ChE 496/696, ME 599 Particles and Particle Systems

- INSTRUCTORS:

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- LECTURES: Tuesdays 1:30 - 4:30 PM, 2166 DOW

- OFFICE HOURS: Albert Liu is available by appointment.

Grading

ACTIVITY	Weight
Attendance and Participation*	20%
In-class Presentations	30%
NSF Fellowship Proposal	15%
Invention Disclosure (group)	15%
Final Project (group)	20%

*Class attendance is mandatory and will be taken. Students are expected to actively participate in class (this will particularly be emphasized and assessed during class presentation days). To achieve full credit for attendance and participation, students must:

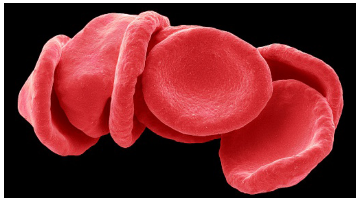
1. Attend lecture, be prepared for, and actively and respectfully participate in each class.
2. Ask and answer questions and contribute critiques and analysis of readings and topics covered in course.

Attendance

- If you will need to be absent for class on a date when team activities are occurring, please let Albert Liu know in ASAP. The teaching staff will determine if you can contribute to your team's preparation remotely or determine an alternate plan to make up your contributions.
- Each class we will have a poll question on a related concept. You will need a digital device with a camera (to scan QR code) and internet access to answer these poll questions which are mandatory. Bonus participation points will be provided if 60% (or more) of these poll questions are answered correctly throughout the semester.

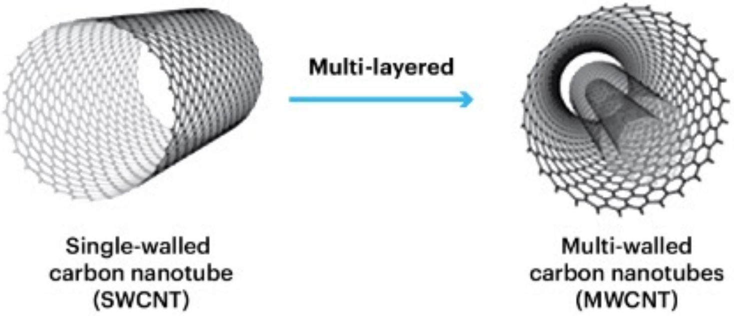
You need to log in using your umich.edu account in order to access this poll

Lecture 1 Poll: Particle Scales



Without consulting the internet, picture the dimension of a human red blood cell (RBC), and the radii of a typical single walled carbon nanotube (SWCNT). Please estimate the ratio of the thickness of an RBC over the radius of a SWCNT.

- A. 0.1
- B. 10
- C. 1,000
- D. 100,000



Long URL https://forms.gle/MnRxozcRcPbSrg2J7

Short URL https://shorturl.at/bguI9

Answer: C

- The discocyte shape of human RBCs is approximately 7.5 to 8.7 μm in diameter and 1.7 to 2.2 μm in thickness.

  MRS Bull. 2010 May; 35(5): 382–388.
  doi: 10.1557/mrs2010.571

- Single-walled carbon nanotubes (SWCNTs) are tubular nanostructures of covalently bonded carbon atoms, with typical diameters near 1 nm and lengths in the micrometer range.

  https://www.pnas.org/doi/10.1073/pnas.0904
  148106

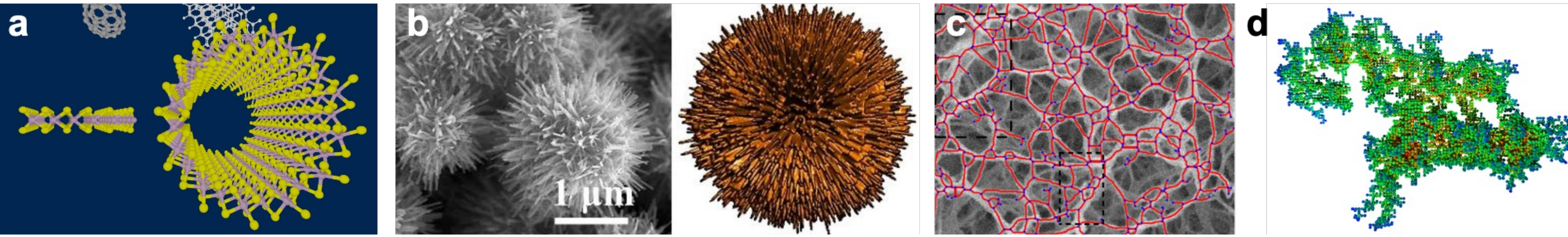
Participation and in-class presentations

- Journal club: we will be reading seminal papers on related topics every week using an online platform (Perussal), and presenting them to the rest of the class.
- Youtube videos: we will be learning from each other on how concepts learned in class can be applied in real world scenarios through youtube video clips.
- Final group project

Scientific communication and practice

- NSF Fellowship Proposal: we will learn how to write academic proposals in a compelling fashion.
- Group Invention Disclosure: we will learn the importance of Intellectual Property, how to work in a team and reduce scientific concepts to practice.

