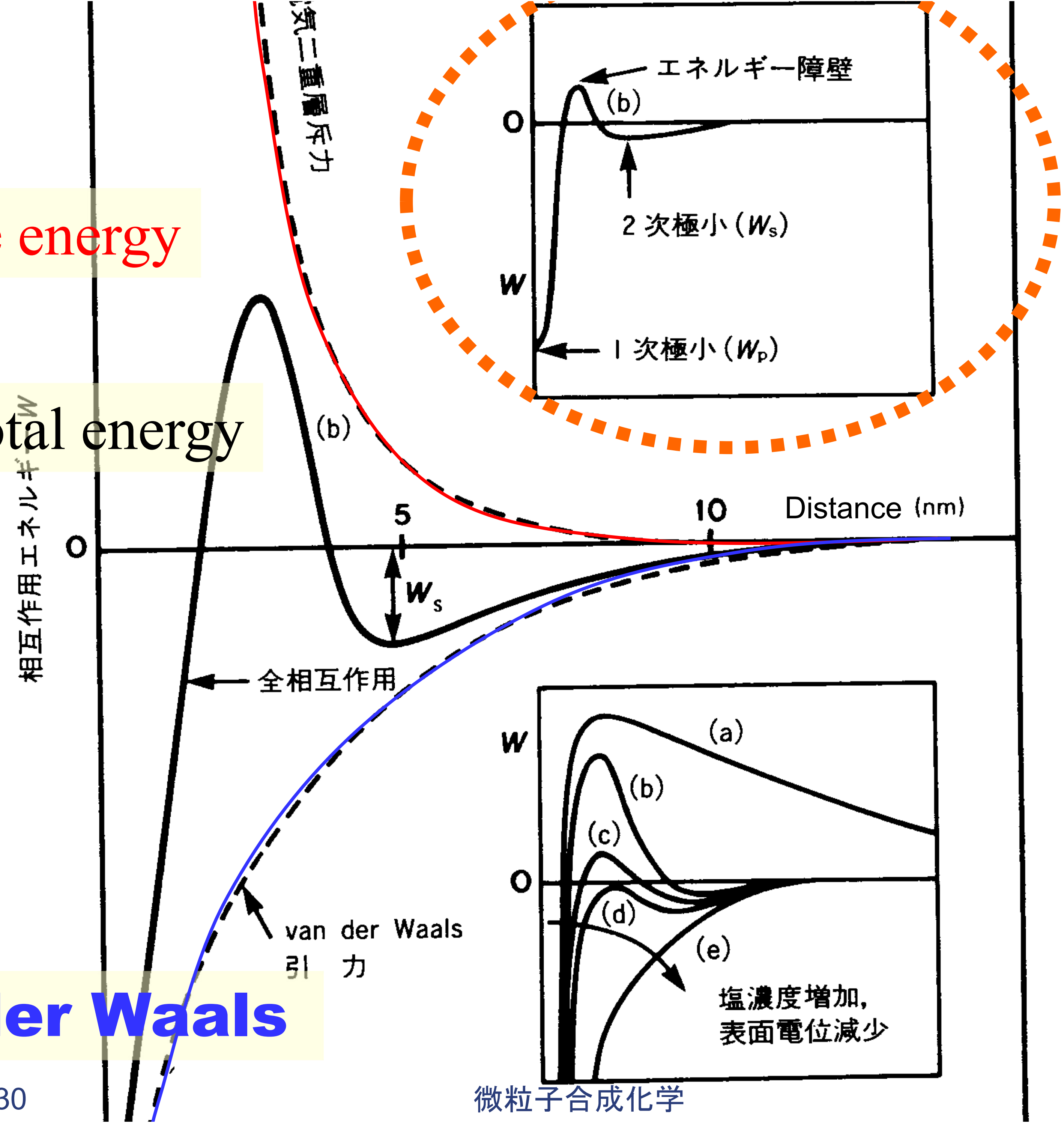
$\downarrow$

κ 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.

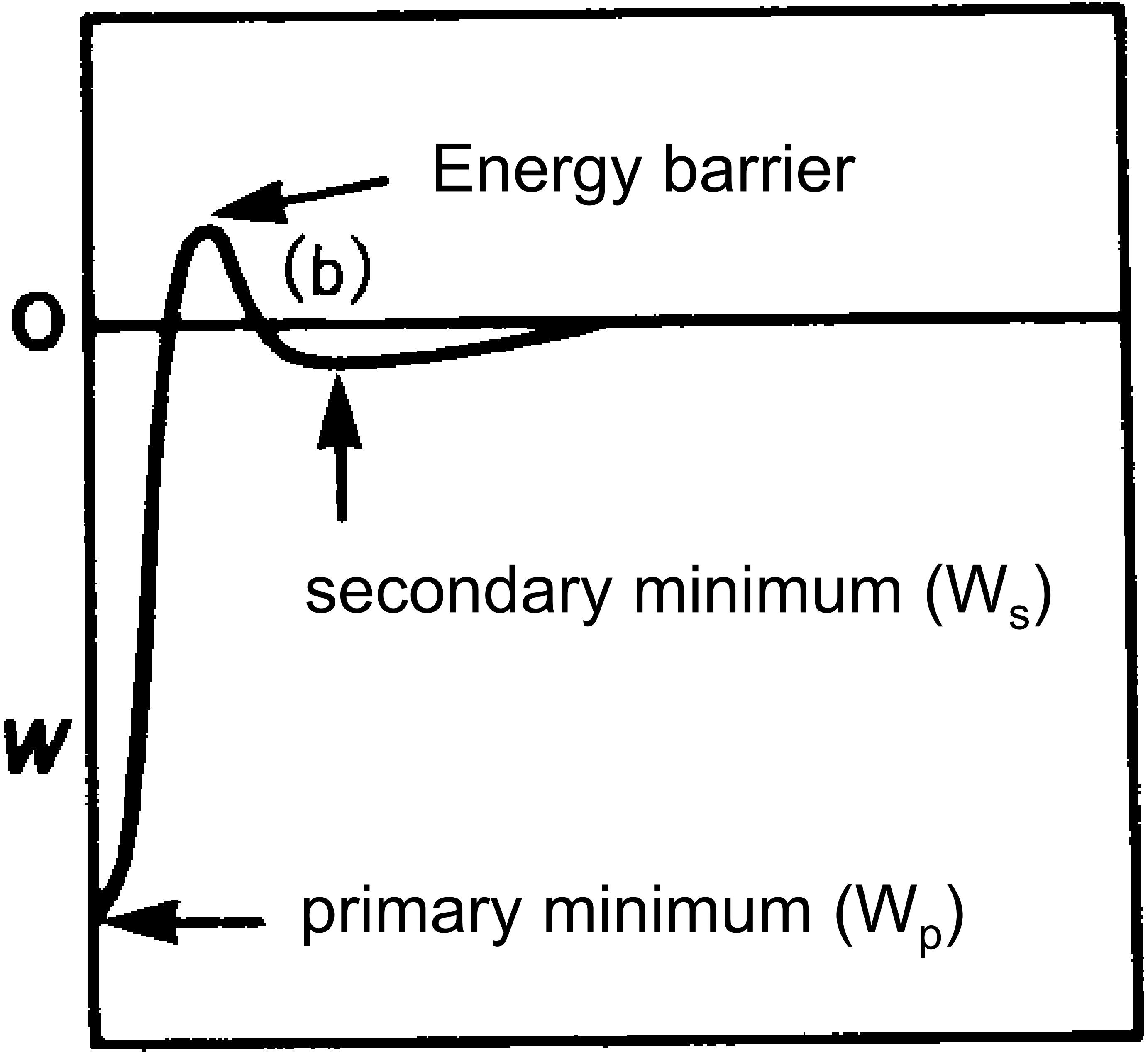
Schematic diagram of the energy versus distance profile of the DLVO interaction



Repulsive energy

Total energy

van der Waals

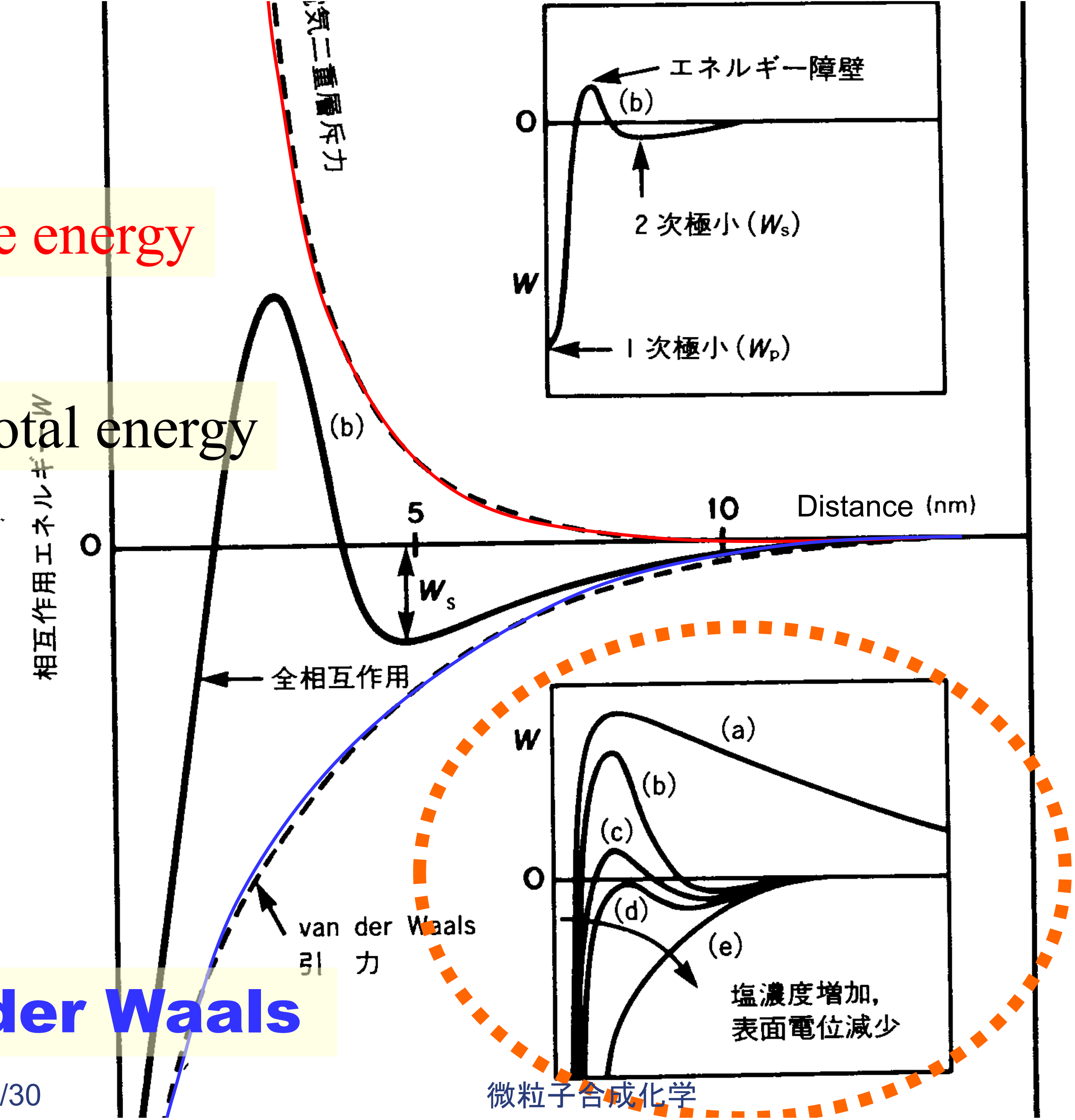


Energy barrier

secondary minimum (W_s)

primary minimum (W_p)

