Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

http://www3.tagen.tohoku.ac.jp/~mura/kogi/

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Objectives

- Acquire physicochemical knowledge related to the synthesis of fine particles.
- Consider phenomena related to surface chemistry and surface chemistry around us in physical chemistry.
- Acquire knowledge of surface chemistry such as colloidal dispersion and aggregation, and catalytic reactions such as adsorption and surface reactions.

Outline

- Physical chemistry on surfaces and interfaces, which is fundamental knowledge for fine particle synthesis research, will be lectured.
- We also consider the dispersion and aggregation of colloidal particles based on the DLVO theory.
- On the other hand, we will also deepen our understanding of physical phenomena, adsorption, and surface reactions on solid surfaces.

Target

- (1) To Acquire physicochemical knowledge mainly on the fine particle formation mechanism from aqueous solution
- (2) To understand that physical chemistry can explain phenomena related to surface chemistry and surface chemistry around us.
- (3) To understand the mechanism of nanoparticle catalysts
- (4) Understanding that these phenomena can be explained by physical chemistry

Processing

- What is physical chemistry
- Let's start with colloid phenomena around us
- Let's think about particles and colloids based on physical chemistry

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

Basic Knowledges

Physical chemistry

- Physical (adjective)
- [1] material, material, material world, natural
- [2] bodily, physical, physical, human
- [3] Desire for the other's body, lustful
- [4] physics, physics, physical
- [5] Natural science according to the laws of nature

What is physical chemistry?

- Chemistry that captures the movement of materials
- Let’s go to the world of equilibrium and kinetics!

Equilibrium and Kinetics

- The equilibrium theory is, so called, the story of the paradise utopia world. The energy difference between this world and the present is exactly the Gibbs free energy change. The equilibrium theory is a study that tries to define the most energetically stable situation under given conditions. The equilibrium theory is the numerical analysis of where we are now between the ideal and reality.

Equilibrium and Kinetics

- Kinetics expresses the degree of effort to reach the paradise. More details will be discussed later in the lecture.

- In short,
- Physical chemistry is to formulate and understand the movement of materials.

Equilibrium and Kinetics

- Equilibrium and Kinetics
  - In equilibrium, the forward and reverse reaction rates are the same.
  - Processes include irreversible and reversible ones.

Chemical potentials

- They indicate the contribution of the energy change of each components to the Gibbs free energy change of the whole system. Expressed as the following,
- $G = f(T, P, V, n1, n2, n3 \ldots)$
- $dG = (\partial G/\partial T)\, dT + (\partial G/\partial P)\, dP + \Sigma (\partial G/\partial ni)\, d\, ni$

Chemical potentials

- When T,P,nj is to be constant, $(\partial G/\partial ni) = \mu$ is called Chemical potential of component i.
- You can think of it as indicating the degree of Gambari of a component i.

What is the definition of 1 mol?

- Until the 1970s, the definition was 1 mol for 12g of 12C at 0° C and 1 atm. To be changed.
- Definition was revised in 2019.
- Until then, "amount of matter in a system containing as many elementary particles as there are atoms in 0.012 kilograms of C12"
- Furthermore, before that, it was "a system of substances composed of as many elementary particles or assemblages of elementary particles (limited to those with a defined composition) equal to the number of atoms in 0.012 kilograms of C12."

What is the definition of 1 mol?

- n(X)mol = N(X) / N_a [X is elementary particles, N is a number]
- 1 mol contains exactly $6.02214076 \times 10^{23}$ elementary particles
- This number is the Avogadro constant NA expressed in units of mol^{-1}, and is called the Avogadro number.
- Unlike the uncertainty up to that point, from 2019 onwards, the Avogadro constant, NA, is assumed to be a value with no uncertainty.

Avogadro constant

N_A, L

Value	$6.022\ 140\ 857 \times 10^{23}\ mol^{-1}$
Standard uncertainty	$0.000\ 000\ 074 \times 10^{23}\ mol^{-1}$
Relative standard uncertainty	1.2×10^{-8}
Concise form	$6.022\ 140\ 857(74) \times 10^{23}\ mol^{-1}$

Value of Avogadro's constant in the new SI : $6.022\ 140\ 76 \times 10^{23}\ mol^{-1}$
Resolution of the General Assembly of Weights and Measures in November 2018
Scheduled to enter into force on May 20, 2019

Definition of pH

$$pH = -\log_{10} a_{\mathrm{H}}$$

- a_H is the activity of proton.
- Expanded uncertainty U(k =2) for pH measurement by glass electrode method is 0.025 to 0.030
- ~0.01 if the primary pH standard solution is used and can be considered to have the same composition as this standard solution;
- Expanded uncertainty using differential – potentiometric cell is ~0.004

What is the activity?

- A concept conceived as a bridge between the ideal solution and the actual solution.
- It's the same unit as a concentration, but it's not a correction of a concentration.
- For example, if the protons of 1 mol/L hydrochloric acid had 100% activity, it would have an activity of 1 mol/L, which is not the case in a real solution. At 80% activity, we call it an "activity" of 0.8 mol/L.

What is the activity?

- Compare rattled train with crowded train.
- Volume, pressure, temperature are constant.
- Envision your own and other passengers' range of activities.
- The rattle train allows you to choose where you want to be overwhelmingly more freely.
- This is the activity.
- Born to connect ideal and real solutions.

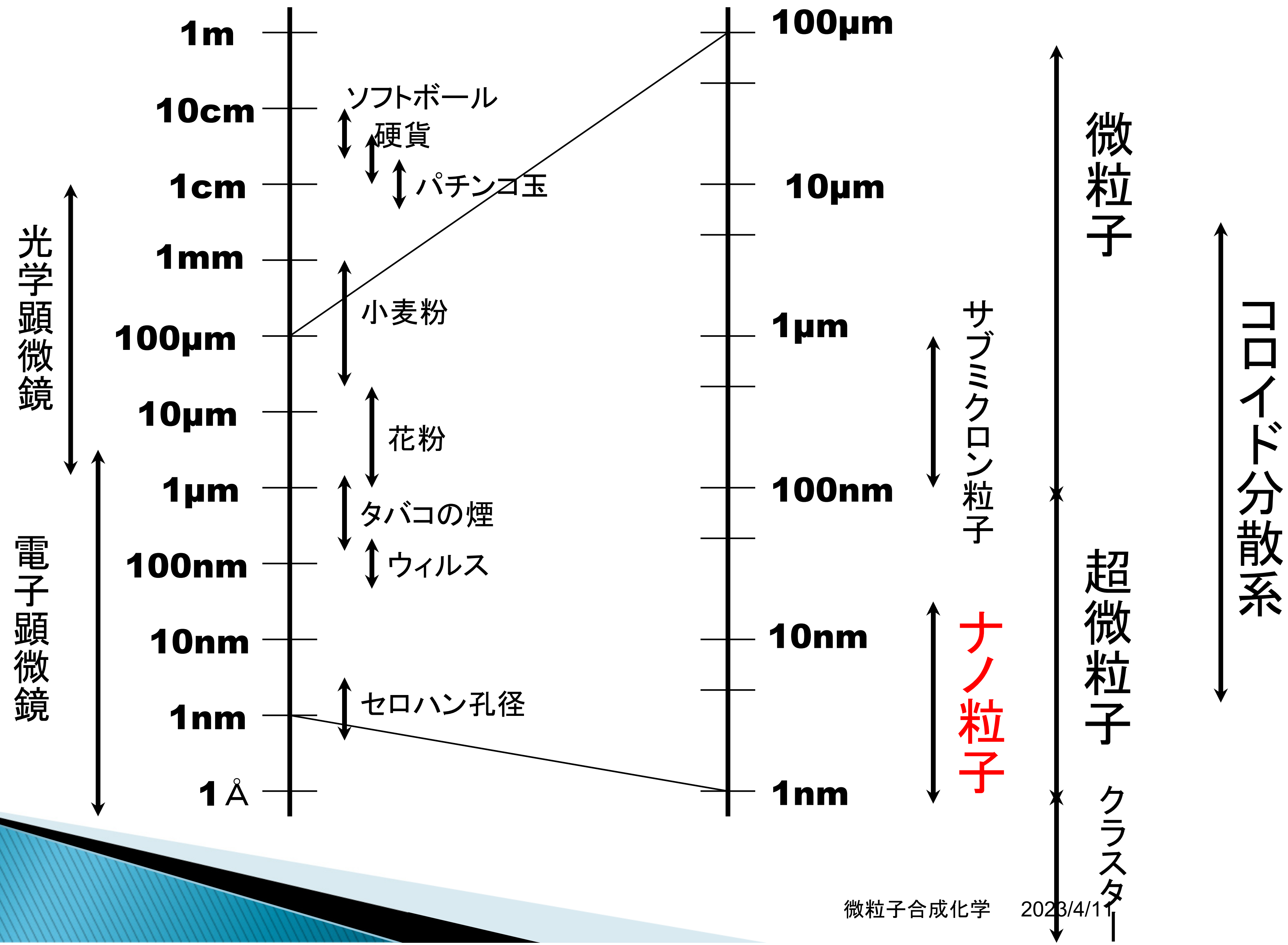
- The concept of fugacity is basically the same.

Invitation to Colloidal Chemistry

What is a Colloid?