Virtual Reality in Complex Particle Systems



- The fields of Chemical Engineering and Mechanical Engineering are rapidly evolving, with programmable matter emerging as a central theme in the core curriculum.
- By incorporating VR, we aim to redefine the way that we can engage with complex materials and network structures, fostering educational equity by providing an immersive learning experience for all.

Learning Outcomes

- Apply theoretical and practical aspects of the fundamental principles that govern the behavior of particles across scales and their interactions with one another, as well as with the surrounding environment.
- Formulate mathematically and solve complex problems related to apply this knowledge to various practical applications in fields such as materials science, biotechnology, and environmental engineering.

Why should I care about Particles and Particle Systems?

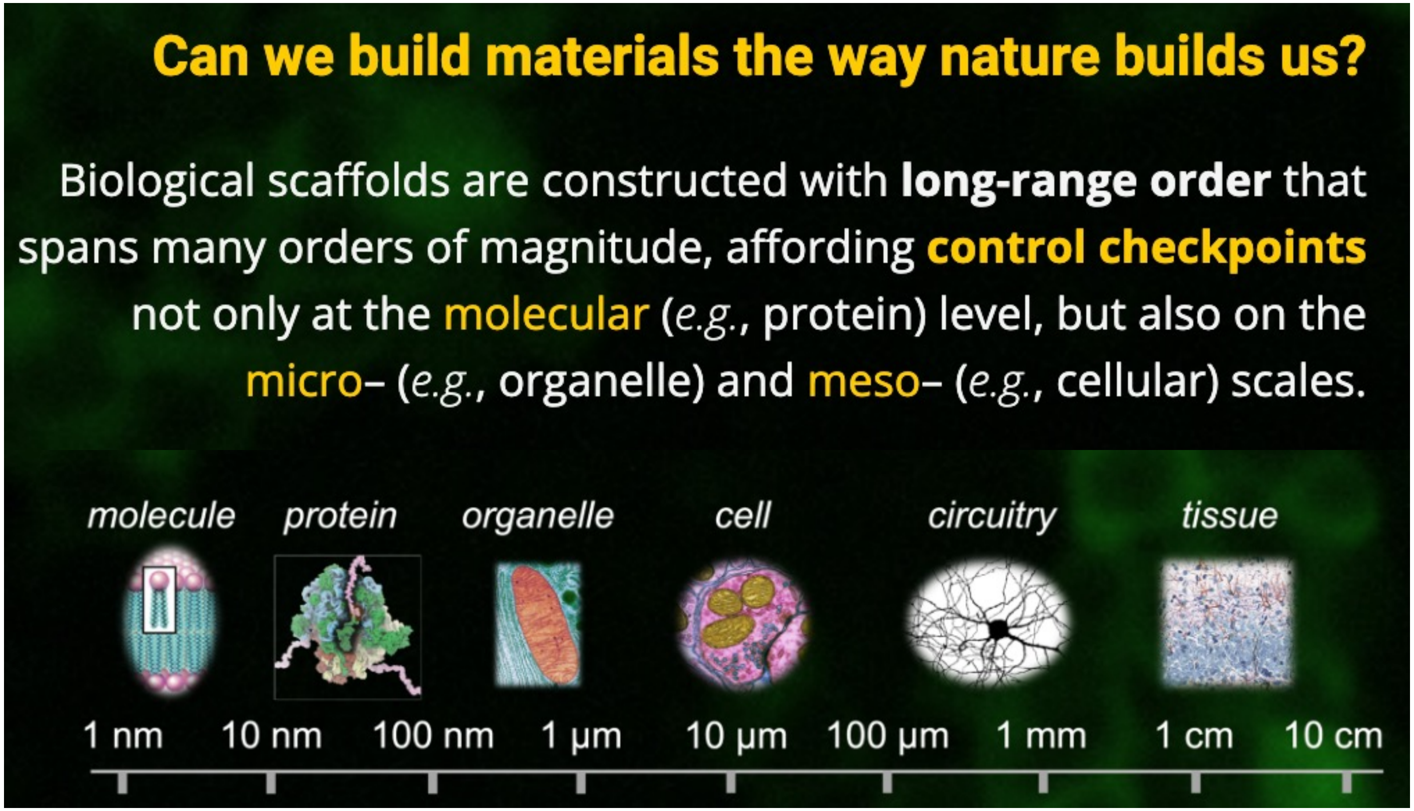
- the story of materials is really the story of civilization.
- Everything is made of something. The material world is not just a display of our technology and culture, it is part of us, we invented it, we made it and it makes us who we are.
- The fundamental importance of materials is made clear from the naming of ages of civilisations – the **stone**, **iron** and **bronze** ages – with each new era being brought about by a new material.