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

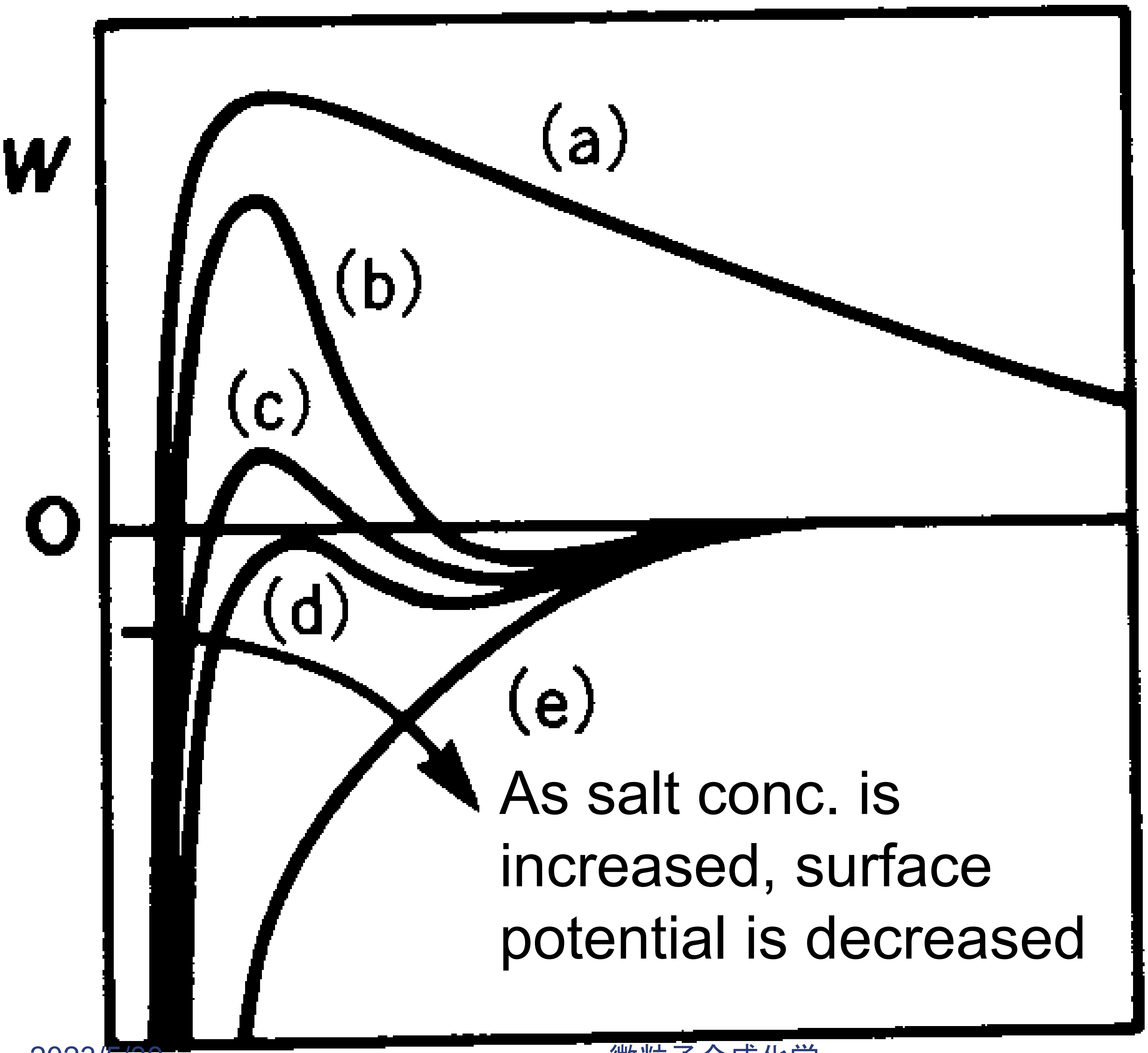


Repulsive energy

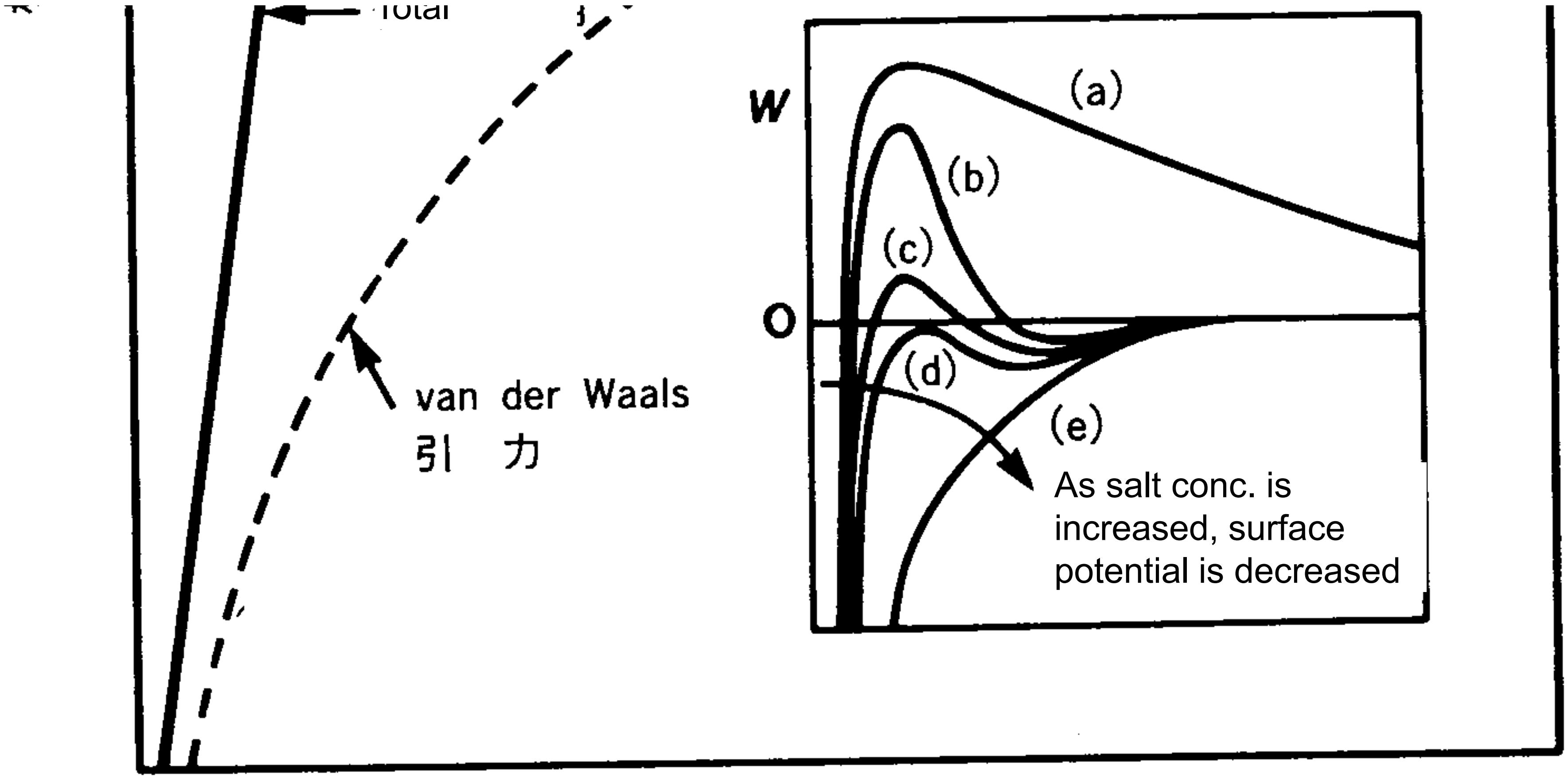
Total energy

van der Waals

als



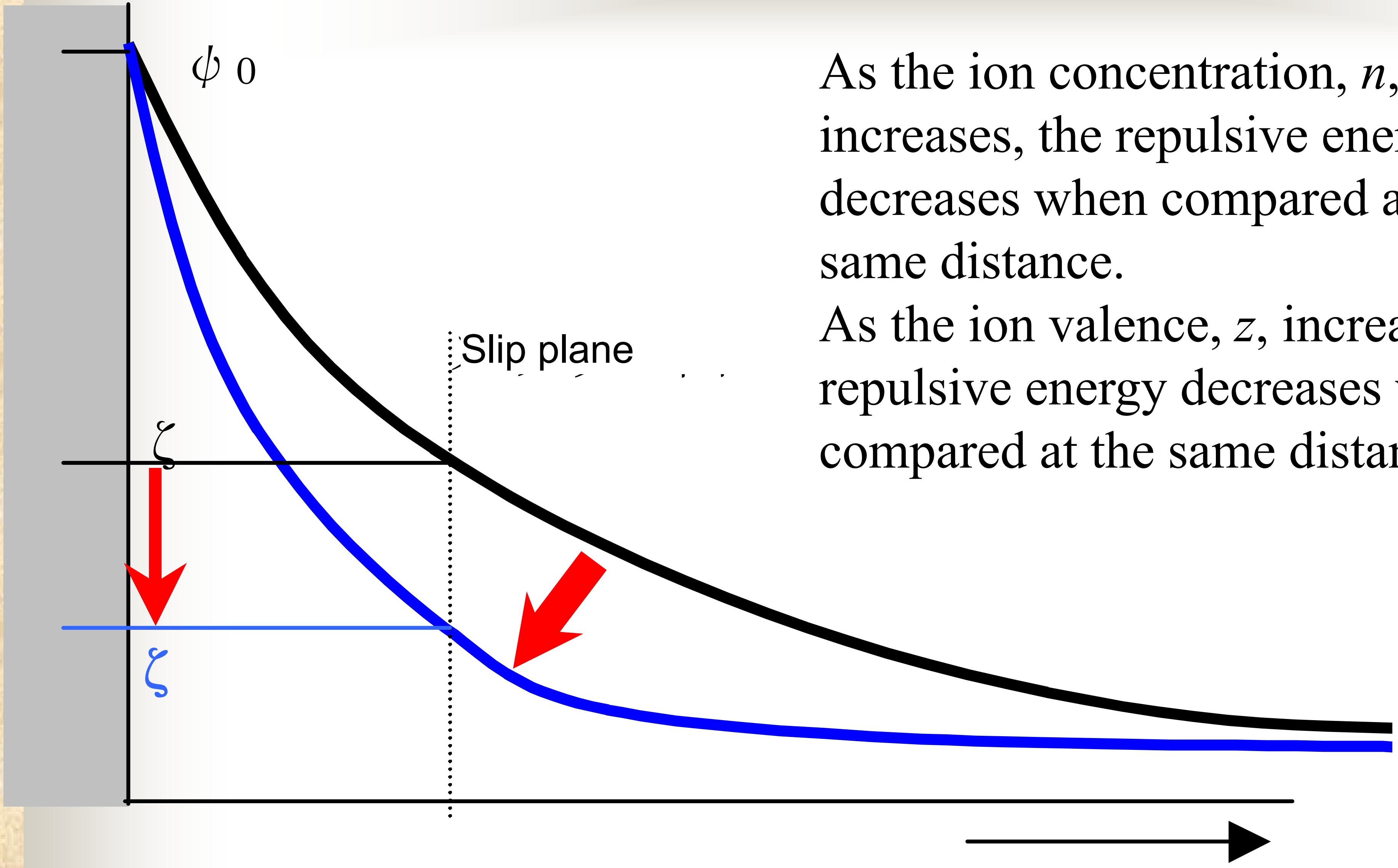
As salt conc. is increased, surface potential is decreased



As salt conc. is increased, surface potential is decreased

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.



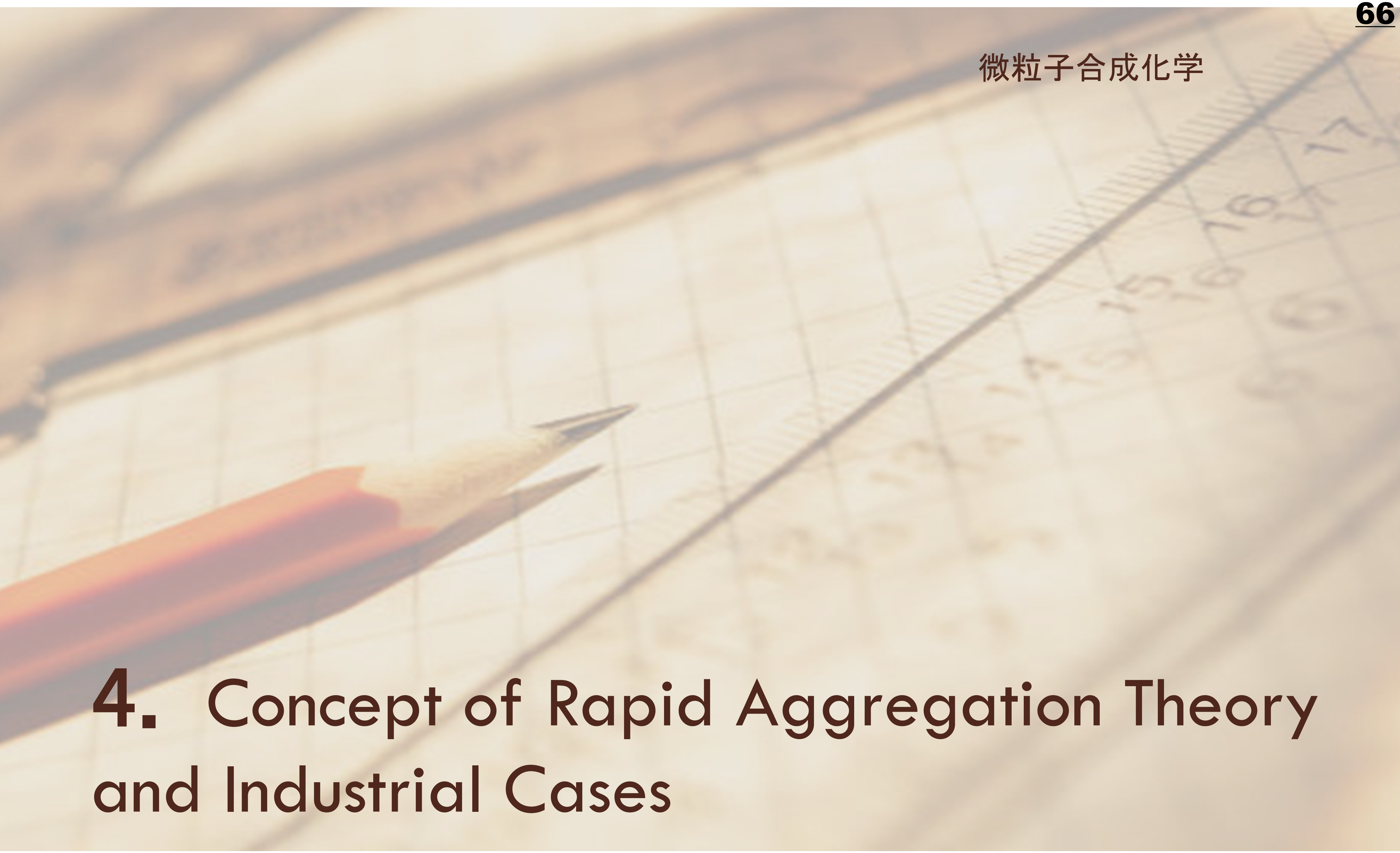
As the ion concentration, *n*, increases, the repulsive energy decreases when compared at the same distance.

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

ζ potential is decreased.

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

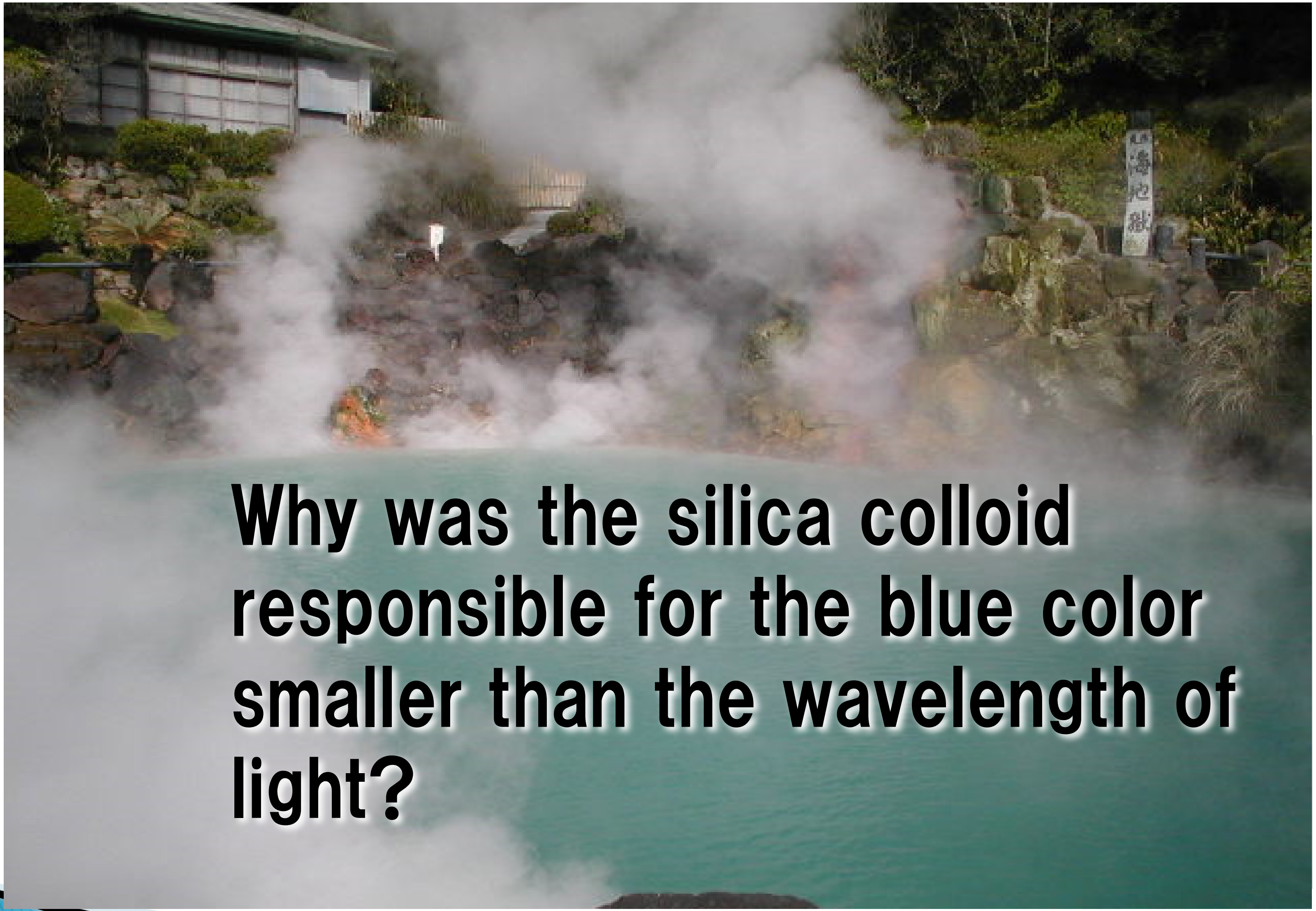
This phenomenon is proved by the DLVO theory.



4. Concept of Rapid Aggregation Theory and Industrial Cases

Use aggregation

Go back to Beppu sea hell



Why was the silica colloid responsible for the blue color smaller than the wavelength of light?

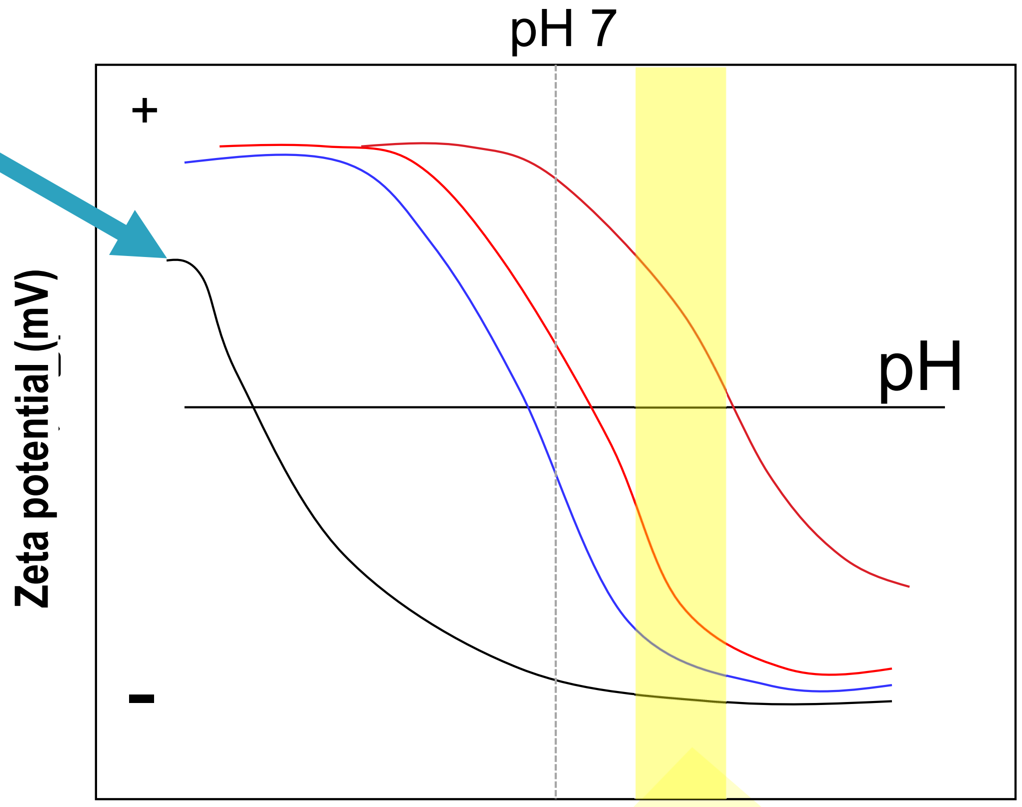
Why were the silica particles smaller than the wavelength?
That's because it didn't aggregate and was stably dispersed in water!

Isoelectric point of oxides

depending on crystal plane, structure, etc.