- Colloid in physics and chemistry dictionary
- We can say, it is in a colloidal state when it is dispersed as particles larger than atoms or small molecules that cannot be seen by ordinary light microscopy.
- Colloidal particles themselves are difficult to define, and only when they are in a dispersed state can be defined as a colloidal state.
- Then, what is different from the dissolution of macromolecules?

Particle classification by particle size



COLLOIDS IN LIFE

2023/4/11

Let's take a look at the colloids around us

Colloids around us

Hot spring

Beppu Hell Tour [Blood Pond Jigoku]

What is the cause of this red hot spring?

Beppu Hell Tour [Blood Pond Jigoku]

- Amount of discharge: about 1,800 kl/day
- Spring quality: Acidic meridian spring
-   = Acidic-Fe(II)-sulfate spring
- Hot spring temperature: about 78 ℃

The red color is caused by oxidation of ferrous ions (Fe(II)), hydrolysis, and then precipitation of solid-phase iron hydroxide $Fe(OH)_3$ or hydrous iron oxide FeOOH. Part of it is hematite Fe_2O_3.
They are particles of several microns to several millimeters, and are dispersed.

Beppu Sea Jigoku

What is the cause of this blue hot spring?

Beppu Sea Jigoku

- Conventionally, it was considered to be the blue color of ferrous sulfate (officially still)
- However, upon component analysis, there are almost no iron ions.
- why is it blue?

- In "Kanwaen" near Umi Jigoku, color is paler.

神和苑 温泉水 分析結果

京都大学地球熱学研究施設

	露天風呂流入口 (1997年11月4日)	露天風呂 #1 (1997年11月6日)	露天風呂 #2 (1997年11月9日)
水温 (℃)	75.6	42.1	43.5
pH	7.7	7.8	7.7
Na (mg/l)	1120	1140	1170
K (mg/l)	151	153	158
Ca (mg/l)	34.2	47.3	47.9
Mg (mg/l)	14.2	7.3	7.2
Cl (mg/l)	1680	1700	1700
SO_4 (mg/l)	401	400	421
SiO_2 #3 (mg/l)	466	444	406

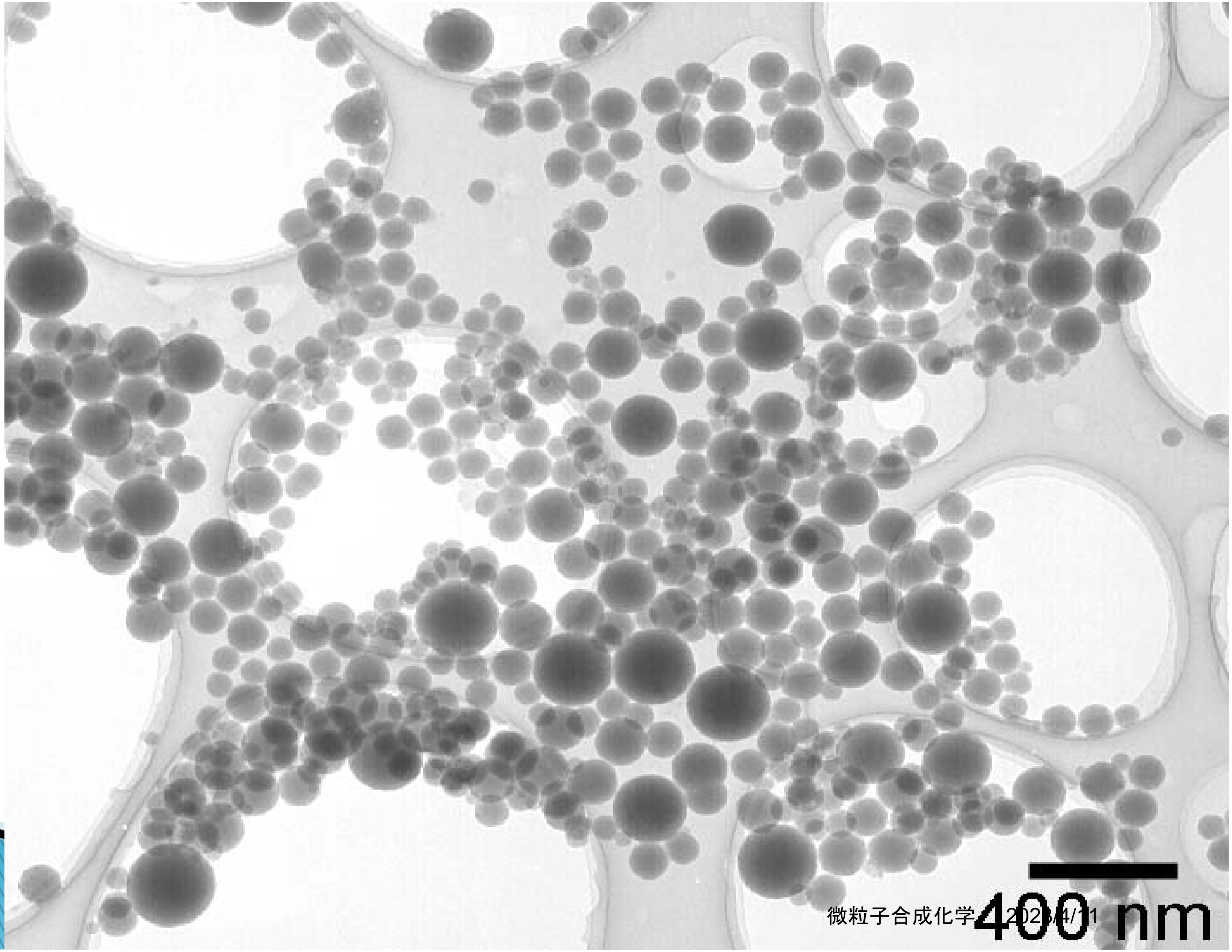
#1　3日目：透明感のある青色
#2　6日目：白っぽい青色
#3　全シリカ

分析者：大沢信二・川村隆夫

Blue = Silica colloid

- This silica colloid was so small that it looked like a solution.
- smaller than the wavelength of light.
- Could it be explained by the scattering phenomenon of light?

TEM photo of the silica colloid



SiO_2(silica) fine particles

- It was found by X-ray analysis that the particles were amorphous.
- FT-IR analysis revealed that it had a SiO2 (silica) composition.
- Since spherical silica particles are synthesized by hydrolysis in a high alkali region, it is presumed that they are produced deep underground at high alkali and high temperature.

Why is it blue?

- It can be explained by the concept of Rayleigh scattering.
- The smaller the particle size, the easier it is to scatter short wavelengths, namely blue.
- Blue light is scattered by silica of several tens of nanometers or less →Suspension turns blue

Size parameter α is

$$\alpha = \frac{\pi d}{\lambda}$$

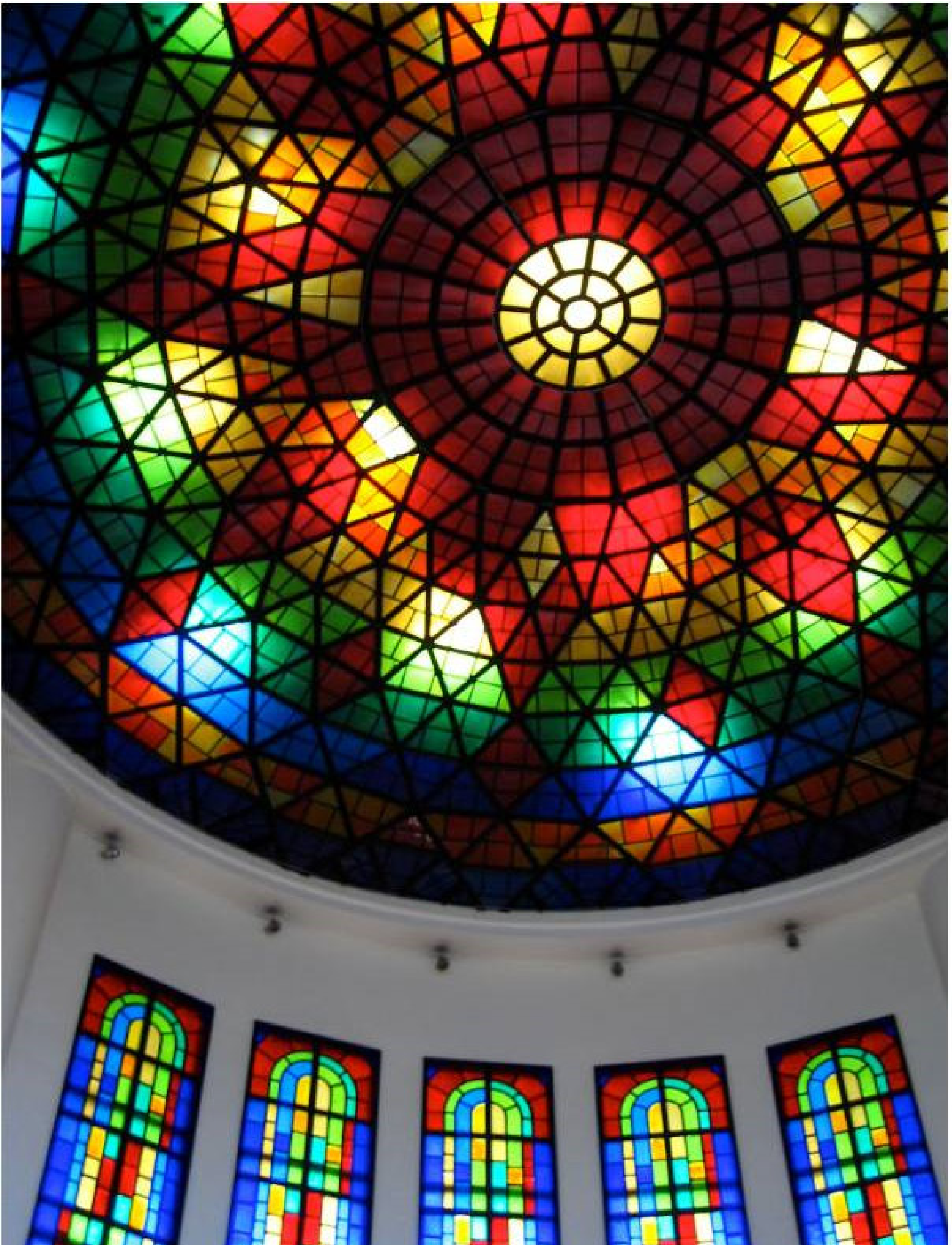
$$\alpha \ll 1 \quad Rayleigh\ scattering$$
$$\alpha \approx 1 \quad Mie\ scattering$$
$$\alpha \gg 1 \quad geometric\ optics\ approximation$$