https://www.theguardian.com/science/2014/sep/14/story-of-materials-human-civilisation-mark-miodownik

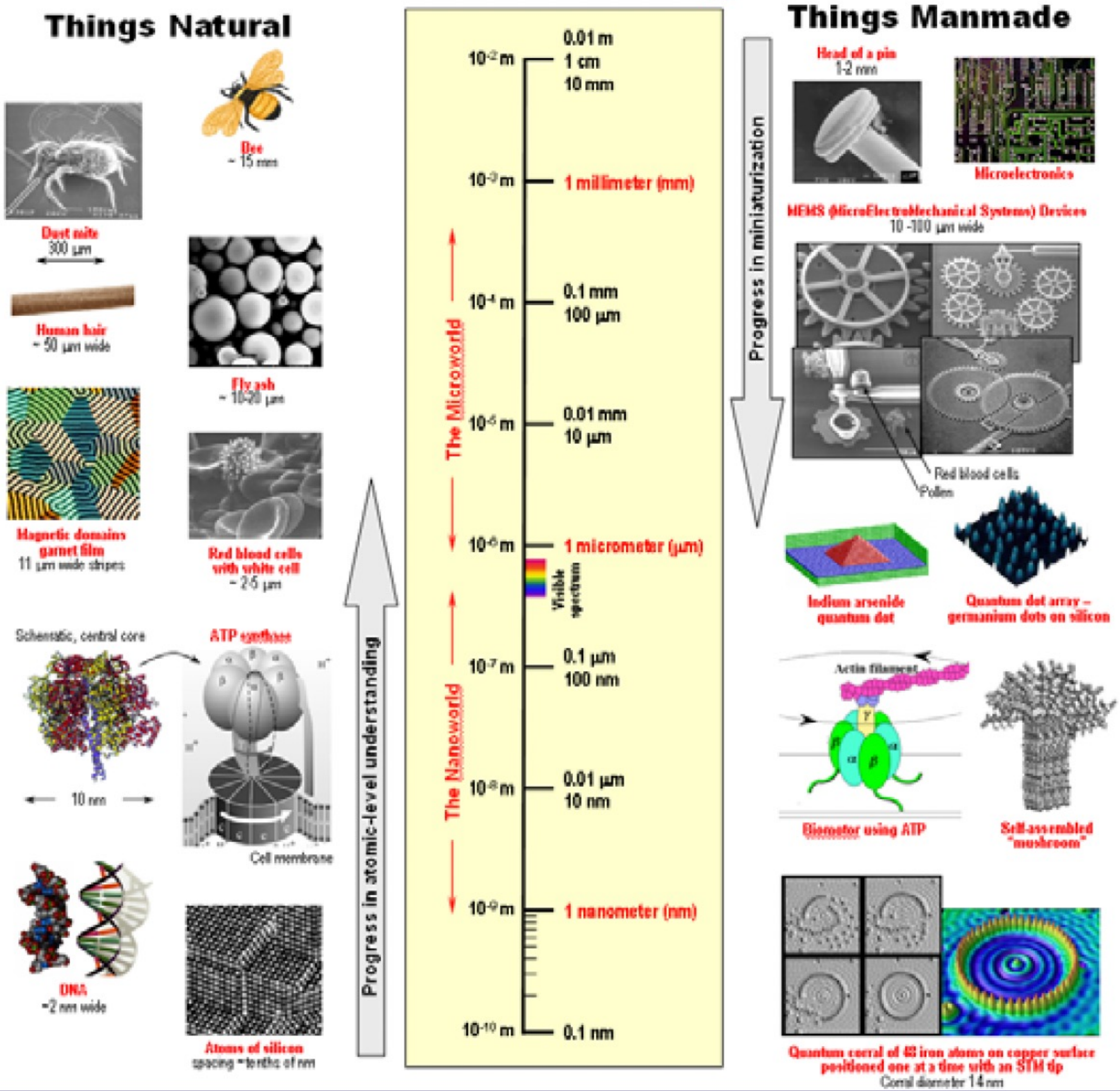
Why should I care about Particles and Particle Systems?