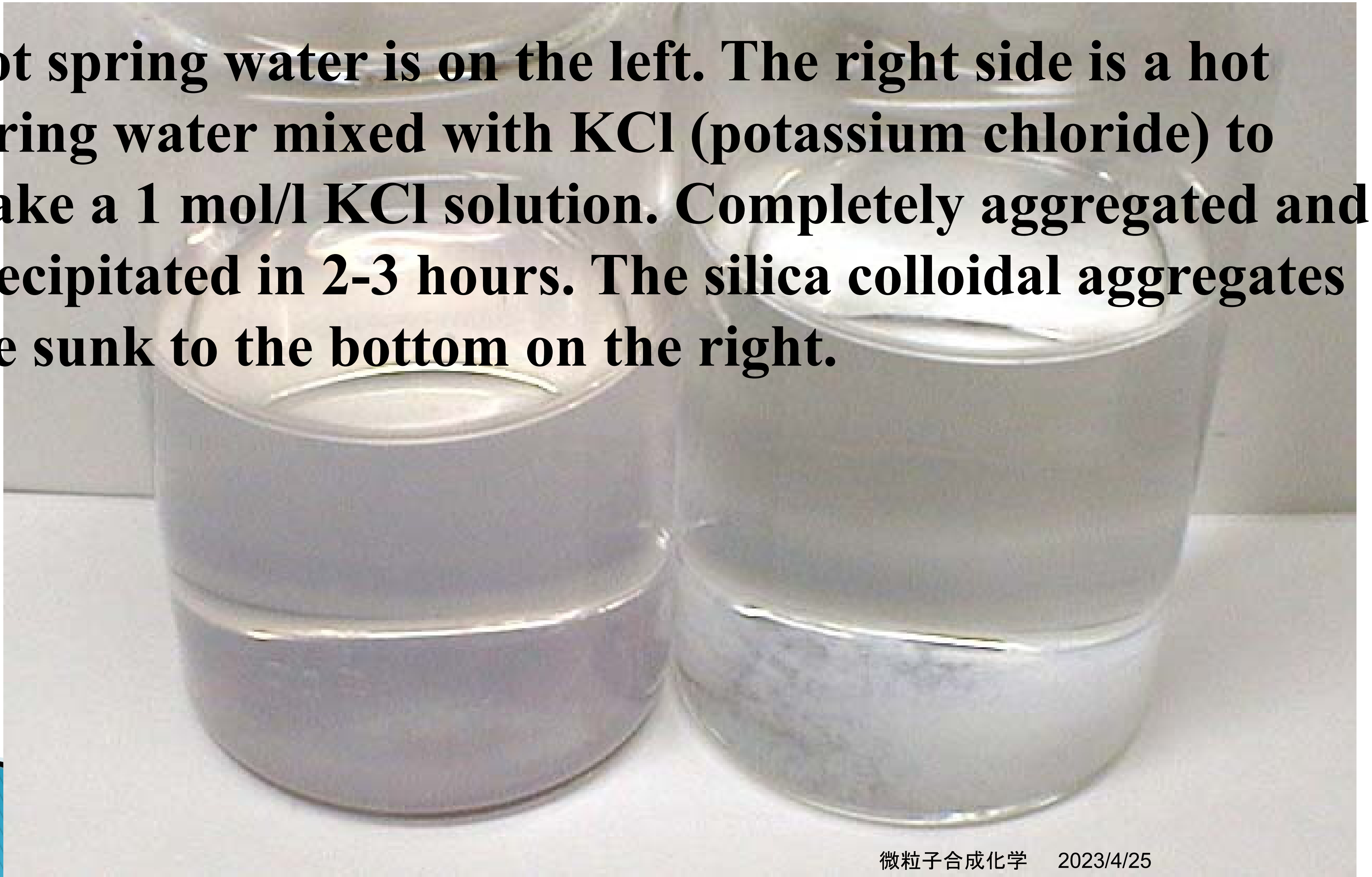
SiO_2	2～3
TiO_2	6～8
Fe_2O_3	6～8
ZrO_2	7～9
Al_2O_3	7～9
MgO	9～11

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



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!

嬉野温泉環境協会のWeb http://www.spa-u.net/shopping.html?cate=3

Ureshino specialty! Hot spring tofu

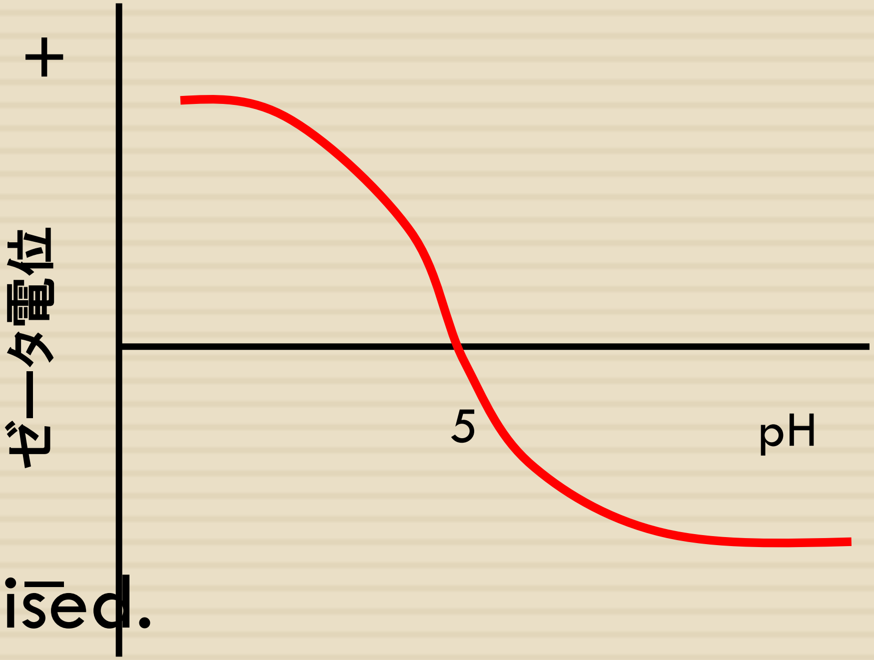
The secret of Ureshino Onsen tofu

- 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.

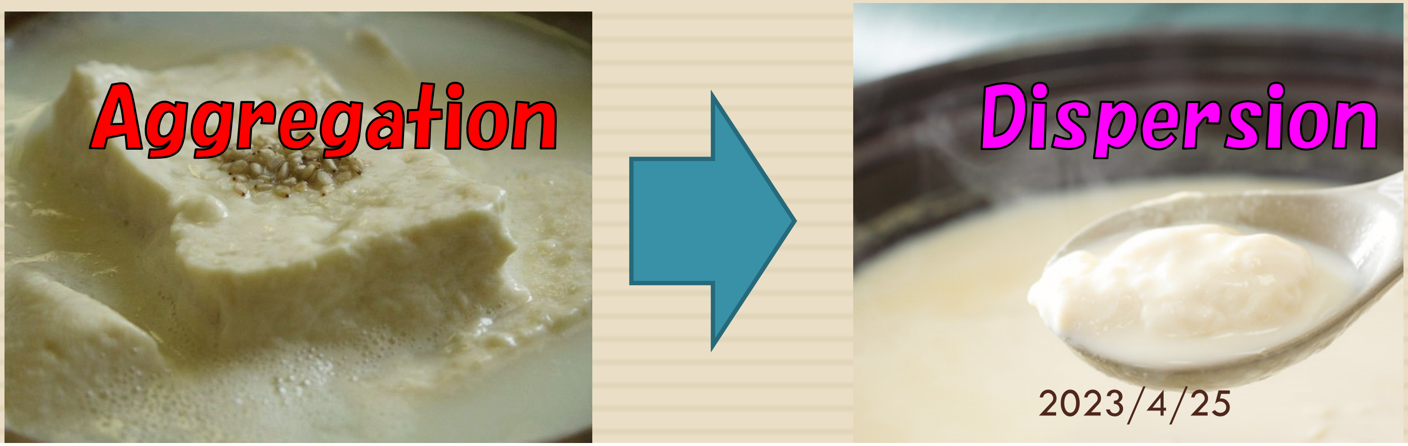
- The main ingredient of nigari, which is used to harden tofu, is magnesium chloride with a small amount of magnesium sulfate.
- Magnesium and calcium dissolve as divalent cations.
- The sulfate ion of magnesium sulfate is a divalent anion.
- In general, when substances aggregate, there is a certain 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.

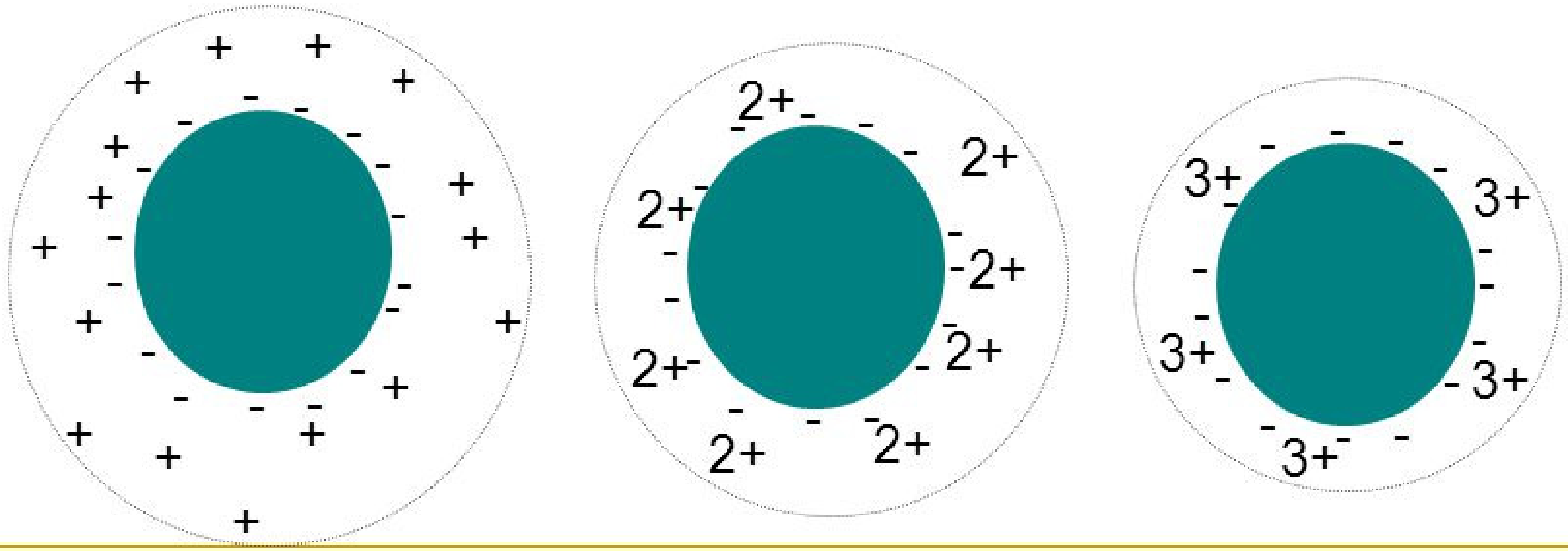
Ingredients of Ureshino Onsen

- 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 Cl, C2, and C3 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/Cl: 1/C2: 1/C3 = 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.

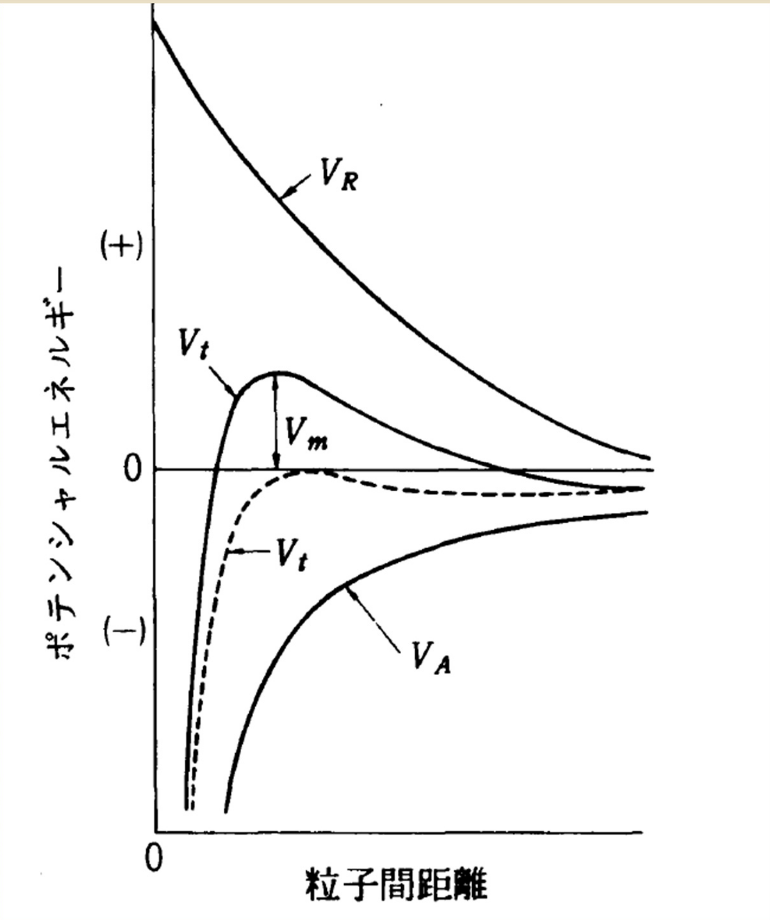
Schulze-Hardy rule

- 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 Vm appears in the figure.
- This is the critical coagulation Concentration (C_C), which is expressed by the following equation. .

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



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.

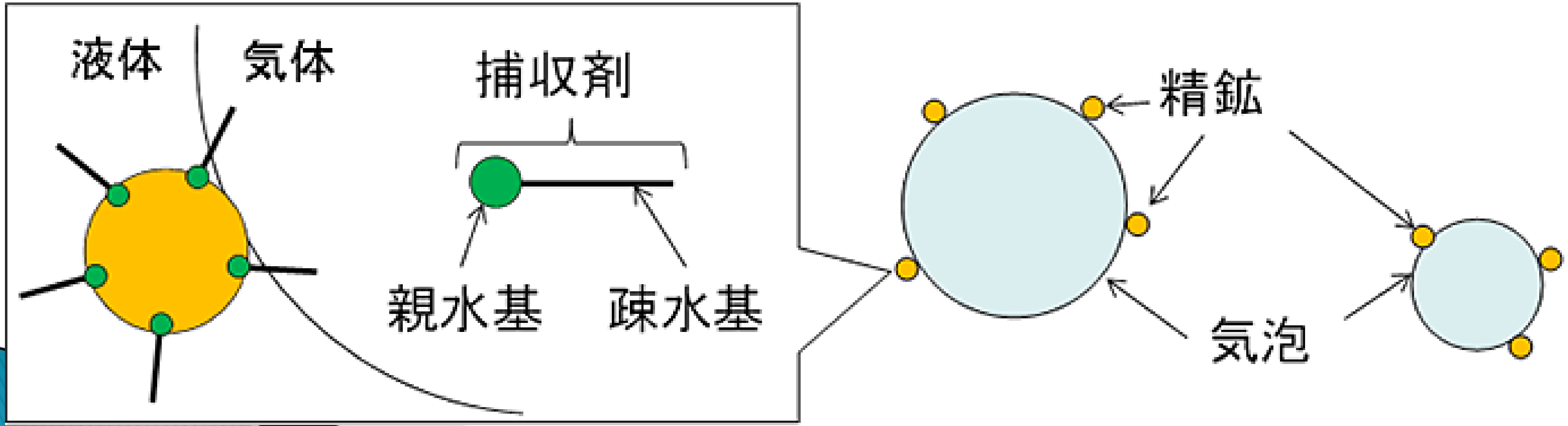
Sanuki Udon

The fabric is stable and does not sag too much.

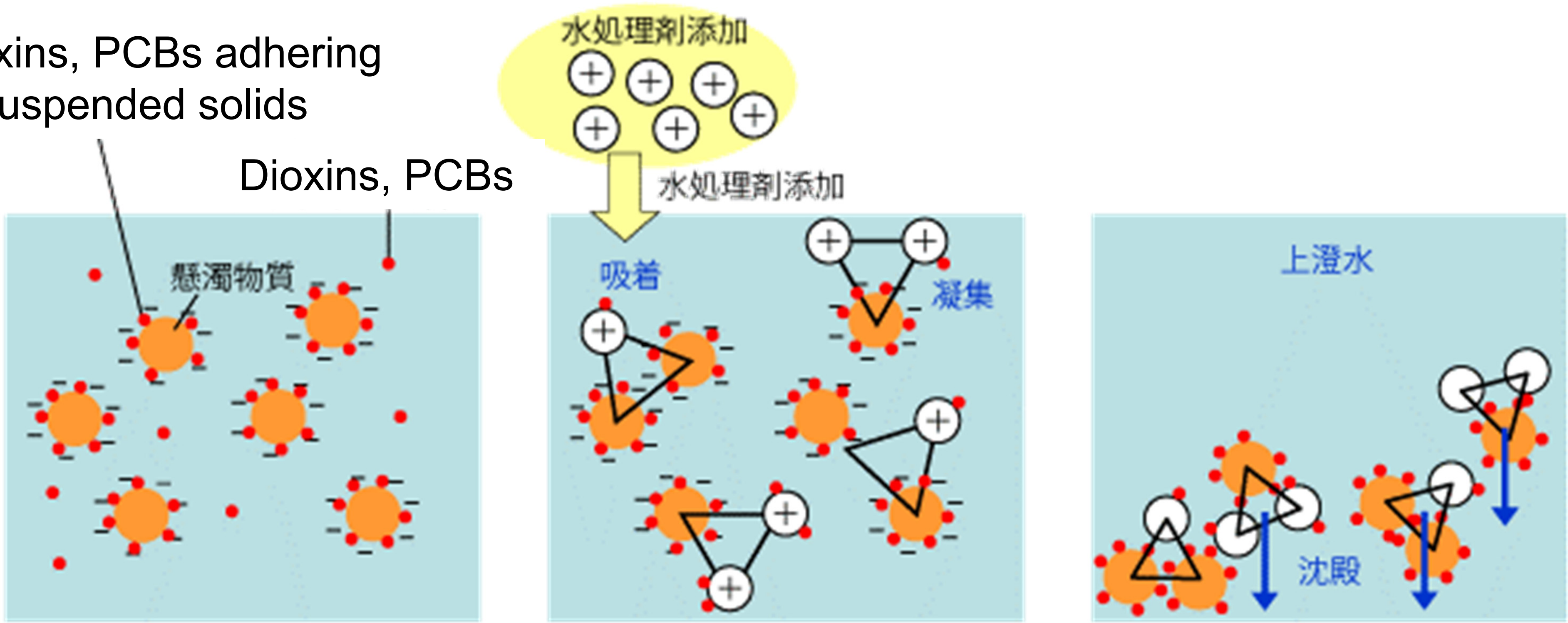
- Wheat flour can be kneaded in fresh water to form gluten, but salt water produces stronger gluten.
- This is called the astringent effect of salt, and it becomes the base of the udon noodles.
- The salt helps keep the dough from getting mushy if it's ripened for the right amount of time.