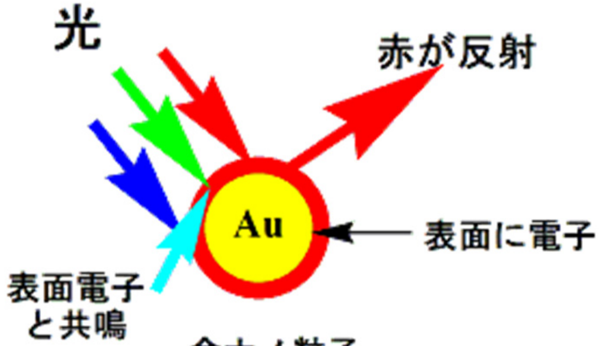
Rayleigh scattering coefficient k_s

$$k_s = \frac{2\pi^5}{3} n \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \frac{d^6}{\lambda^4}$$

n:particle number, *d*:particle diameter,
m:reflection constant, λ:wave length

The color of the stained glass is due to surface plasmon resonance of gold nanoparticles...

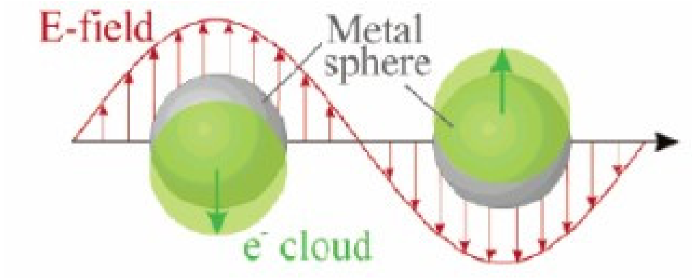


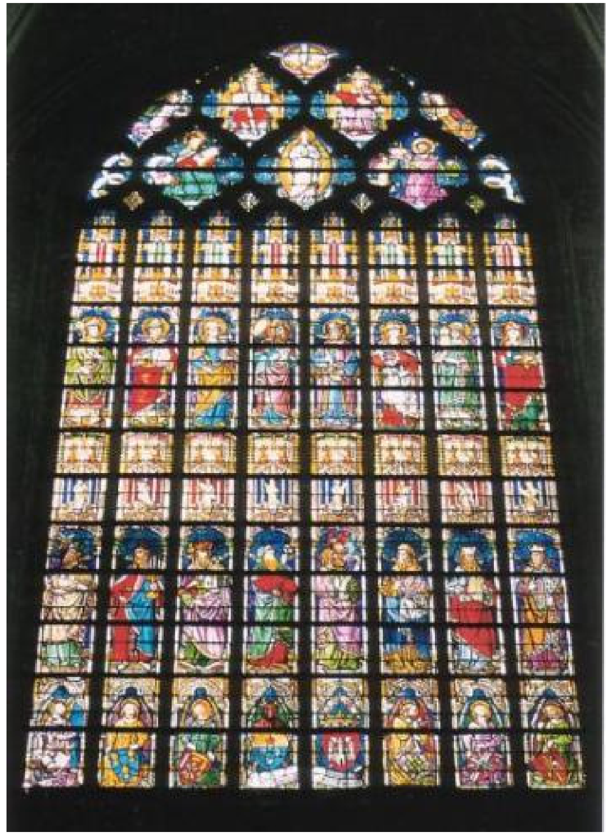


Colored gold nanoparticles

Surface plasmon resonance

A phenomenon in which electrons in a metal interact with light. When a metal has a special structure in which the tips of nanometer-sized particles or needle-like protrusions are arranged periodically, conduction electrons and light resonate in these fine regions, It produces effects such as bringing a very high light output that overturns