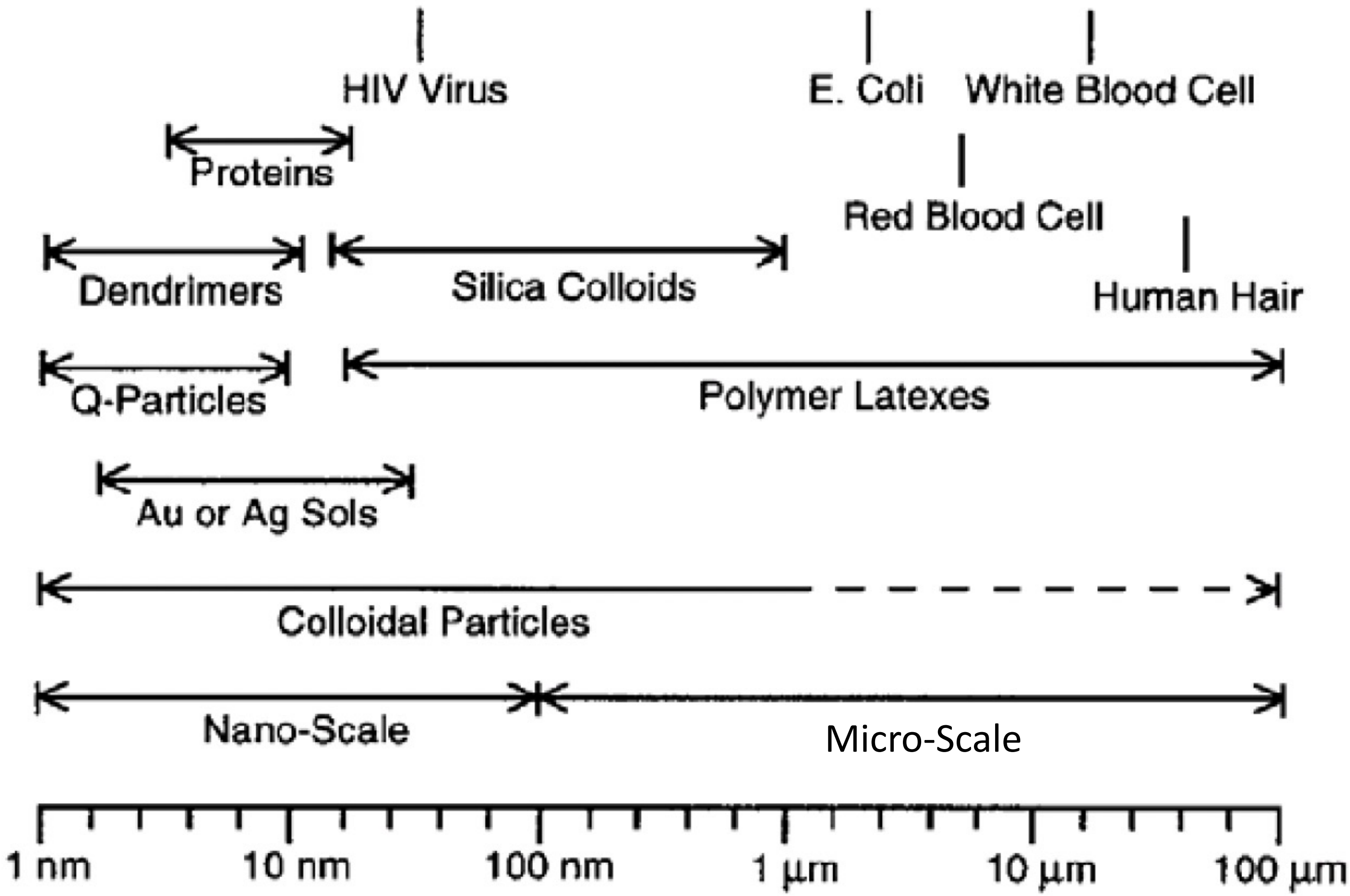
- **Steel** was the defining materials of the Victorian era.
- The 20th century is often hailed as the age of **silicon**, after the breakthrough in materials science that ushered in the silicon chip and the information revolution.
- What's next?

Why are Particles and Particle Systems so powerful?