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

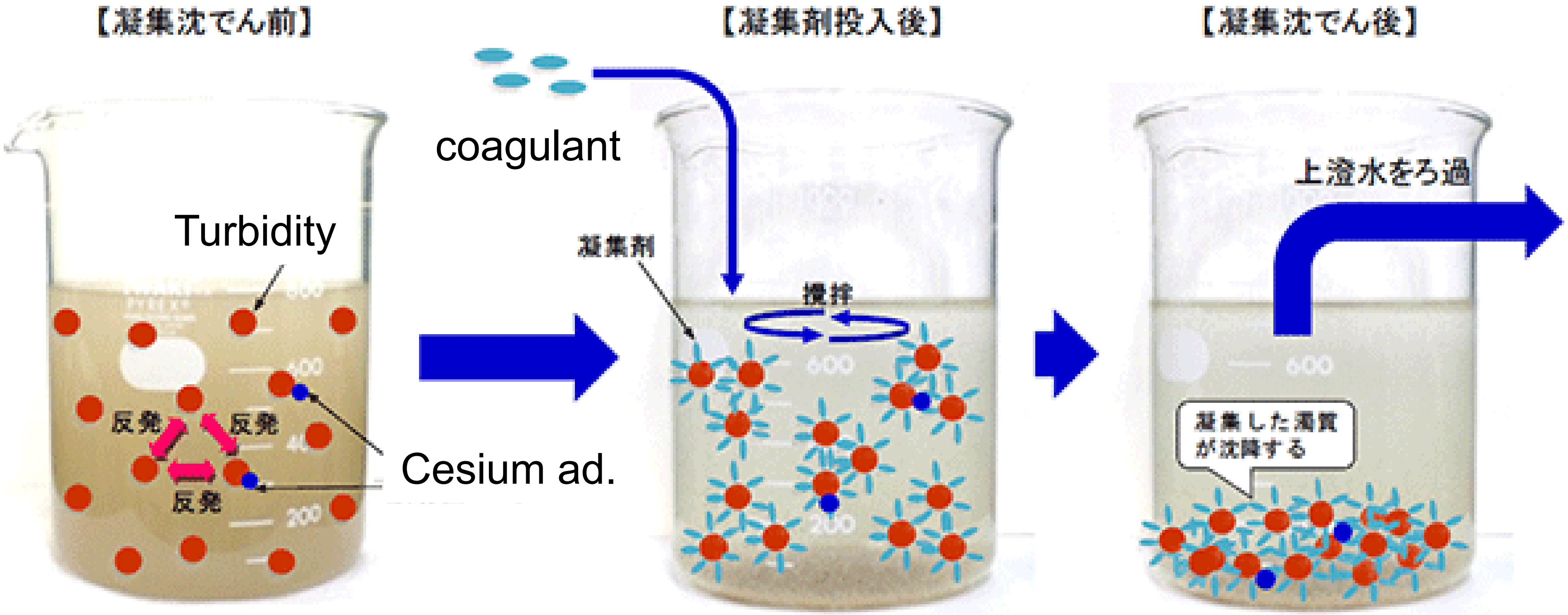
Dioxins, PCBs

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.

微粒子合成化学

Synthesis method of nanoparticles

2023/6/6

ITO nanoparticles, etc.

Nano world： What is “nano”？

1 m の 1/1000 → 1 mm

1 mm の 1/1000 → 1 μm

1 μm の 1/1000 → 1 nm

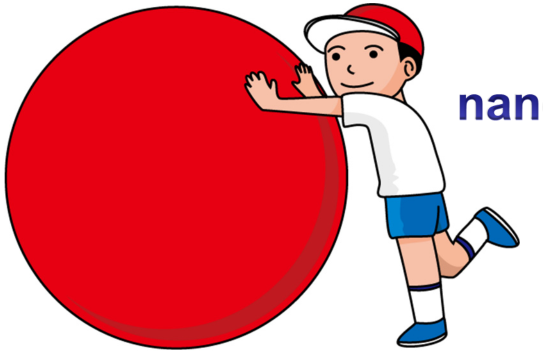
1 nm = 1/1,000,000,000 m (= 1/10^9 m) → billionth of a meter is 1 nm !!!

Earth 12,000 km = 12 x 10^9 mm

I want to see the marbles on the earth!

Observed at 10^9 times

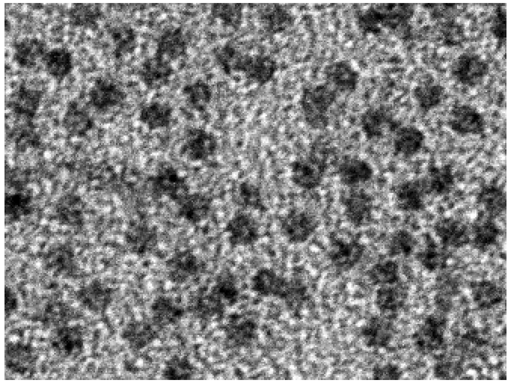
Marbles 12 mm



big ball rolling 1.5 m = 1.5 x 10^9 nm

I want to see the nanoparticles in Ootama!

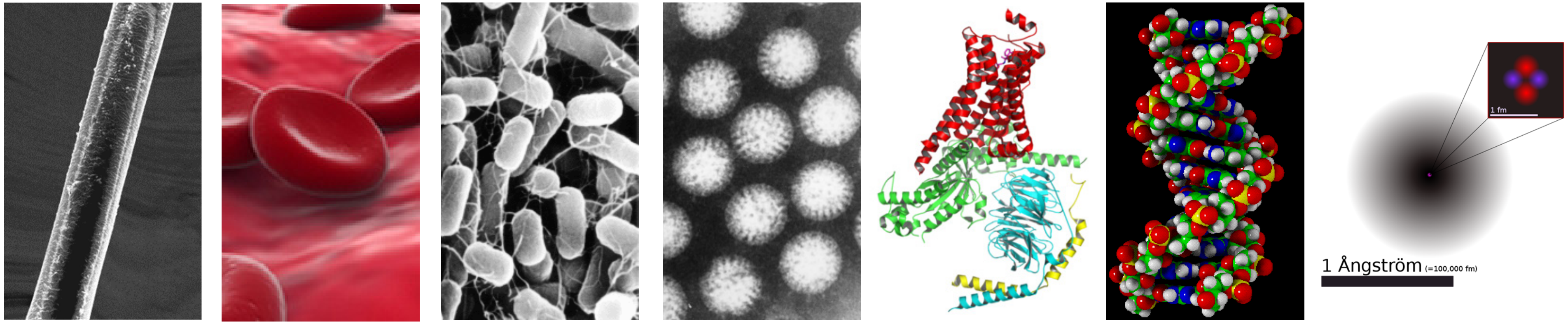
Observed at 10^9 times

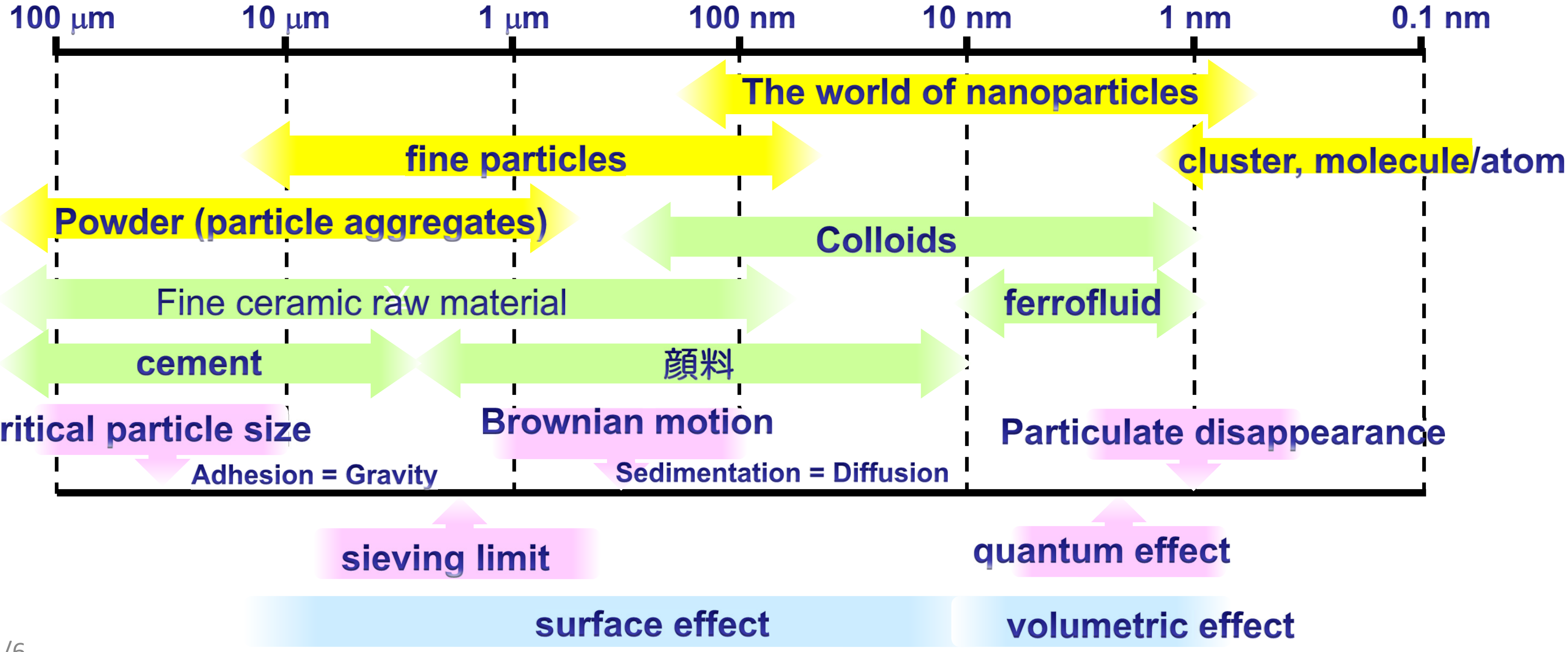


Nanoparticles 1.5 nm

The world of various sizes and the world of particles

hair | **red blood cell** | **Escherichia coli** | **virus** | **protein** | **DNA** | **He**





100 µm | **10 µm** | **1 µm** | **100 nm** | **10 nm** | **1 nm** | **0.1 nm**

The world of nanoparticles

fine particles

cluster, molecule/atom

Powder (particle aggregates)

Colloids

Fine ceramic raw material

ferrofluid

cement

顔料

critical particle size

Adhesion = Gravity

Brownian motion

Sedimentation = Diffusion

Particulate disappearance

sieving limit

quantum effect

surface effect

volumetric effect

What's monodispersed particles

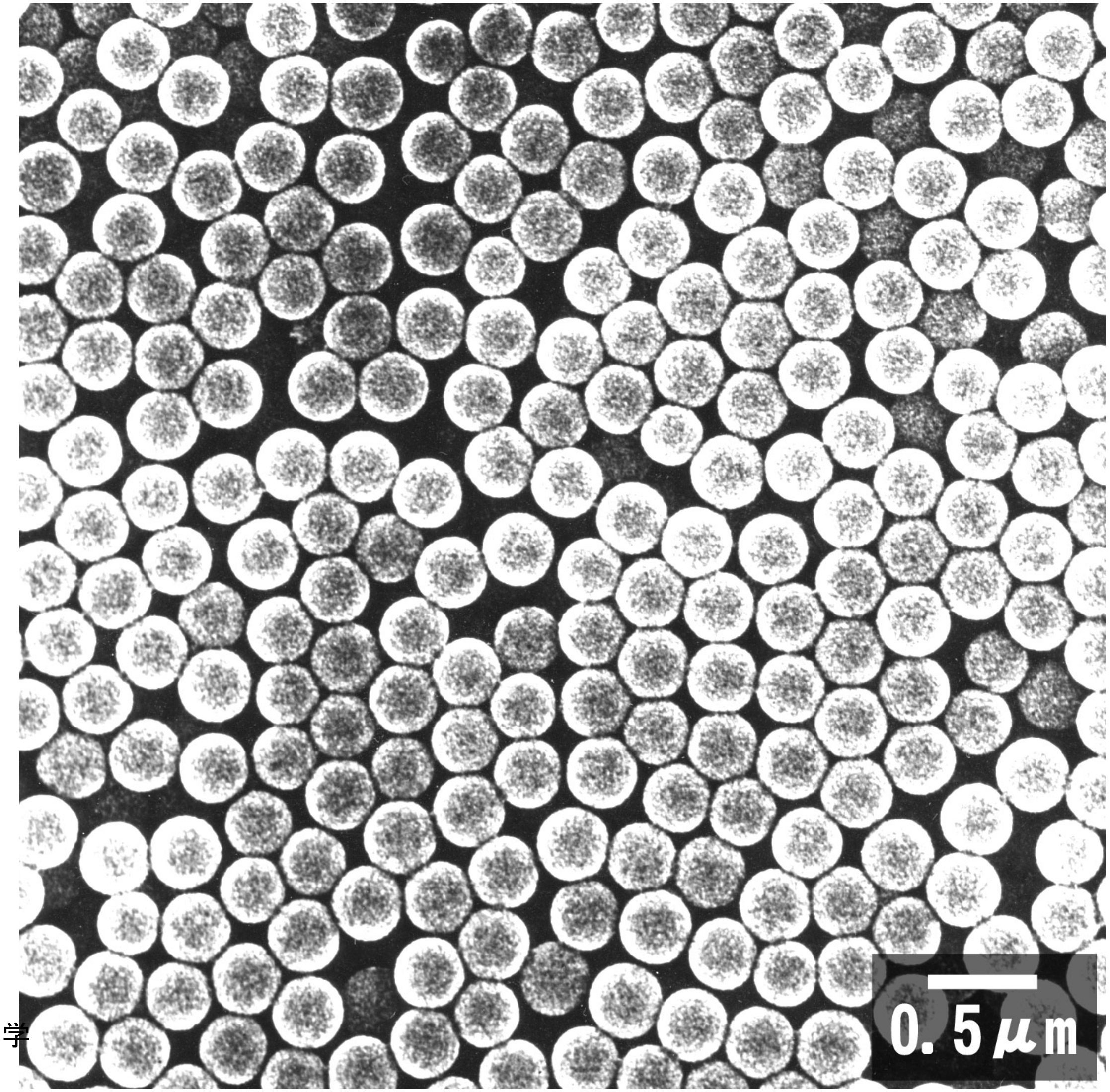
Monodispersed particles refer to a group of particles that are uniform in size, morphology, structure and composition.

In general, the standard deviation of size is within 10%.

Since monodisperse particles have uniform properties as described above, they themselves can be used as functional materials. This is because the characteristics of each individual particle are reflected as they are, rather than being averaged over the whole.

For example, if iron oxide (α-Fe2O3) is not monodisperse particles, it is a bright red paint called red iron oxide. The size is about 1 μm, and if the shape is long, it will be yellowish, and if it is flat, it will be bright red.

Stöber Silica fine particles



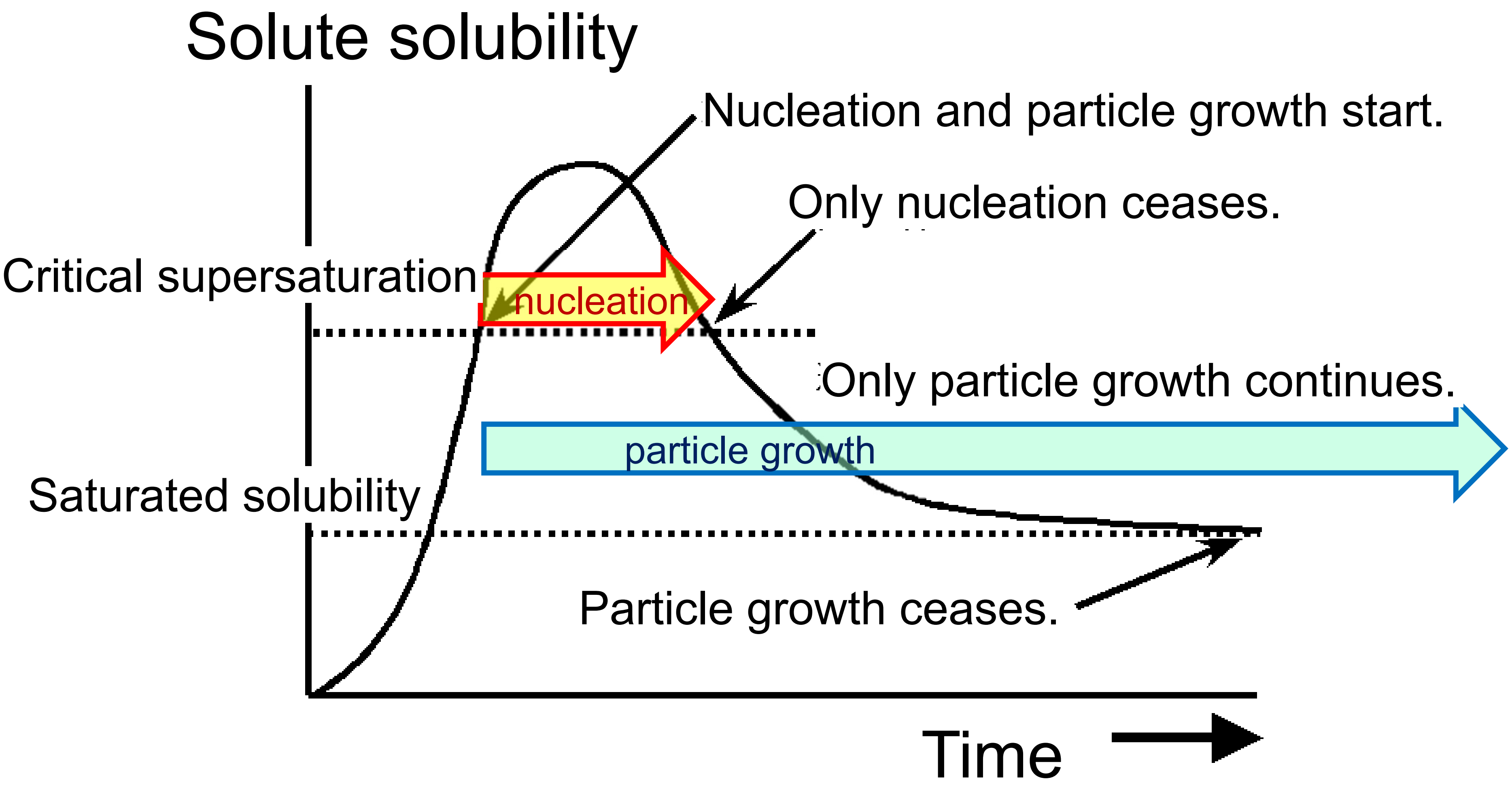
They are beautiful monodisperse particles and are widely used industrially.