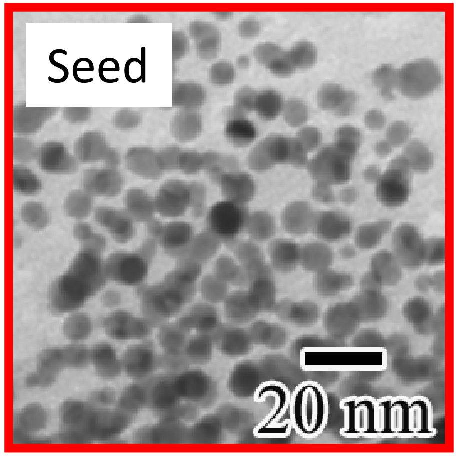
church stained glass

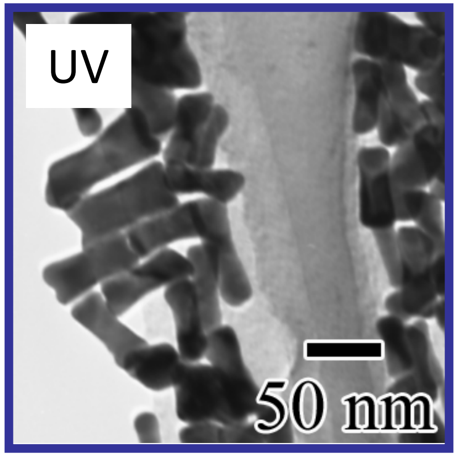
Late Roman Lycurgus Cup

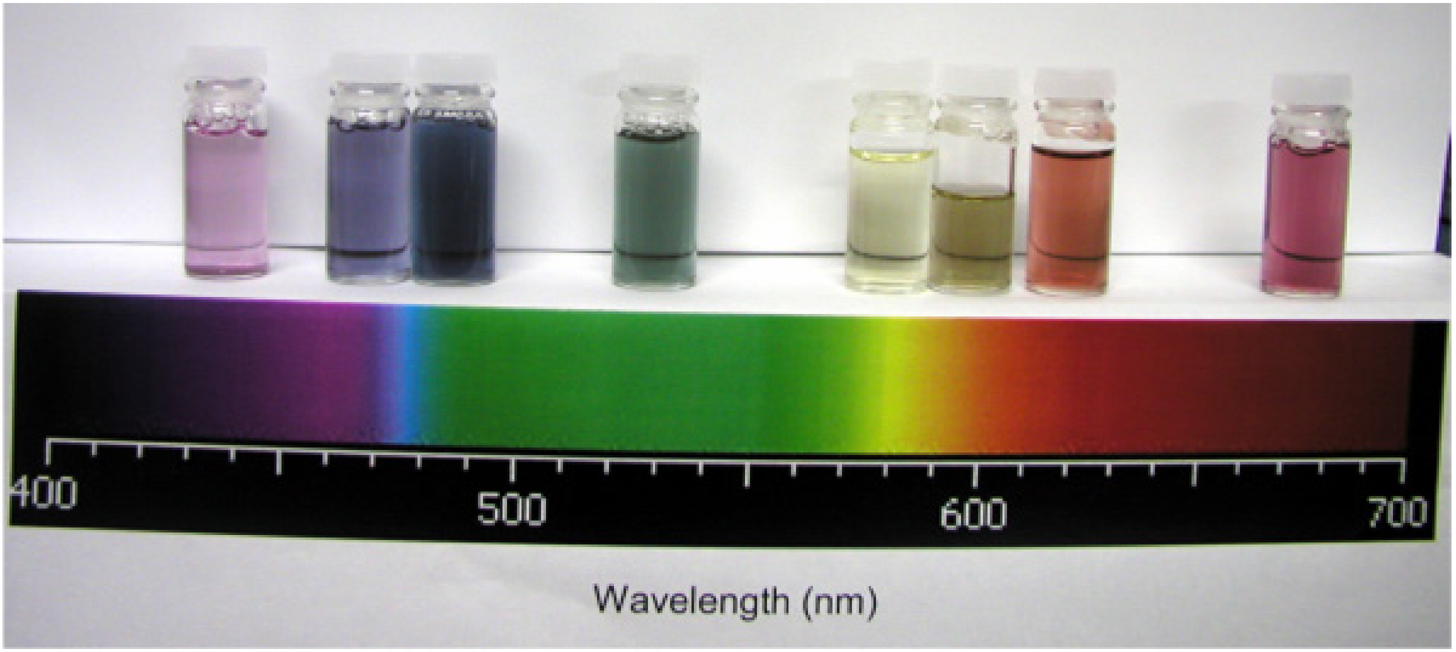
Baroque Ruby Glass

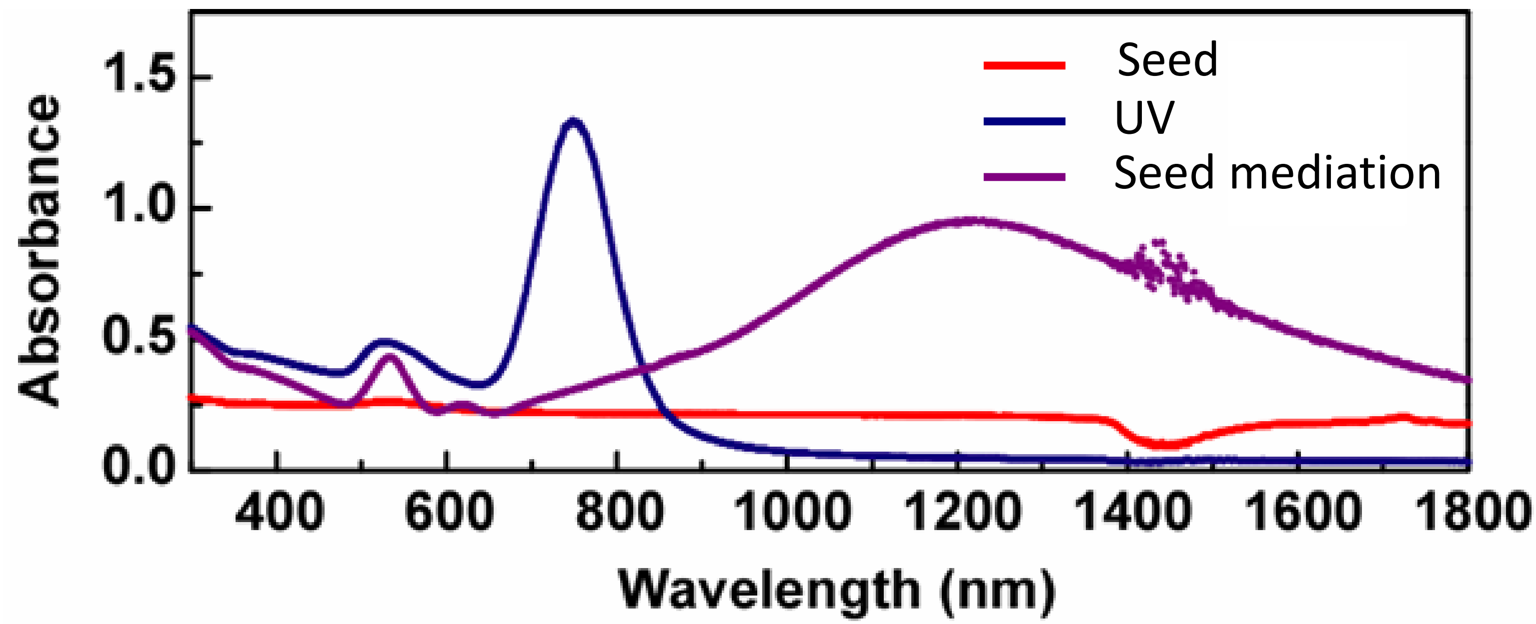
Colloidal dispersion of gold nanoparticles