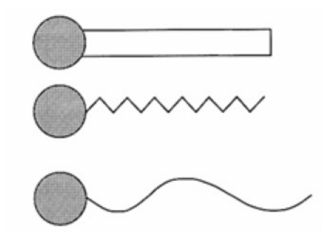
Scale of Things

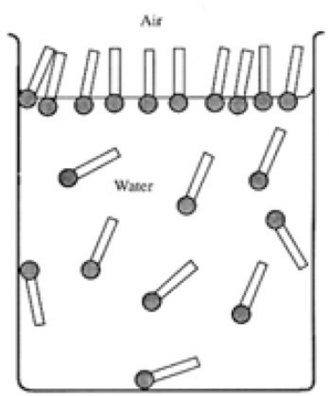


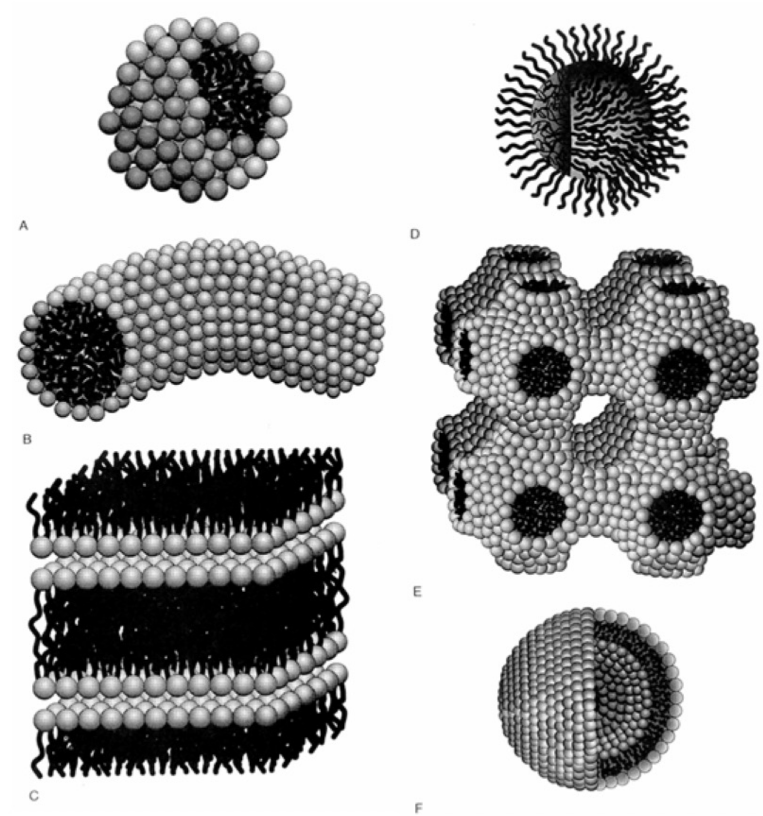

HIV Virus
E. Coli
White Blood Cell
Proteins
Red Blood Cell
Dendrimers
Silica Colloids
Human Hair
Q-Particles
Polymer Latexes
Au or Ag Sols
Colloidal Particles
Nano-Scale
Micro-Scale
1 nm
10 nm
100 nm
1 µm
10 µm
100 µm

Types of colloidal particles

- **Molecular**
  - **Surfactants**



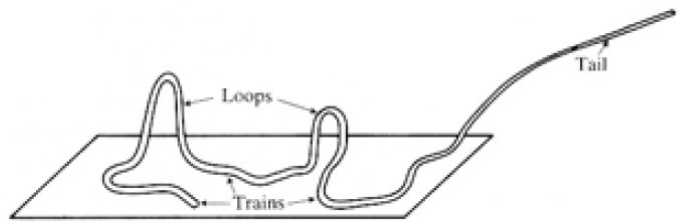


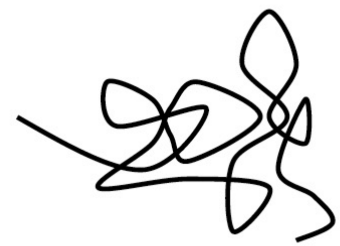


Self-assemble in a variety of structures

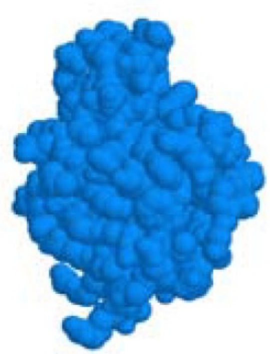
Types of colloidal particles

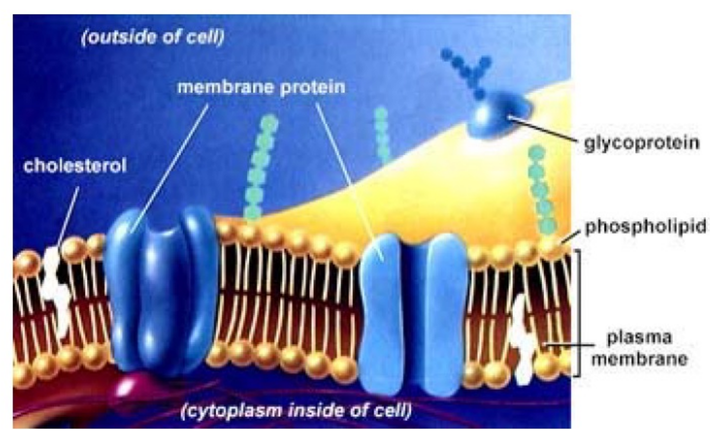
- **Molecular colloids continued**
  - **Polymers**