General guidelines for monodisperse particle synthesis

1. Separation of nucleation and particle growth
2. Prevention of inter-particle coagulation
3. Storing particle precursors

(T. Sugimoto, Adv. Colloid Interface Sci. 28, 65 (1987).)

LaMer model - kinetics



"Separation of Nucleation and Grain Growth"
Nucleation and particle growth can apparently be separated by increasing the time difference between them.

Gibbs-Thomson effect

The Gibbs-Thomson effect on the particle size dependence of solubility is expressed by the following equation.

$$\ln(C_r/C_\infty) = 2\gamma V_M / (rRT)$$

where Cr is the equilibrium solute concentration for a particle of radius r, C∞ is the equilibrium solute concentration for an infinite plane (solubility), γ is the surface free energy (more precisely, the interfacial free energy at this solid/liquid interface), VM is the molar volume (volume of 1 mol of substance, ie molar mass/specific gravity), r is the particle radius, R is the gas constant, and T is the temperature.

Roughly speaking, it can be seen that the Gibbs-Thomson effect appears in fine particle systems of about 1 μm or less. At 1 nm, the value is extremely large. At this size, the application of macroscopic thermodynamics is problematic in itself.

Size of stable nuclei

Nucleation

Formation of embryo → Unstable nuclei

Stable nuclei are generated according to the uncertainty principle.

Size of stable nuclei depends on solubility.

A material with high solubility has a large stable nucleus size.

The stable nucleus size of materials with low solubility is small and may not grow.

Separation of nucleation and particle growth

Supersaturation control

- Dilute System or Reservoir
- The supersaturation required for homogeneous nucleation is usually greater than for heterogeneous nucleation

Control of nucleation period

- Remarkably shorten the nucleation period compared to the growth period, etc.

Growth speed control
~ 2 growth modes

Surface reaction controlled growth

- If the growth reaction on the particle surface is rate-determining, it grows in proportion to the 1/2 power of time
- Growth is slow in principle.

Diffusion controlled growth

- If diffusion is rate-limiting, it grows squarely with time. (parabola)
- In principle, it grows quickly.

Homogeneous nucleation

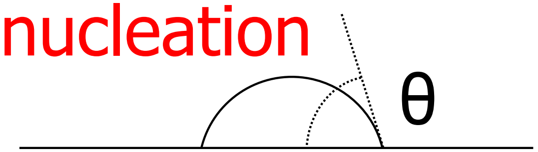
When n mol of solute precipitates in a solution and a crystalline phase (solid phase) with radius r is formed (homogeneous nucleation), the free energy change ΔG(n) is as follows.

$$\Delta G(n) = 4\pi r^2 \gamma - n\Delta\mu$$

γ is the liquid-solid interfacial energy, Δμ is the free energy per mol, and Δμ is the function of supersaturation. As supersaturation increases, Δμ also increases. Assuming that the precipitated crystal phase is spherical, the following can be written with v being the molar volume of the crystal phase.

$$\Delta G(n) = 4\pi r^2 \gamma - \left(4\pi r^3 \Delta\mu\right)/3v$$

Heterogeneous nucleation



If the wetting angle between the solute and the plane is θ, and the radius of curvature is r, the energy change ΔG'(r) associated with the precipitation is expressed as follows.

$$\Delta G'(r) = \left\{4\pi r^2 \gamma - \left(4\pi r^3 \Delta\mu\right)/3v\right\} \times f(\theta)$$

$$f(\theta) = \left\{(1 - \cos\theta)(2 - \cos\theta - \cos^2\theta)\right\}/4$$

$$\therefore 0 \le f(\theta) \le 1$$

Differentiate with respect to r and equal to 0. Here, the value of r that maximizes ΔG(r) is called the critical radius (critical radius of curvature) and is expressed as r*.

$$r^* = 2\gamma v / \Delta\mu$$

In other words, it is the size of the stable nucleus.

If the critical radius of curvature is r*, then the volumes of precipitation nuclei are as follows.

Homogeneous $(4\pi/3)\times(r^*)^3$

Heterogeneous $(4\pi/3)\times(r^*)^3\times f(\theta)$

The heterogeneous nucleus always has a smaller volume.

The formation rate, J, of homogeneous nucleation and heterogeneous nucleation is as follows.

$$J_{\mathrm{homo}} = N_A \exp\left(-\Delta G\left(r^*\right)/\mathrm{R}T\right)$$

$$J_{\mathrm{hetero}} = N_C \exp\left(-\Delta G'\left(r^*\right)/\mathrm{R}T\right)$$

The rate ratio of homogeneous and heterogeneous nucleation is as follows.

$$N_A \cong N_C$$

$$\therefore J_{\mathrm{homo}}/J_{\mathrm{hetero}} = \exp\left[-\Delta G\left(r^*\right)\left\{1-f(\theta)\right\}\right]/\mathrm{R}T$$

The ratio is always less than one. That is, heterogeneous nucleation is also kinetically advantageous.

Prevention of aggregation

Dilute system

- Aggregation is prevented by the electrostatic repulsive force of the electric double layer caused by lowering the salt concentration.

Protective colloids

- By adsorbing them on the particle surface.

Particle fixation

- Brownian motion is suppressed by immobilization on a gel network.

Storing monomers

Reserver

- Oxide particles：　Water is the reservoir for O in the oxide. Therefore, the release rate of metal ions should be controlled.
- Metallic particles：　Metals have very low solubility, so it is necessary to devise ways to grow them.

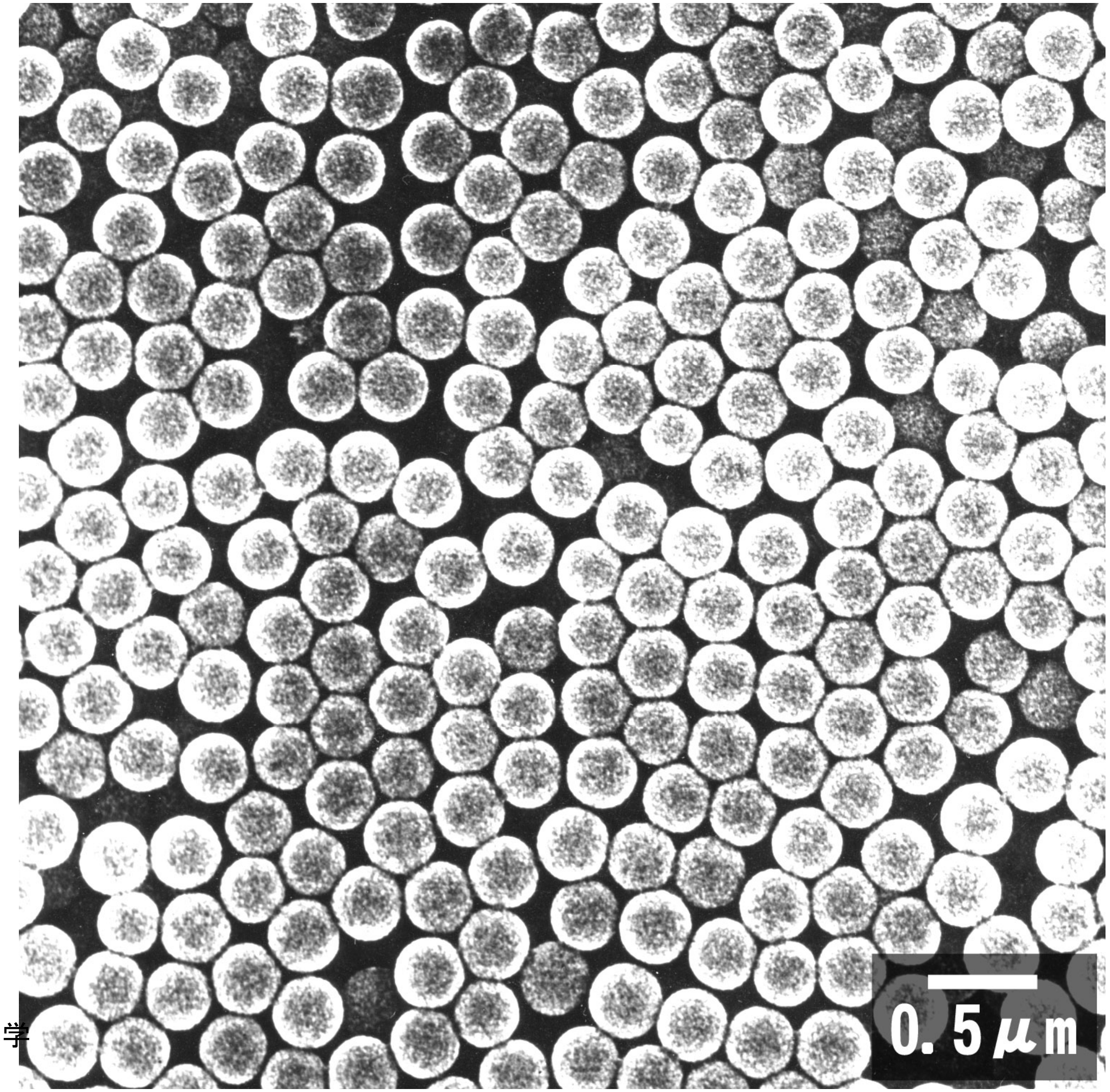
Addition from outside

- Like silver halide, the double jet method is used.

Synthesis methods of monodispersed fine particles

Sol-gel method, dilute system, etc.

Stöber silica



Synthesis conditions：

TEOS=Tetraethylorthosilicate, $Si(-O-C_2H_5)_4$ 0.1～0.5 mol/L

Solvent=ethanol

NH_3 as catalyst = 1～10 mol/L

H2O= 0.5～2.0 mol/L

0～30 ℃

Particles made by sol-gel method

TiO_2, ZrO_2, etc.

Since the temperature is low, many of them are amorphous immediately after preparation. Therefore, it may be subjected to high temperature treatment.

In the amorphous case, the particles are spherical.

SiO_2: W. Stöber, A. Fink, and E. Bohn: J. Colloid Interface Sci. 26, (1968) 62.
TiO_2: E.A. Barringer and H.K. Bowen: J. Am. Ceram. Soc. 67 (1984) C-113.
E. A. Barringer, N. Jubb, B. Fegley, Jr., R. L. Pober, and H. K. Bowen: in "Ultrastructure Processing of Ceramics, Glasses, and Composites," (L. L. Hench and D. R. Ulrich, Eds.), pp. 315-333. Wiley, New York, 1984.
B. Fegley, Jr., E. A. Barringer, and H. K. Bowen: J. Am. Ceram. Soc. 67, (1984) C-113.
ZrO_2: K. Uchiyama, T. Ogihara, T. Ikemoto, N. Mizutani, and M. Kato: J. Mater. Sci. 22, (1987) 4343.
T. Ogihara, N. Mizutani, and M. Kato: Ceram. Intern. 13, (1987) 35.
PZT: T. Ogihara, H. Kaneko, N. Mizutani, and M. Kato: J. Mater. Sci. Lett. 7, (1988) 867.
H. Hirashima, E. Onishi, and M. Nakagawa: J. Non- Cryst. Solids 121, (1990) 404.

Other methods

Dilute system

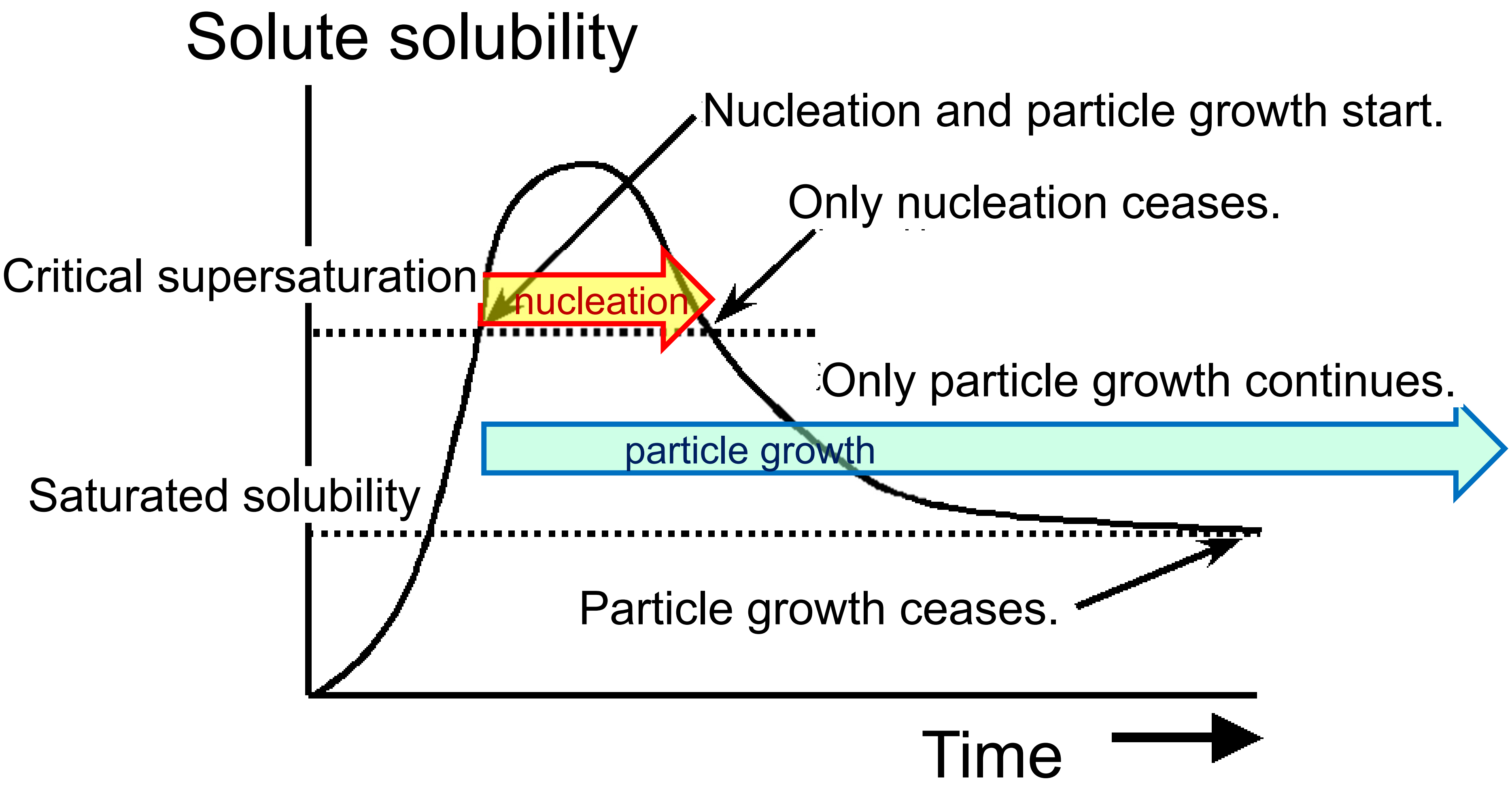
- Matijevic colloids, etc.

Polystyrene latex

- polymerization reaction
- emulsion
- There is a difference between using and not using a surfactant

Others

LaMer model - kinetics



Solute solubility

Nucleation and particle growth start.

Only nucleation ceases.

Critical supersaturation

nucleation

Only particle growth continues.

particle growth

Saturated solubility

Particle growth ceases.

Time

"Separation of Nucleation and Grain Growth"

Nucleation and particle growth can apparently be separated by increasing the time difference between them.

Gel-sol method

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PROF. SUGIMOTO, ETC.

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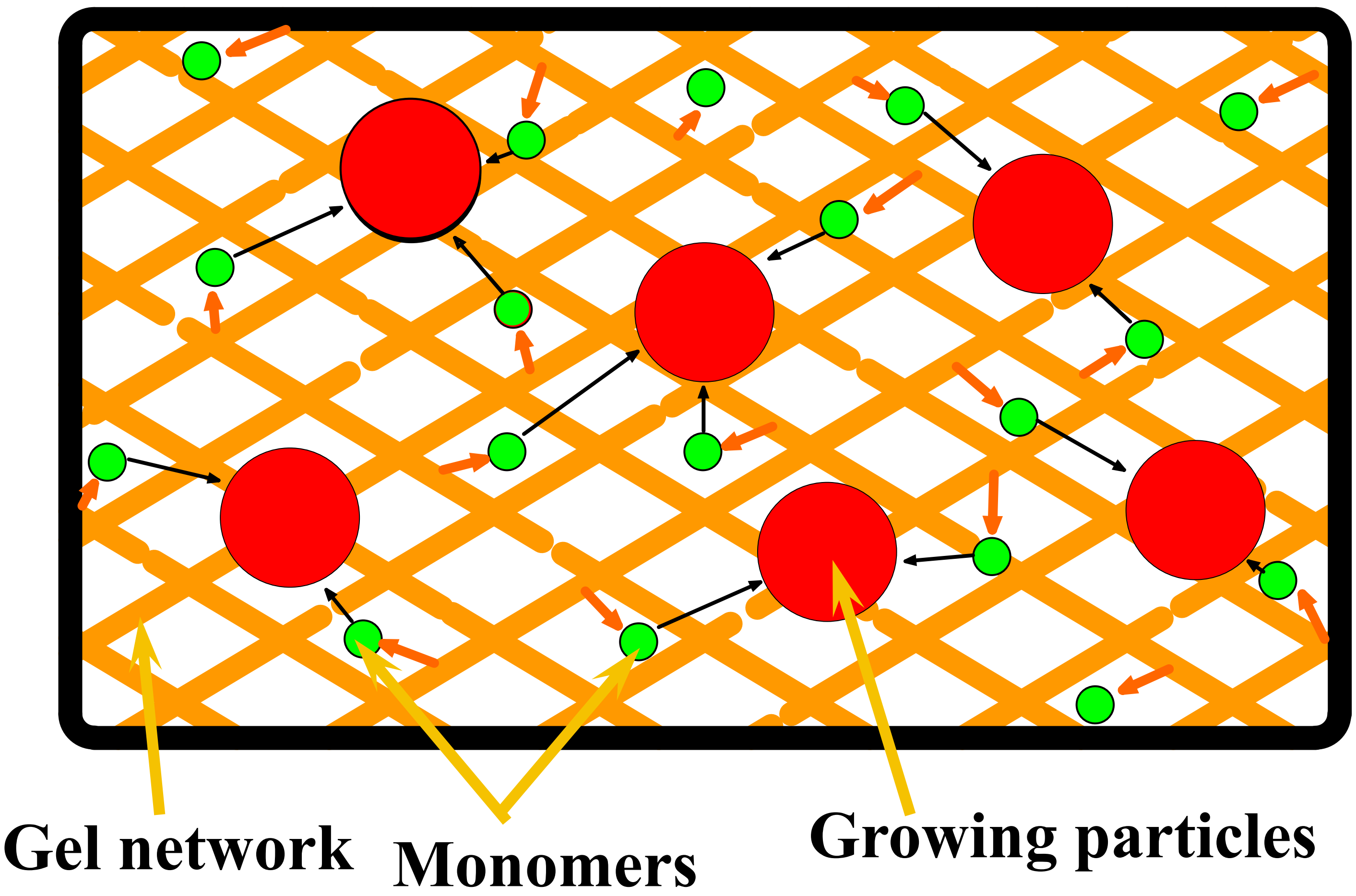
微粒子合成化学

Aggregation prevention mechanism



Hematite (α-Fe2O3) particles are immobilized in the gel network.