Color change due to change in morphology of gold nanoparticles







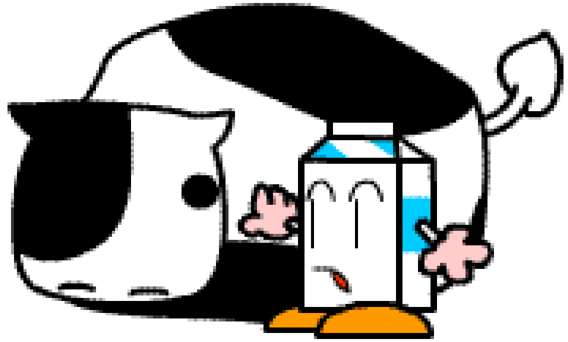


Absorption wavelength shifts to longer as aspect ratio increases

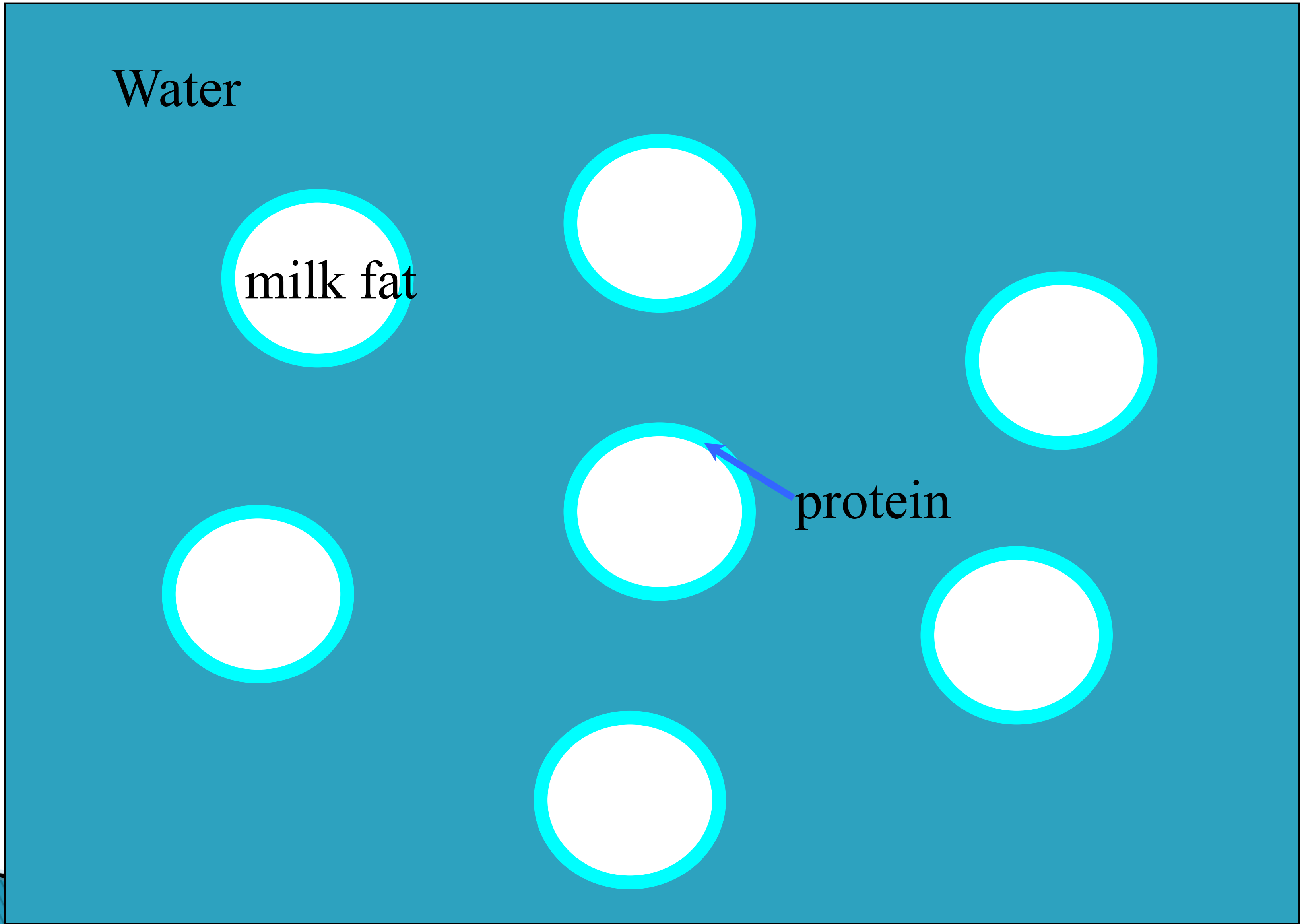
Colloids around us

Milk

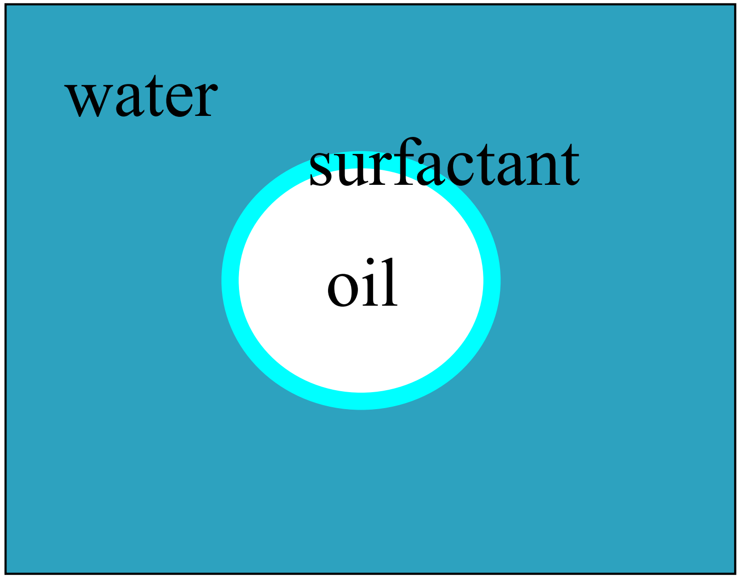
Milk

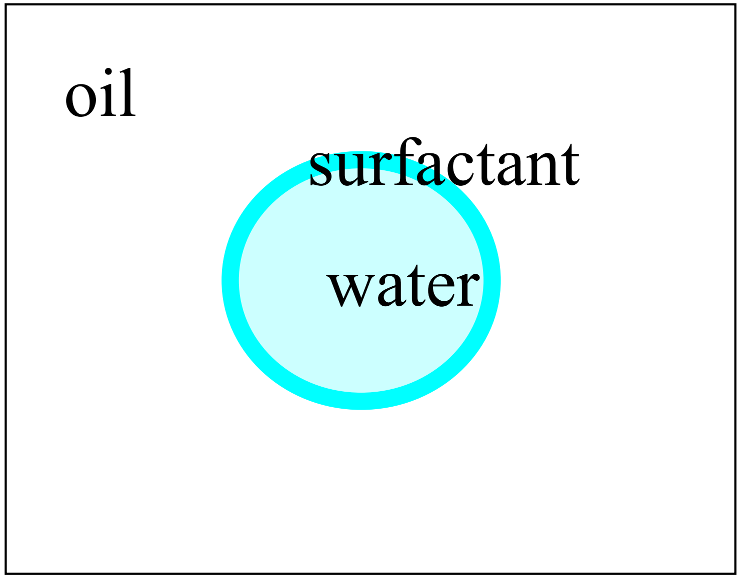


Nutrient energy value	Cow's milk	Human milk
Protein (% of energy)	3.25	1.42
Fat (% of energy)	3.61	3.64
Lactose (% of energy)	4.88	6.71
Casein (% of protein)	2.51	0.37
Whey (% of protein)	0.57	0.76
Energy value (kcal/g)	674	677
Vitamin A (ug/100 ml)	35.2	60
Vitamin D (ug/100 ml)	0.29	0.01
Vitamin E (ug/100 ml)	113.5	0.35
Vitamin C (ug/100 ml)	1530	380
K (mg/l)	1204	491
Na (mg/l)	504	15
Ca (mg/l)	1287	35
P (mg/l)	996	15
Mg (mg/l)	134	2.8