  - **Biomolecules**

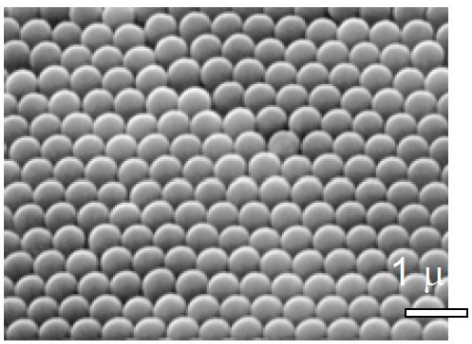




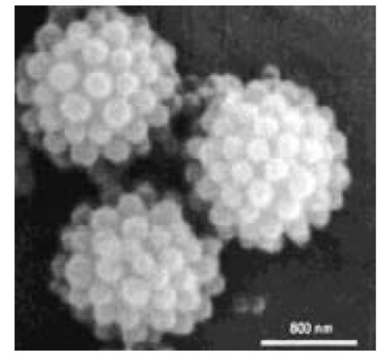
Types of colloidal particles

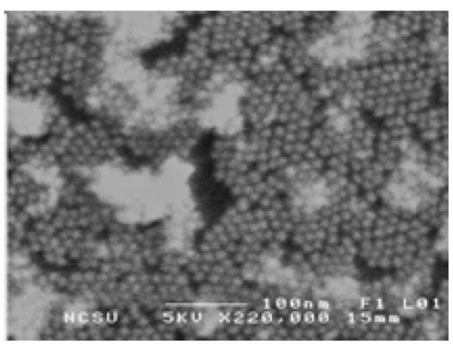
- **Dispersions**
  - **Suspensions – spherical colloids**