Gel network of β-FeOOH (intermediate product)

For example, in the synthesis of hematite (α-Fe2O3) particles, a dense amorphous iron hydroxide gel is used as a precursor solid, and the phase transition occurs in two steps: amorphous iron hydroxide → hydrated iron oxide (akaganite) → hematite. do. In this case, the intermediate product, iron oxide hydrate, serves as a reservoir for the hematite precursor and has an effect of suppressing aggregation. In addition, the control of the shape of hematite is achieved by the coexistence of adsorptive ions such as sulfate groups and phosphate groups.

Choice of reservoir

Solute is supplied during grain growth.

Choose a solid or complex with sufficiently low solubility or release rate.

Ingenuity to prevent aggregation

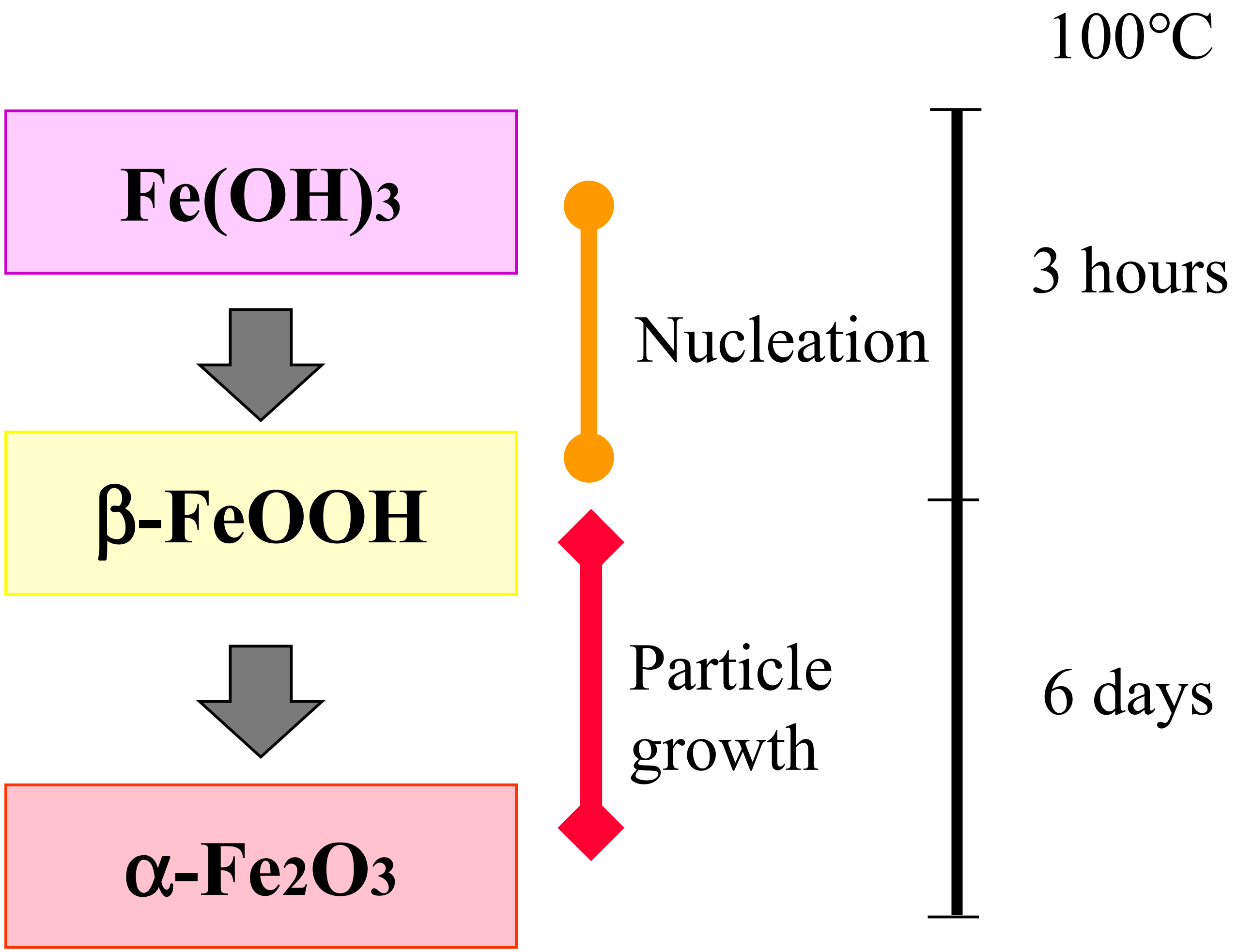
Use of gel network

Addition of aggregation reducing agent

- Addition of protective colloids such as gelatin one solution：

Gel-sol method

Preparation of monodisperse hematite particles



100°C

$Fe(OH)_3$

β-FeOOH

α-Fe_2O_3

Nucleation

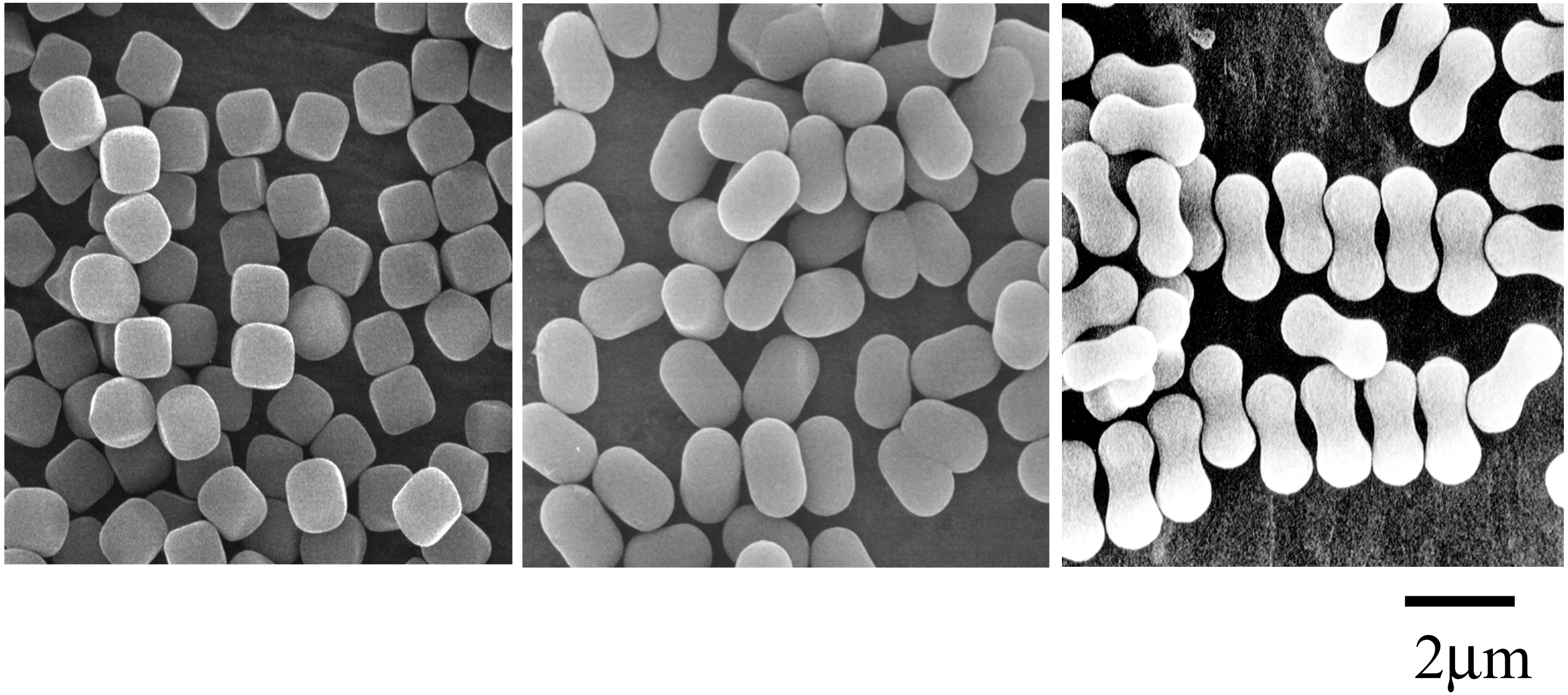
3 hours

Particle growth

6 days

By Gel-sol method

Synthesis of monodisperse hematite particles



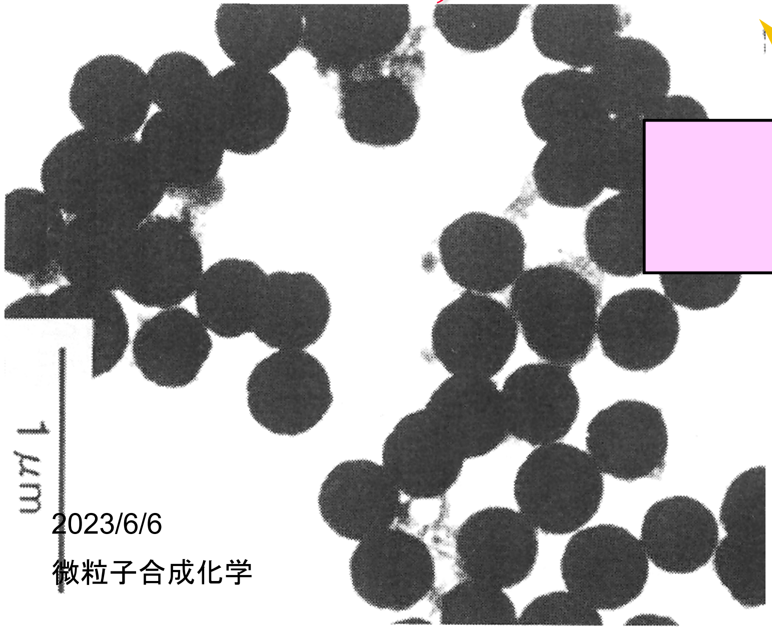
Synthesis of Uniform Metallic Nickel Particles from Concentrated Nickel Hydroxide Suspension

Ni(OH)$_2$ suspension
With PEG

NaH$_2$PO$_2$ addition

50°C, 12 hours

Ni



- 0.1 M Ni(OH)$_2$ + 4 M NaH$_2$PO$_2$
- 0.5 wt% PEG（400,000）

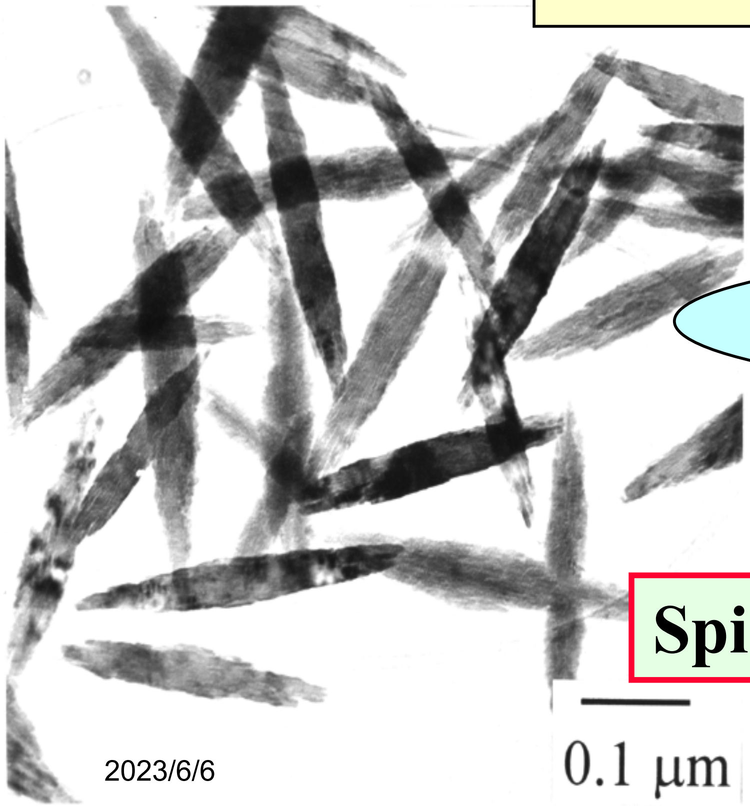
Synthesis of spindle-shaped uniform titania particles by gel-sol method

Titanium isopropoxide: 0.5 M
Triethanolamine: 1.0 M
（inhibitor to rapid hydrolysis）

⇦ 2M NH3 aq.

Highly viscous gel-like substance

Spindle type uniform titania particles



①

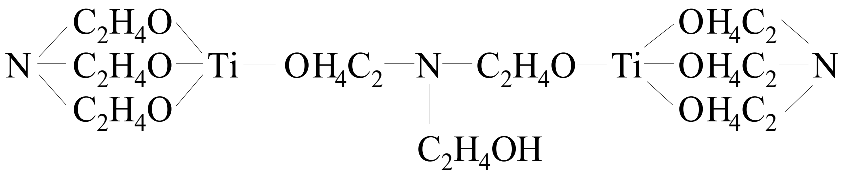
Gel-Sol process

Titanium(IV) isopropoxide (TIPO) [$Ti(OC_3H_7)_4$]

↓ ← Triethanolamine (TEOA) [$N(C_2H_4OH)_3$]

TIPO:TEOA = 1:2
($[TIPO]_0 = 0.25\ mol\ dm^{-3}$)

Stable complex



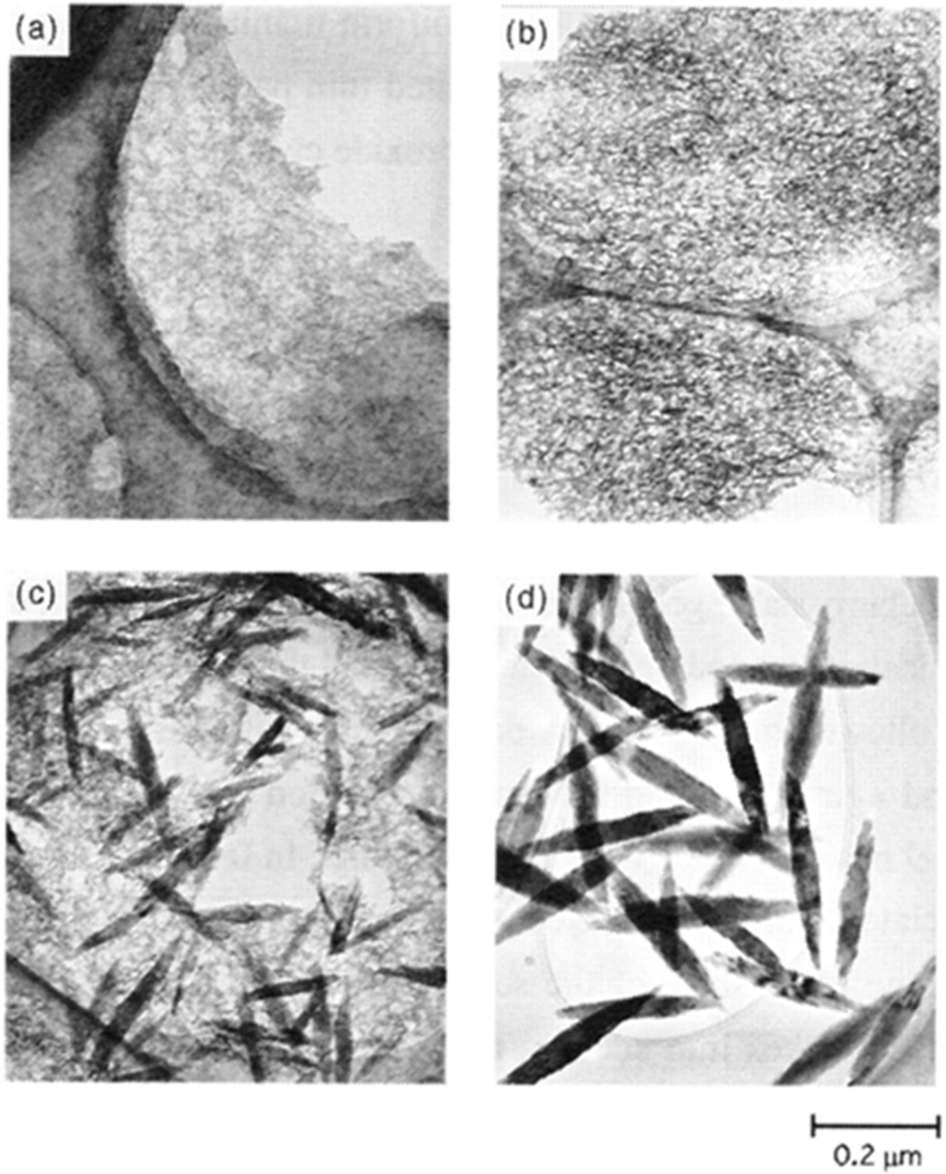
↓ ← H_2O (+$HClO_4$ or + NaOH)