Water
milk fat
protein

Milk is an O/W emulsion





O/W emulsion

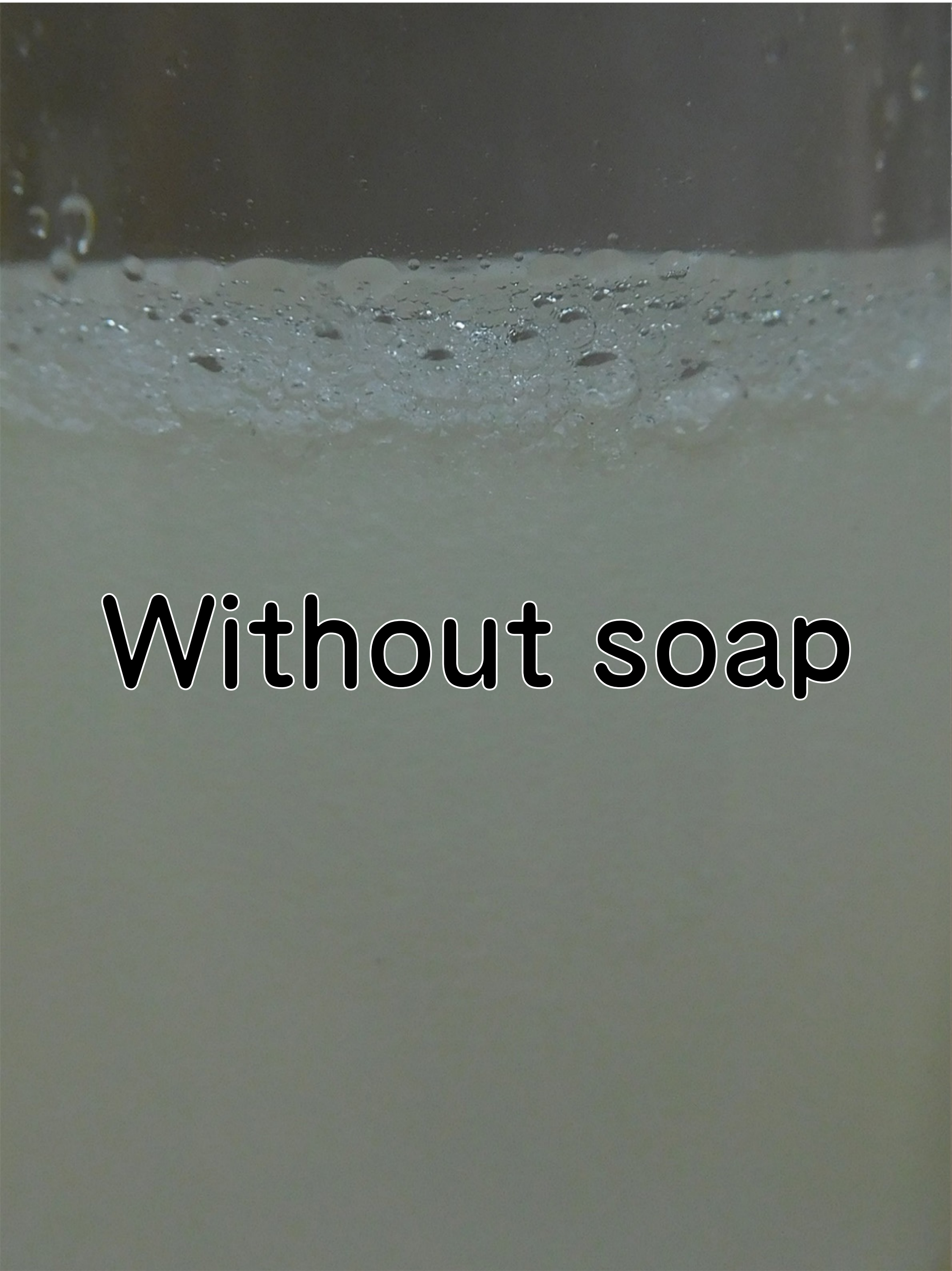
W/O emulsion

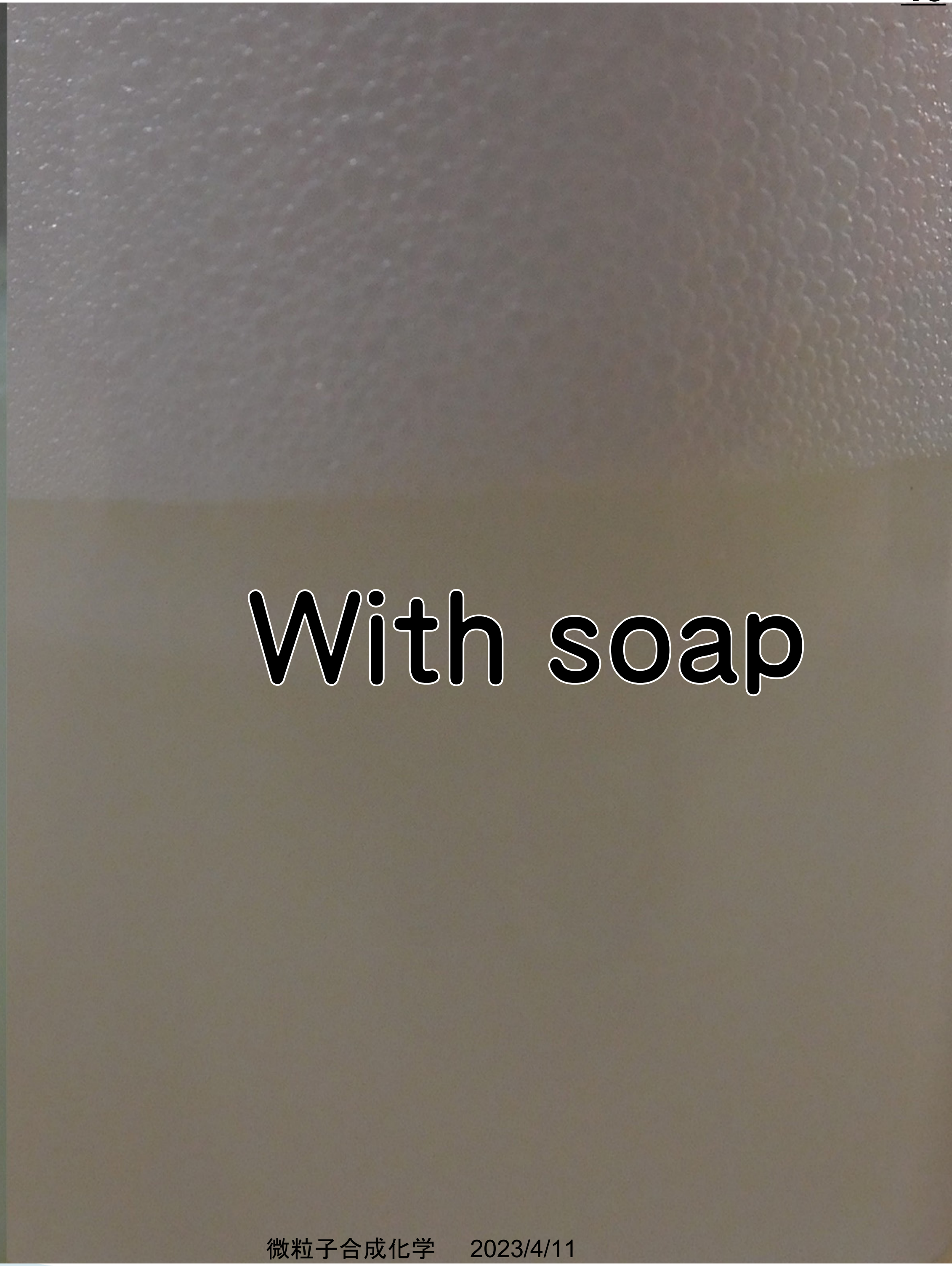

water


Salad oil

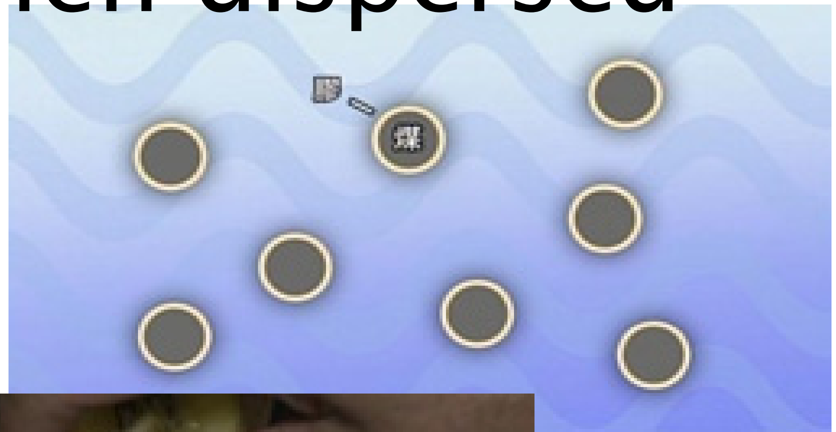

Water
Soap
Salad oil

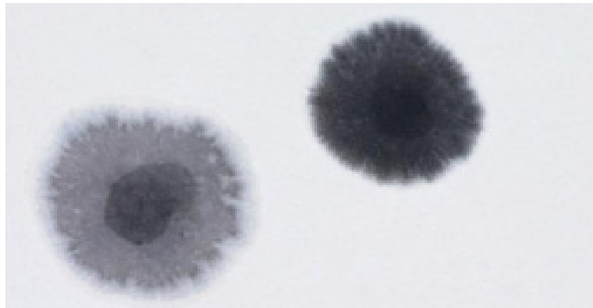

Salad oil
Water


Without soap


With soap

India ink is also an O/W emulsion
~ Glue is adsorbed and then dispersed ~





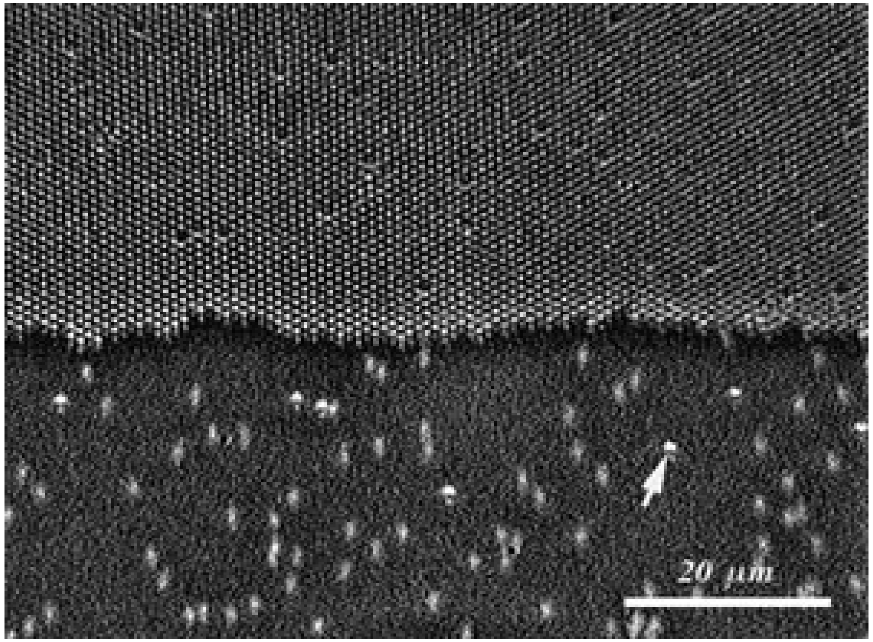
NHK高校講座「芸術（美術Ｉ／書道Ｉ）」第12回 漢字の書(2) ～さまざまな表現～

Colloids around us

Beer

beer foam

Nagayama Project Beer



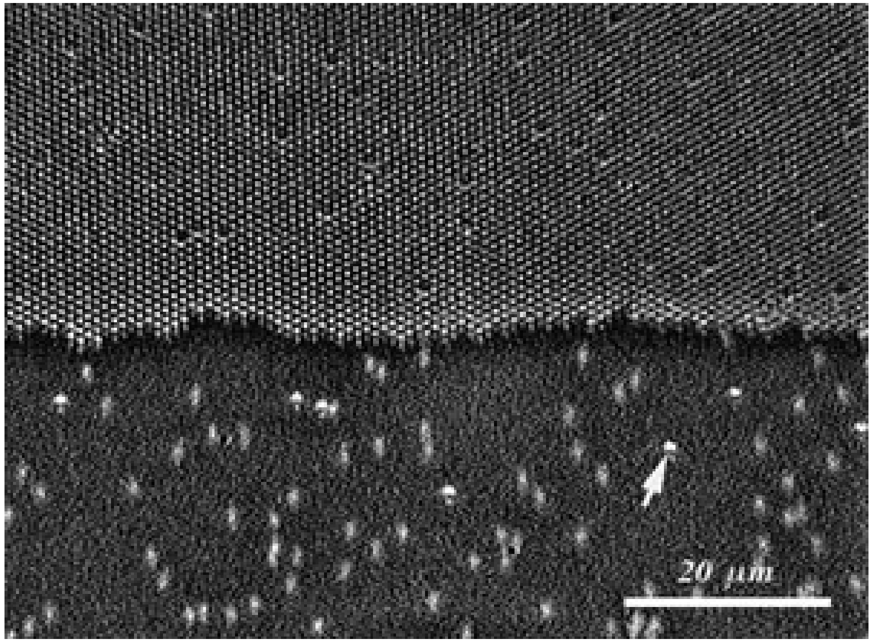
Colloids that are transported from bottom to top by advective accumulation to form a two-dimensional crystal structure. The lower colloid is blurred because it is moving.

bad pour

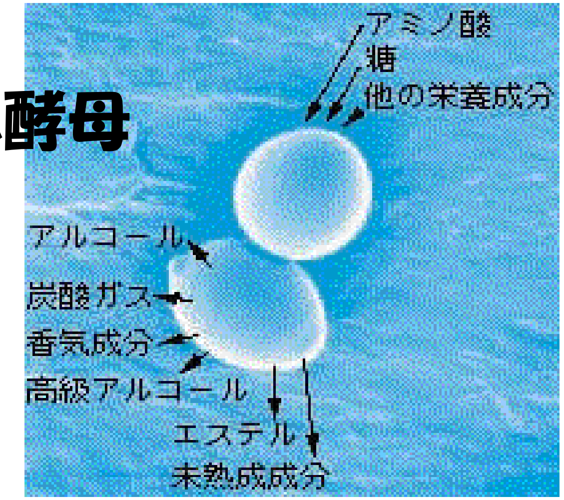
good pour

ビールの泡

- なぜ合一しにくいのか？
  - 分散安定化への指針
  - 泡の表面にホップと麦芽由来のフムロンや塩基性アミノ酸が吸着し、分散剤的な働きをしている



ビール酵母



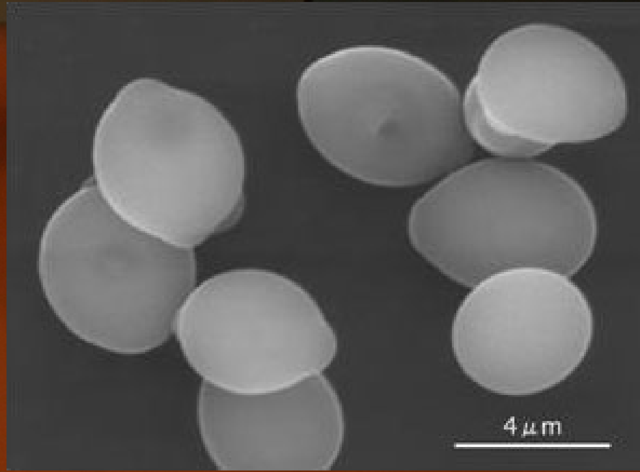
How to pour beer properly

Pour slowly and gently without foaming

Homogeneous nucleation:
Bubbles come out of the solution

Heterogeneous nucleation:

Bubbles come out of disposable chopsticks when inserted



Japanese sake fermentation
The zeta potential of yeast is positively charged.
Go up with negatively charged bubbles along with CO_2 generated by fermentation
Same as top-fermenting yeast in beer

Tyndall effect, Tyndall scattering

- A phenomenon in which light is scattered mainly by Mie scattering when it passes through a dispersion system, and the path of the light appears to shine even when viewed obliquely or sideways.
- It was discovered in the 19th century by British physicist, John Tyndale
- The intensity of Mie scattering is maximized when the particle size and wavelength are nearly equal.
- Since the intensity of Mie scattering does not particularly depend on the wavelength, it looks whitish in the case of sunlight.