Latex: polymer spheres



Silica on polymer

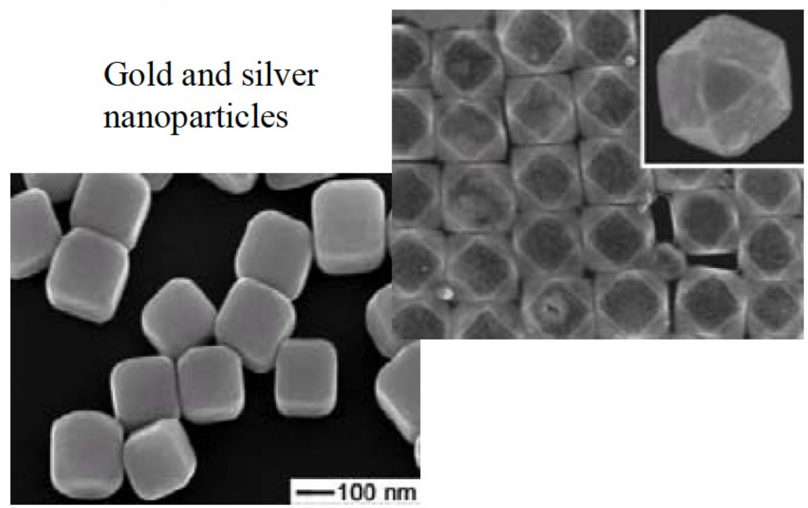




Gold nanoparticles

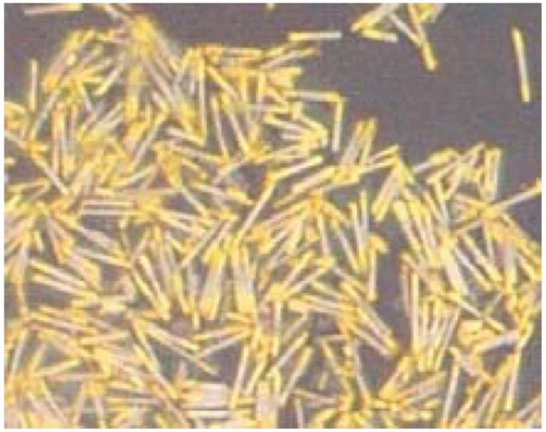
- **Suspensions – cubes, etc.**

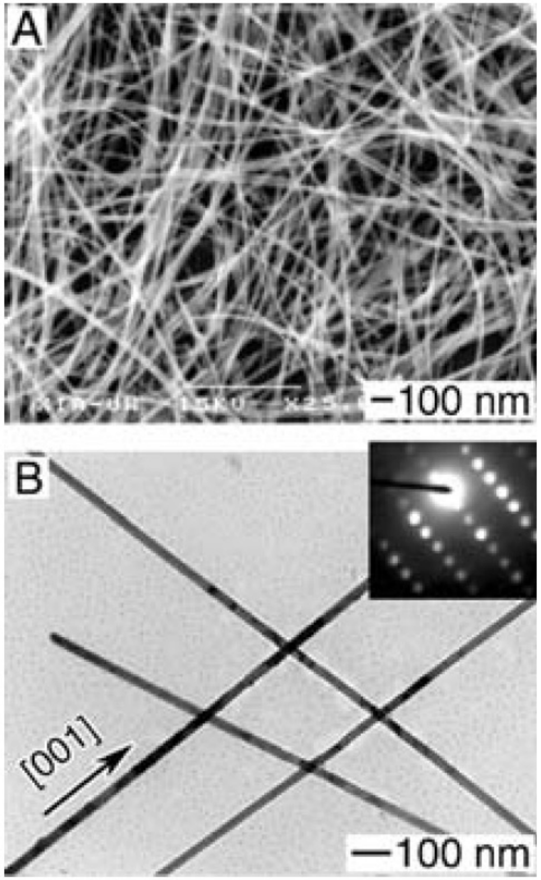
Gold and silver nanoparticles



Types of colloidal particles

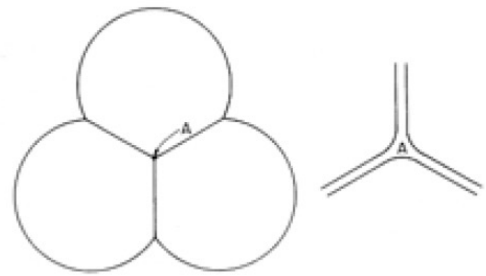
- **Suspensions – rods and fibers**

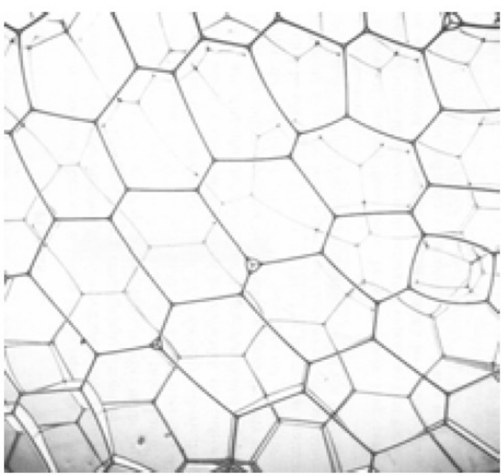


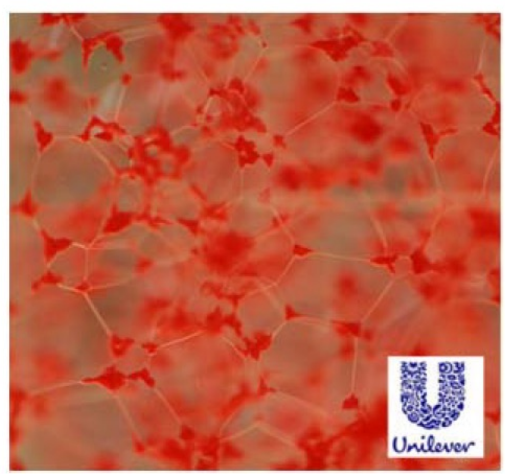


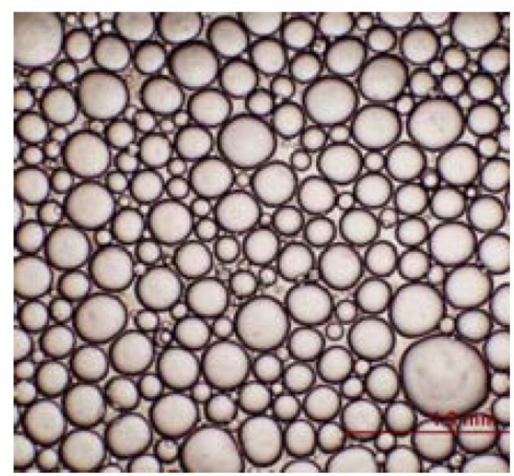
Types of colloidal particles

- **Dispersions contd.**
  - **Foams**
  - **Emulsions**





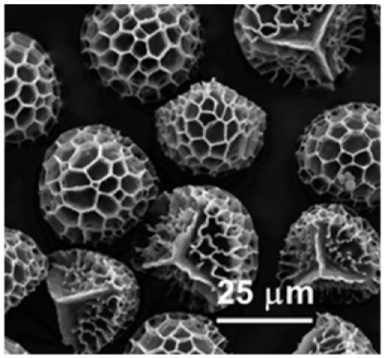




The thin liquid films are of colloidal scale

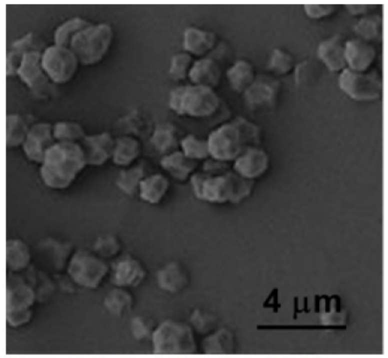
Types of colloidal particles - biological particles

Moss Spore



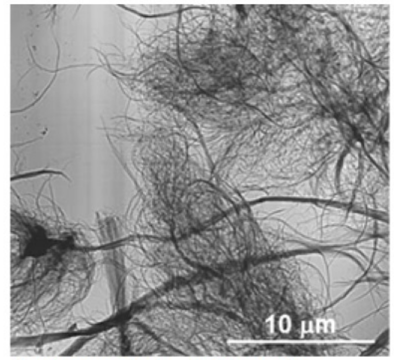
Binks et al., *Langmuir*, **2005**

Quinoa Starch



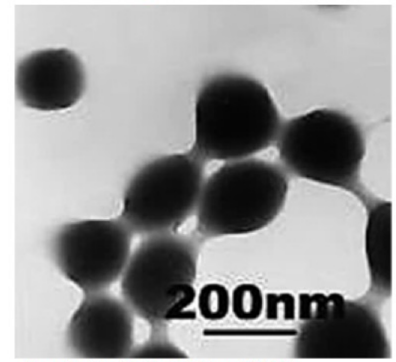
Rayner et al., *J. Sci. Food Agric.*, **2012**