1st aging (100℃, 1 day)

$Ti(OH)_4$ gel

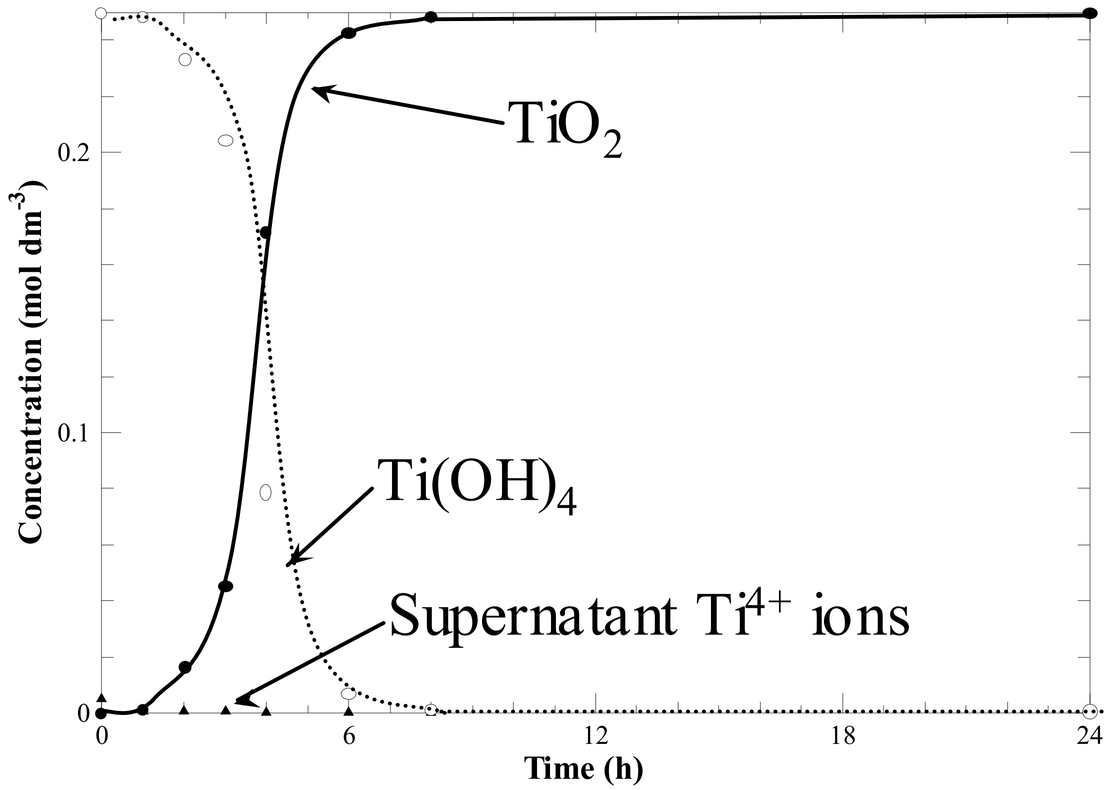
2nd aging (140℃, 3 days)

TiO_2 (anatase) → Pt deposition → Photocatalyst



Time evolution in titania particle synthesis
(a) 0, (b) 1 day, (c) 2 days, and (d) 3 days

② Concentration changes of TiO_2, $Ti(OH)_4$, and supernatant Ti^{4+} ions during the 2nd aging (pH = 10)



Phase transformation: $Ti(OH)_4 \longrightarrow TiO_2$

Monodispersed metal sulfide particles

Reservoir of M^{2+}

Reservoir of S^{2-}

**Cd(OH)$_2$
or
Metal
chelates**

$$\mathrm{Cd(OH)_2 \text{ or Metal chelates}} \Rightarrow \boxed{M(NH_3)_n^{2+}} \rightleftharpoons M^{2+} + S^{2-} \leftleftarrows\!\!\!\rightarrow \boxed{TAA}$$

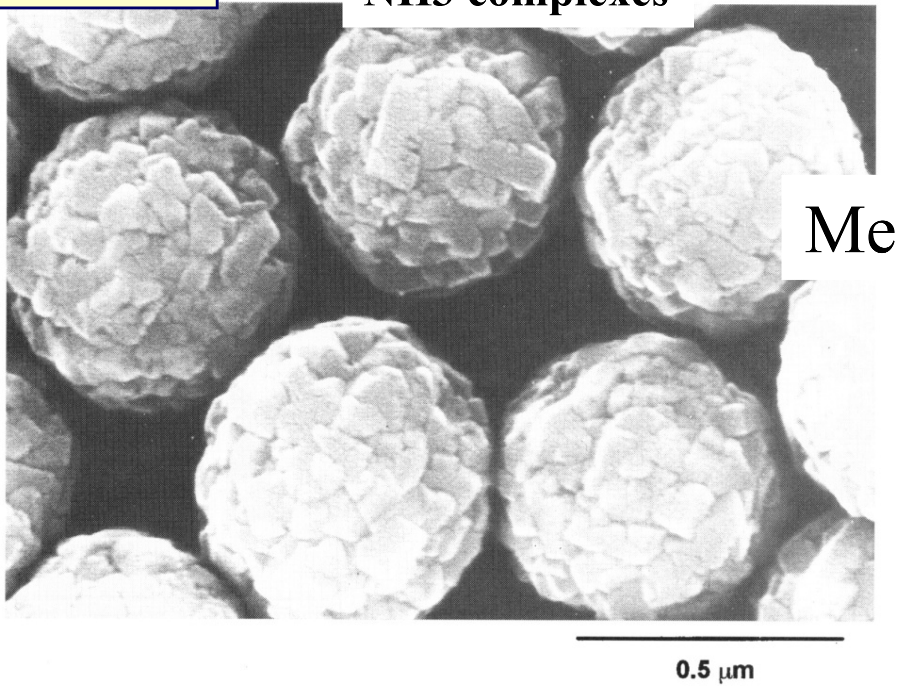
$$M(NH_3)_n^{2+} \rightleftharpoons M^{2+} + S^{2-} \rightleftharpoons TAA$$

NH3 complexes

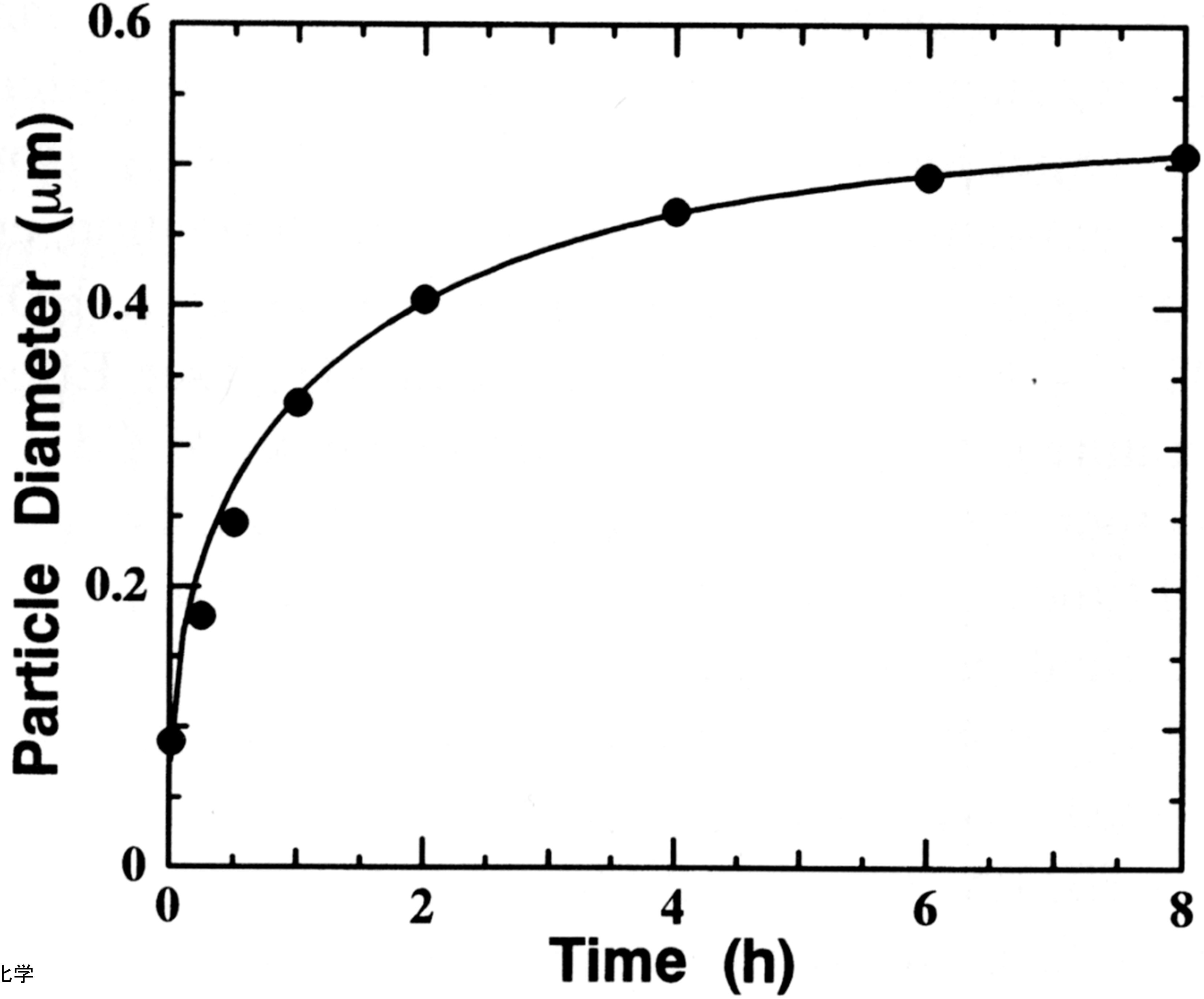
Thioacetamide

Gelatin

Metal sulfides



M=Cd, Zn, Pb etc.


0.6
0.4
0.2
0
Particle Diameter (μm)
0
2
4
6
8
Time (h)

BaTiO$_3$, SrTiO$_3$

Synthesis of perovskite oxides

Direct synthesis from the liquid phase is possible using the gel-sol method.

Commercial products are made by solid phase reaction.

Synthesis method of $BaTiO_3$/$SrTiO_3$ fine particles

gel-sol method

$Ti[OCH(CH_3)_2]_4$
$N(CH_2CH_2OH)_3$
(solution-A)

$Ba/Sr(OH)_2 \cdot 8H_2O$

← de-carbonated water →

Stock solution
(solution-B)

(solution-C)

↓

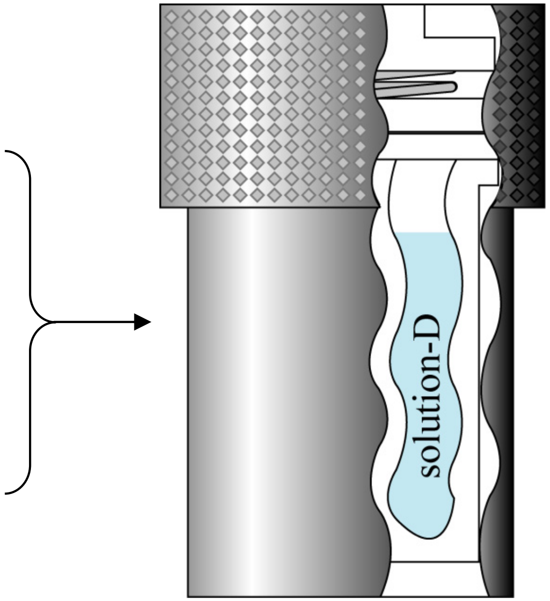
gel formation
stirring:10 min
aging: 1h
(solution-D)

↓

Aging (250 ℃ for 3 hours)

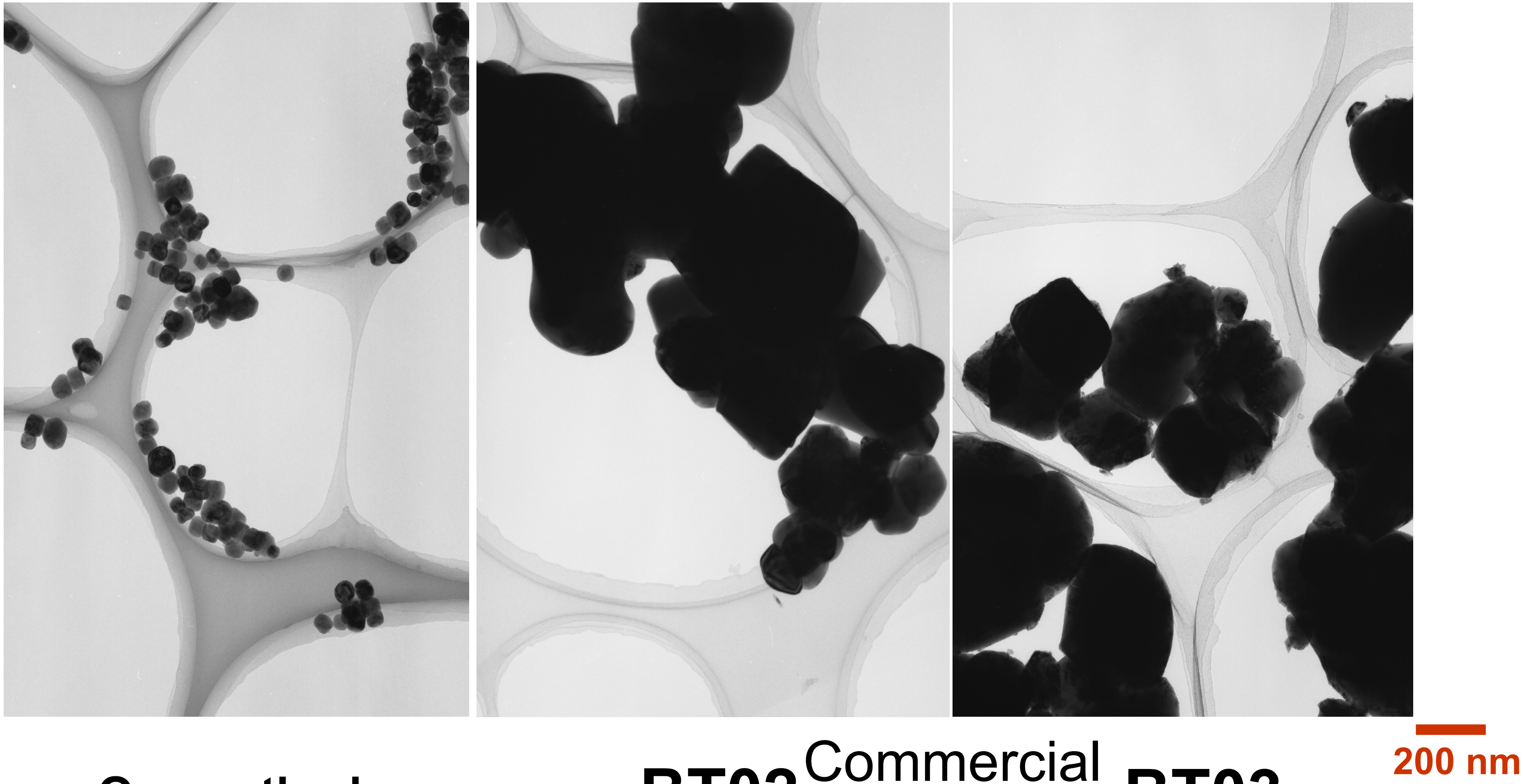
↓

$BaTiO_3$/$SrTiO_3$ fine particles



Schematic drawing of reaction vessel (autoclave)