サイズパラメータαは

$$\alpha = \frac{\pi d}{\lambda}$$

$\alpha \ll 1$ レイリー散乱

$\alpha \approx 1$ ミー散乱

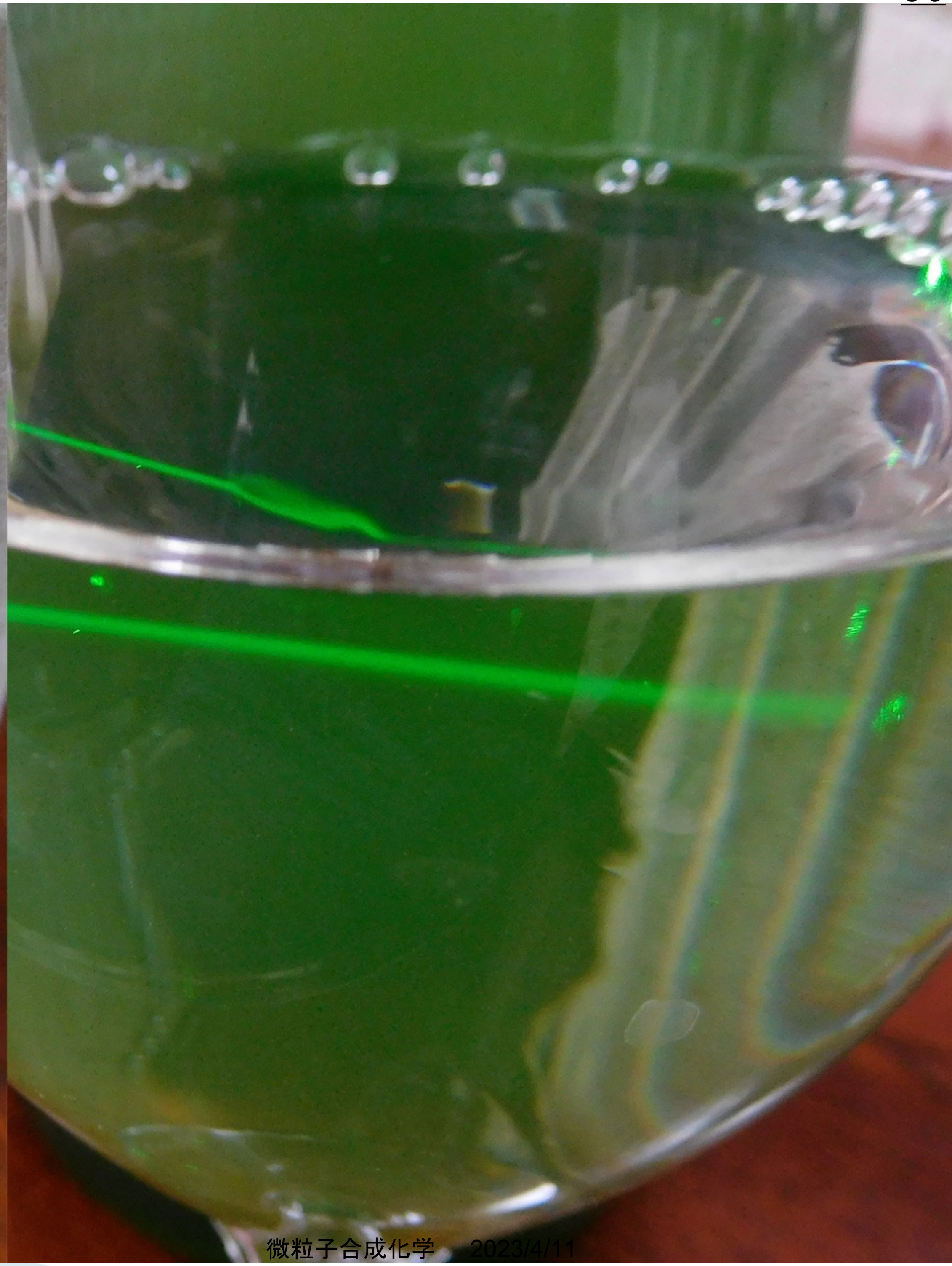
$\alpha \gg 1$ 幾何光学近似

レイリー散乱の散乱係数k_s は

$$k_s = \frac{2\pi^5}{3} n \left(\frac{m^2 - 1}{m^2 + 2}\right)^2 \frac{d^6}{\lambda^4}$$

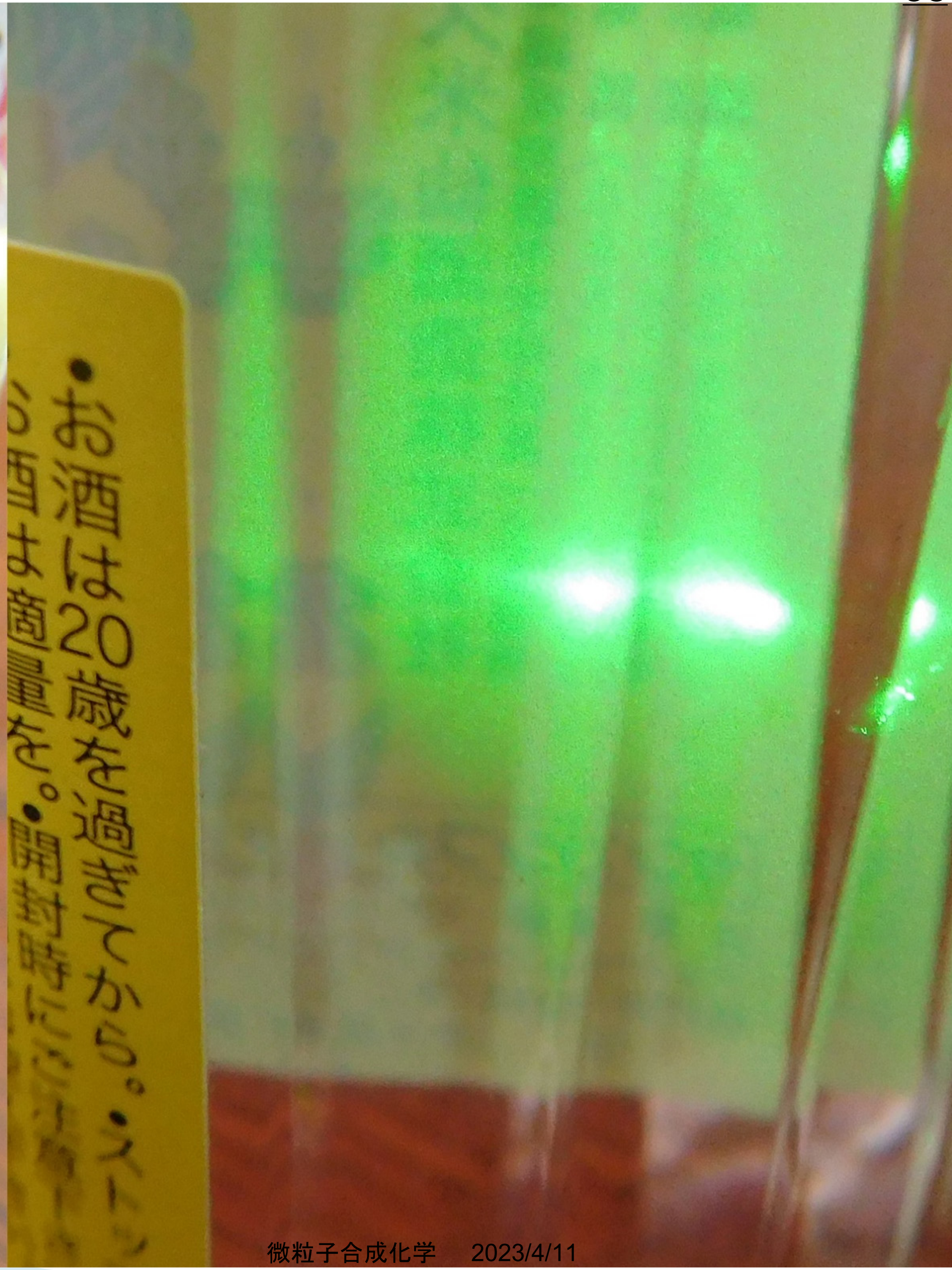
n:粒子数, *d*:粒子径, *m*:反射係数, λ:波長


純米大吟醸

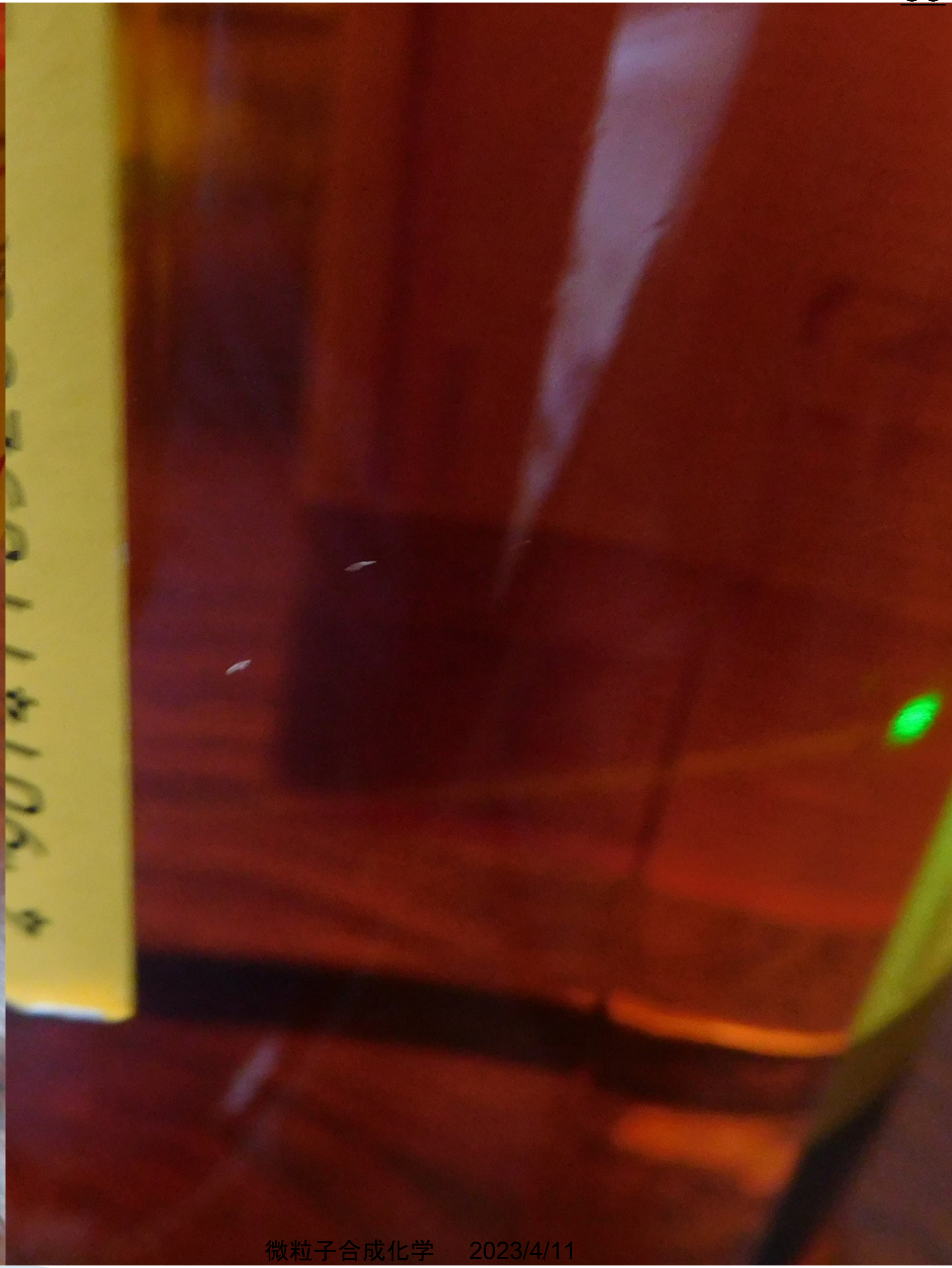



Penfolds
KOONUNGA
HILL
CHARDONNAY
SOUTH AUSTRALIA
2014
In 1976, Penfolds released the first wine to bear the name Koonunga Hill. By applying our long held philosophy of blending select parcels of grapes from South Australia's wine regions, Penfolds wine makers are able to craft wines of distinction without ever compromising on quality.
375ML


琉球泡盛

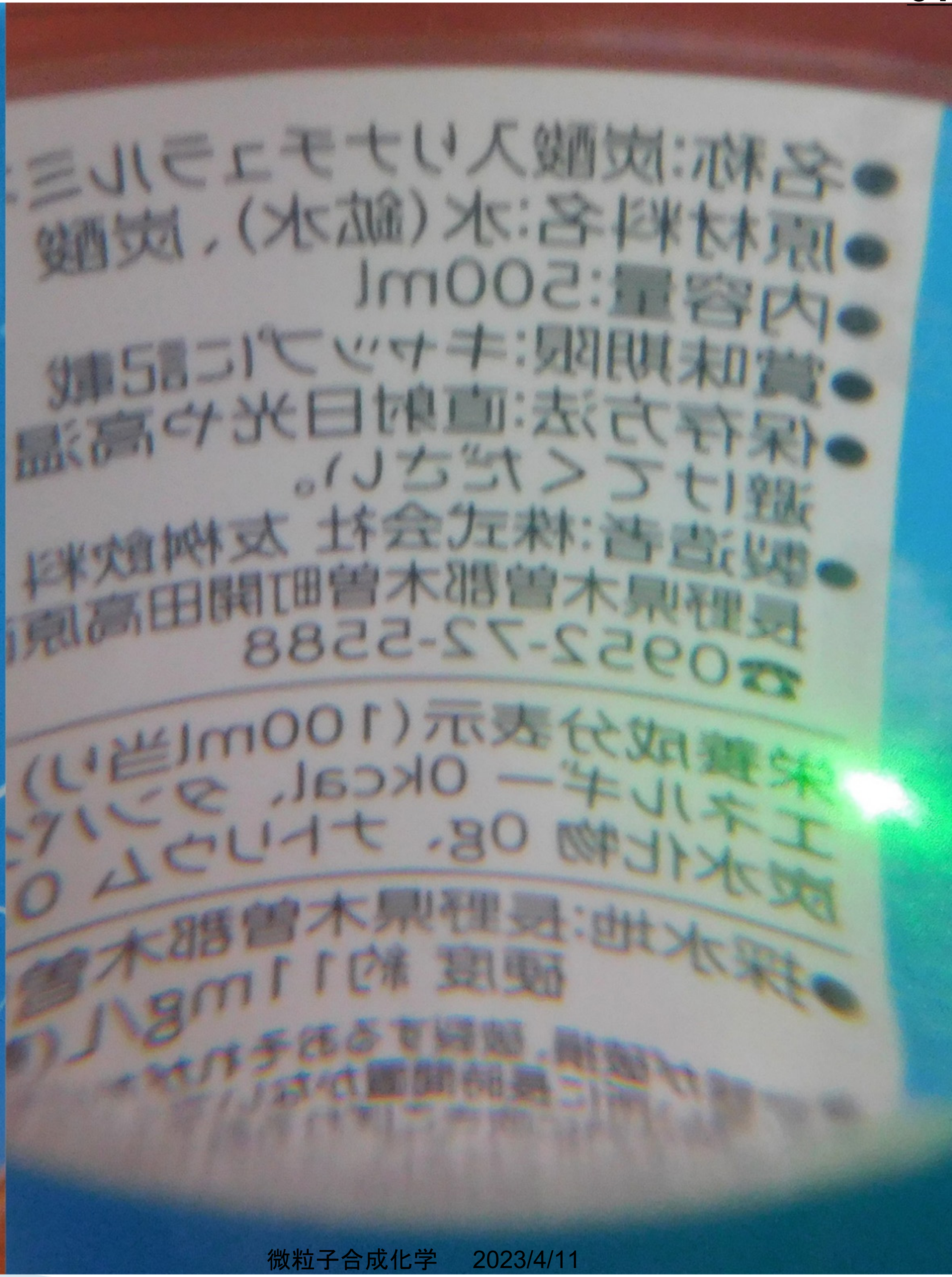

・お酒は20歳を過ぎてから。
酒は適量を。・開封時に


SCOTLAND
WHITE HORSE
Fine Old
BLENDED
SCOTCH WHISKY
WHITE HORSE DISTILLERS




BOTTLED AT THE SOURCE
CRYSTAL GEYSER
NATURAL
ALPINE SPRING WATER
BY CG ROXANE
16.9 FL OZ (1.05 PINTS) 500mL


炭酸水
SPARKL
WATER
信州木曽開田高原
天然湧水使用
0
kcal
500ml


名称:炭酸入りナチュラルミ
原材料名:水(鉱水),炭酸
内容量:500ml
賞味期限:キャップに記載
保存方法:直射日光や高温
避けてください。
製造者:株式会社 友納飲料
長野県木曽郡木曽町開田高原
☎0952-72-5588
栄養成分表示(100ml当り)
エネルギー 0kcal
炭水化物 0g
採水地:長野県木曽郡木曽
硬度 約11mg/L


お〜いお茶


SUNTOR
サントリー
烏龍茶
Rich & Clear Taste
525ml


ジンジャーエール