Cubic $BaTiO_3$



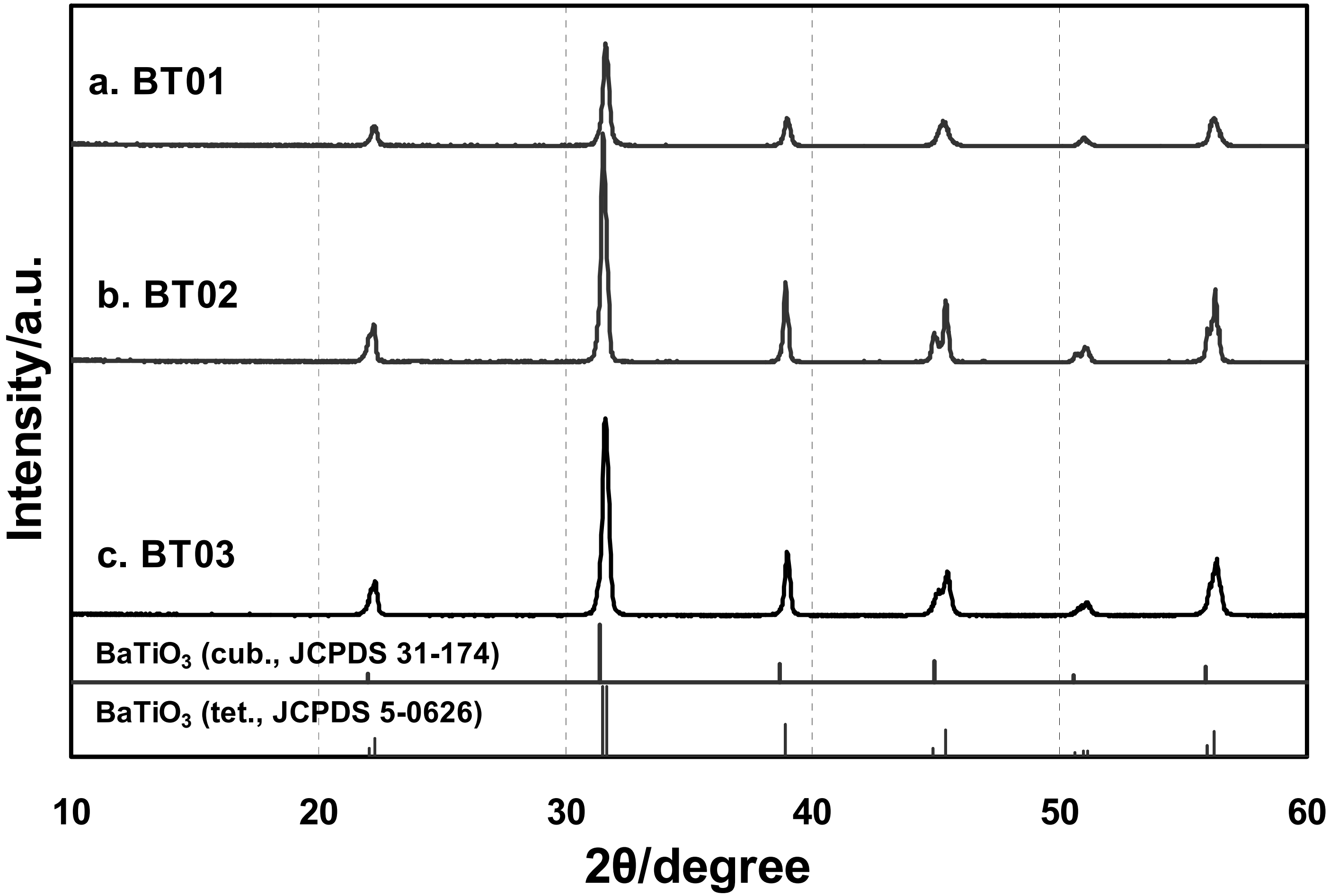
Our method
BT01

Commercial

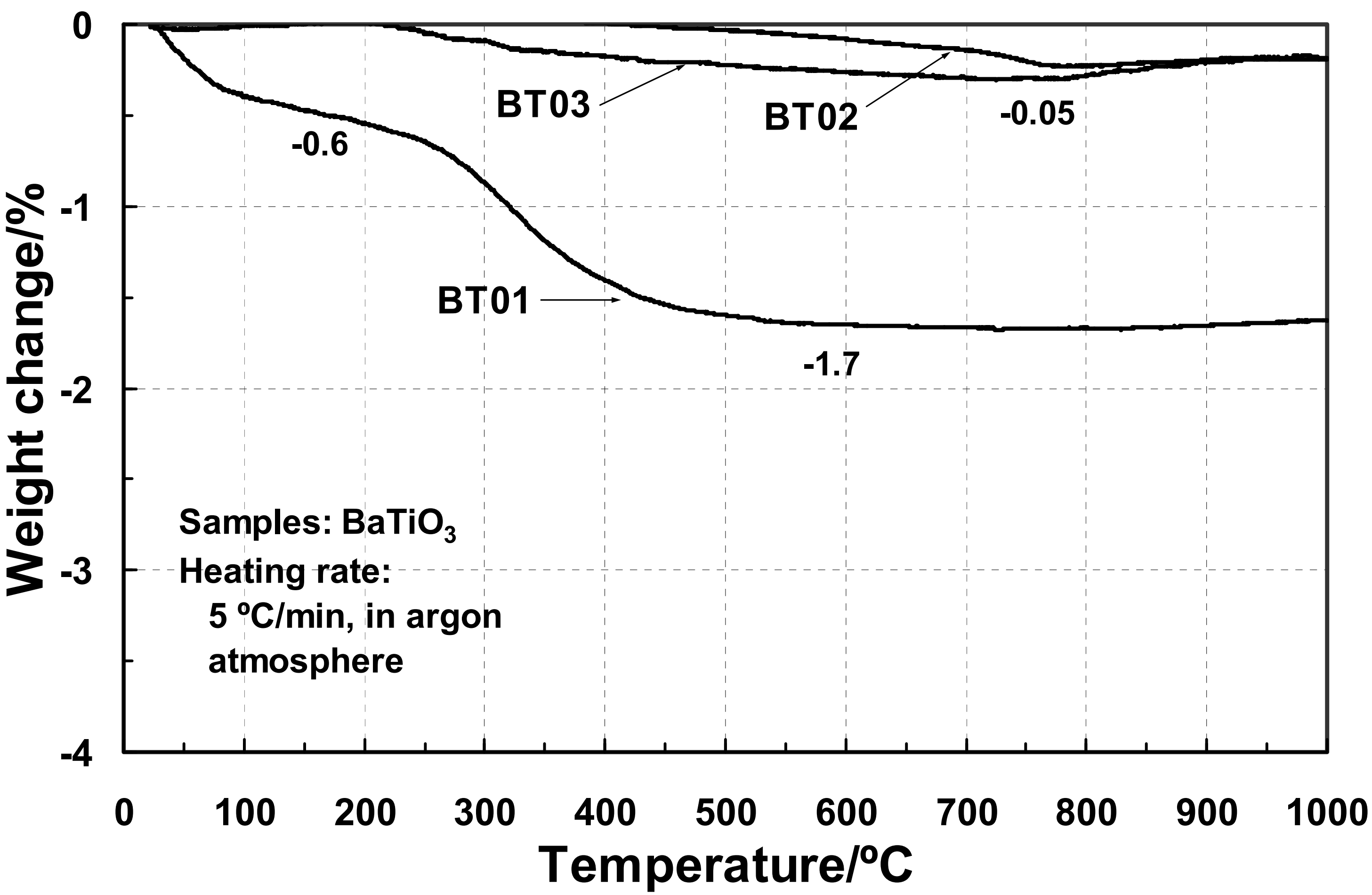
BT02
(High Purity Chemicals)

BT03
(Wako Pure Chemicals)

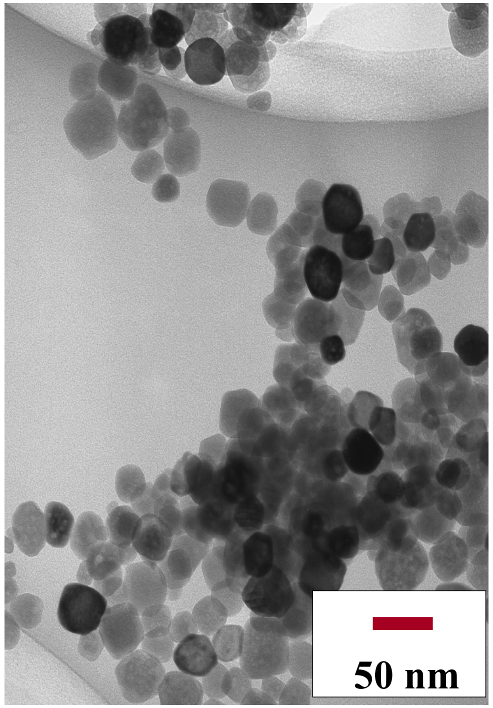
XRD


a. BT01
b. BT02
c. BT03
$BaTiO_3$ (cub., JCPDS 31-174)
$BaTiO_3$ (tet., JCPDS 5-0626)
Intensity/a.u.
10
20
30
40
50
60
2θ/degree

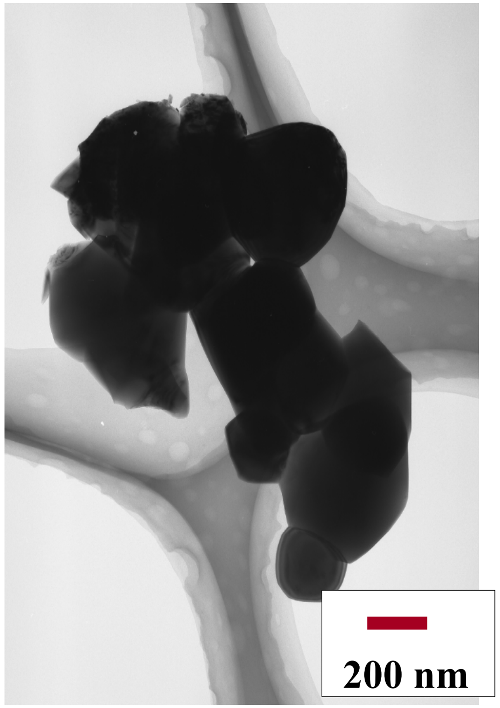
TG curves in Ar



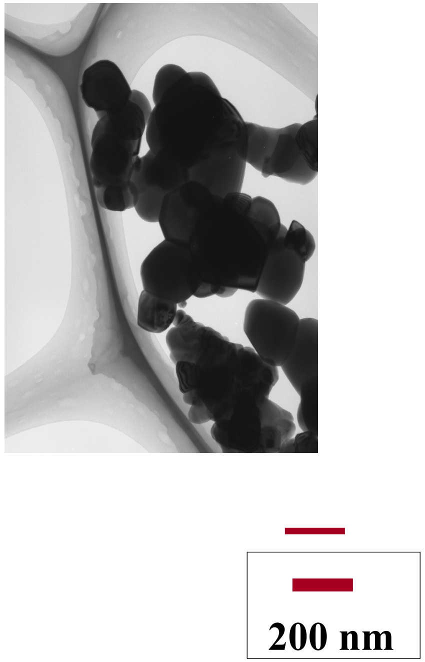
Cubic $SrTiO_3$



SR-01



SR-02

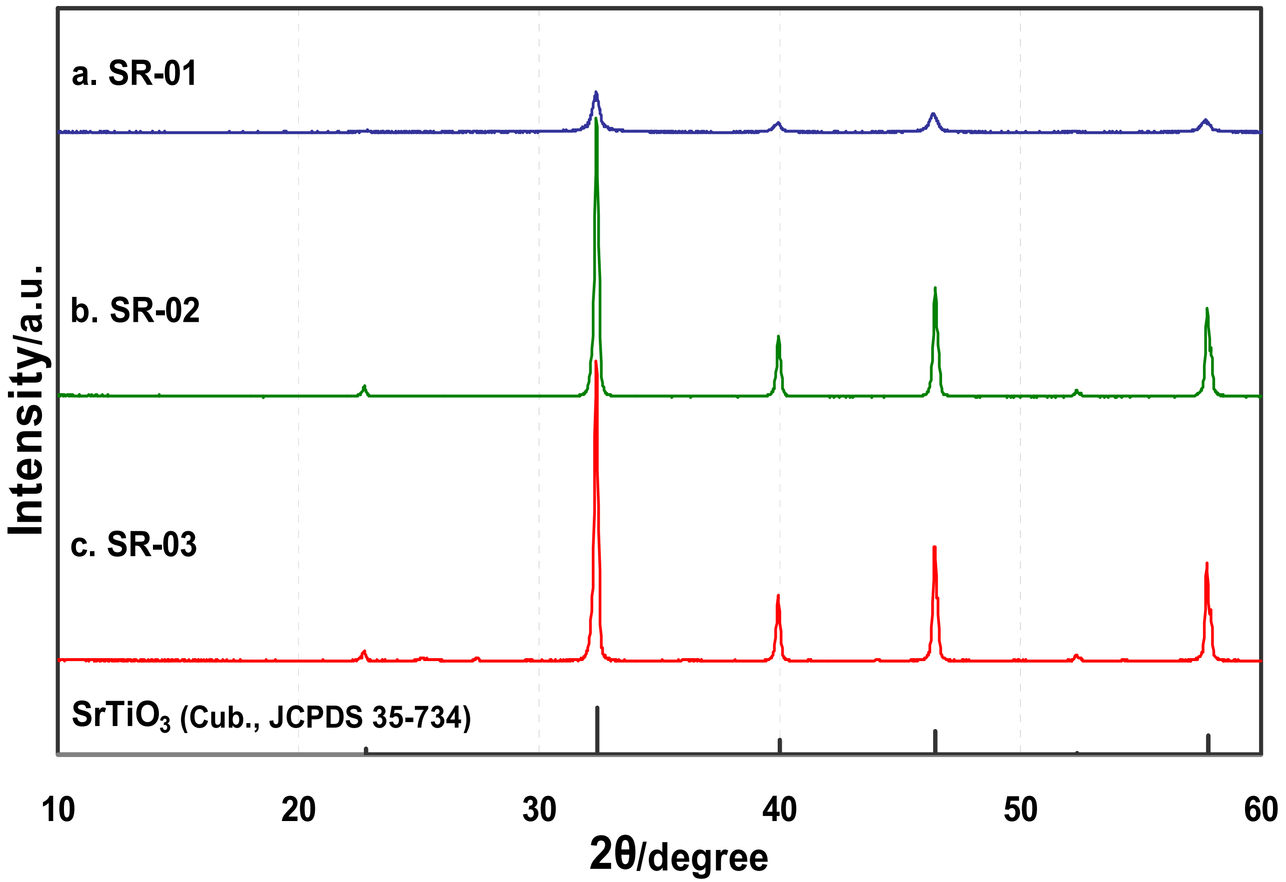


SR-03

Commercial

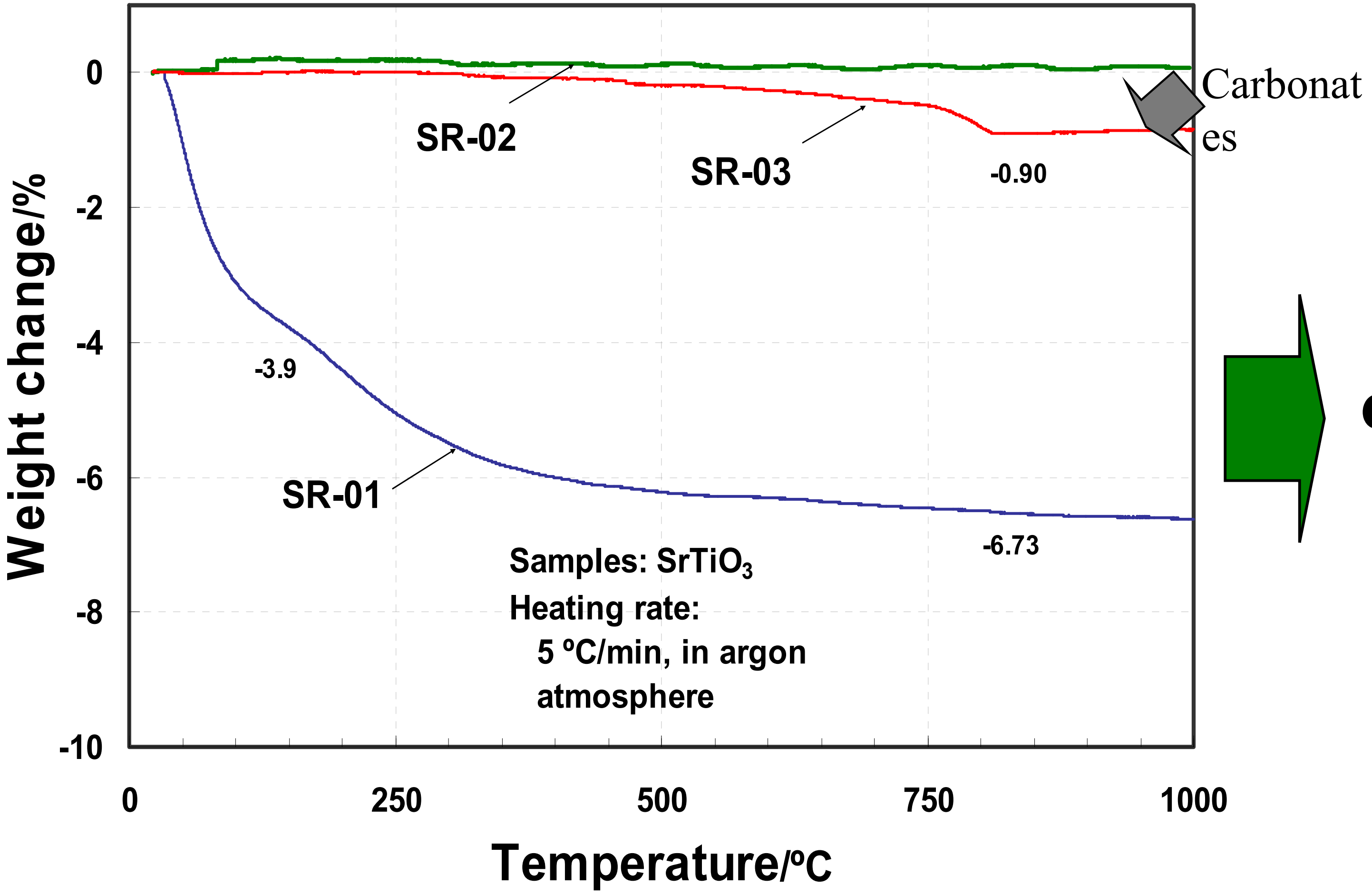
The particle size of SR-01 is smaller than 40 nm.

XRD



A cubic SrTiO$_3$ phase was founded in initial materials .

TG curves in Ar



Samples: $SrTiO_3$
Heating rate:
5 ^{o}C/min, in argon atmosphere

SR-01 only contents 3.9 % of adsorbed water and 2.83 % of OH groups.

particle morphology

Shape in equilibrium or growth

- Equilibrium control or kinetic control

Mostly growth shape

Equilibrium shapes are found in some minerals.

The growth shape is created by the difference in growth speed in the normal direction of each surface.

Therefore, the particle morphology can be controlled by varying the growth rate.