Fibrillated Cellulose



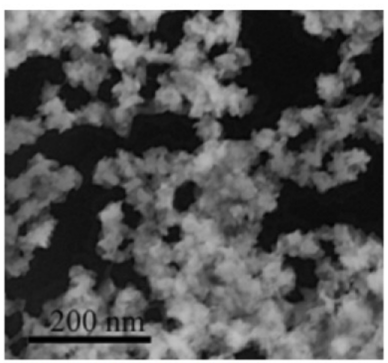
Andresen et al., *J. Dispersion Sci. Technol.*, **2007**

Ethyl Cellulose



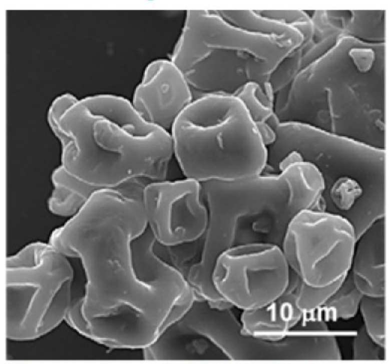
Jin et al., *Soft Matter*, **2012**

Chitosan



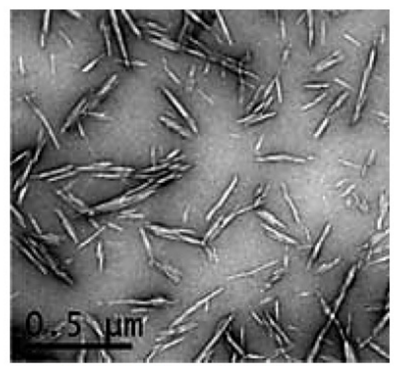
Wei et al., *Polymer*, **2012**

Soy Protein



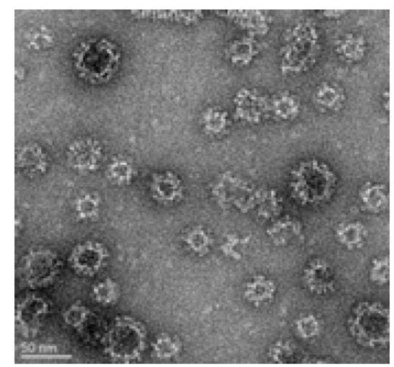
Paunov et al., *J. Colloid Interface Sci.*, **2007**

Cellulose Nanocrystals



Kalashnikova et al., *Soft Matter*, **2013**

Viruses and VLPs



Mertens and Velev, unpubl. **2014**

What makes a colloidal system different?

- **Size range: 1 nm – 10 μm**

  - Is size the main characteristic of a colloid?

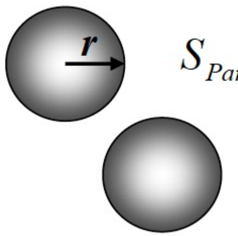
- **A true definition is based on thermodynamics:**

  Colloidal systems are the ones where the macroscopic properties are determined by the action of intermolecular forces on the nanoscale

- **Related to the size: small size → large surface area → large role of the intermolecular (surface) forces**

What makes a colloidal system different?

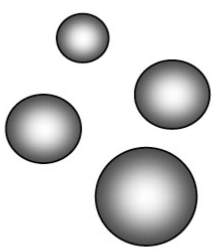
- **Shape, size and volume – monodisperse sample**

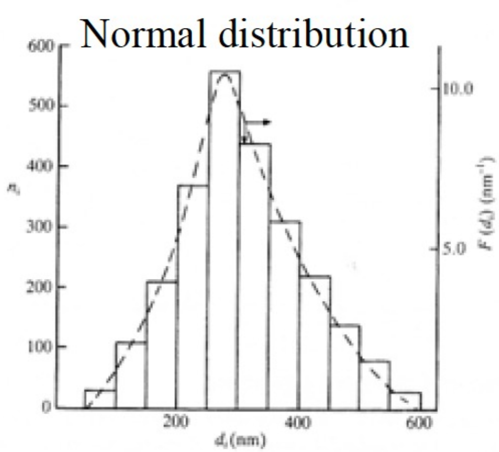


$$S_{Particle} = 4\pi r^2 \qquad V_{Particle} = \frac{4}{3}\pi r^3 \qquad m_1 = V_{Particle}\,\rho$$

$$m_{Total} = N_{particles}\, V_{particle}\, \rho$$

- **Size distribution – polydisperse sample**





Average diameter (size average) $\quad \bar{d} = \frac{1}{N}\sum_i n_i d_i$

Total surface area $\quad A_S = \sum_i n_i \pi d_i^2$

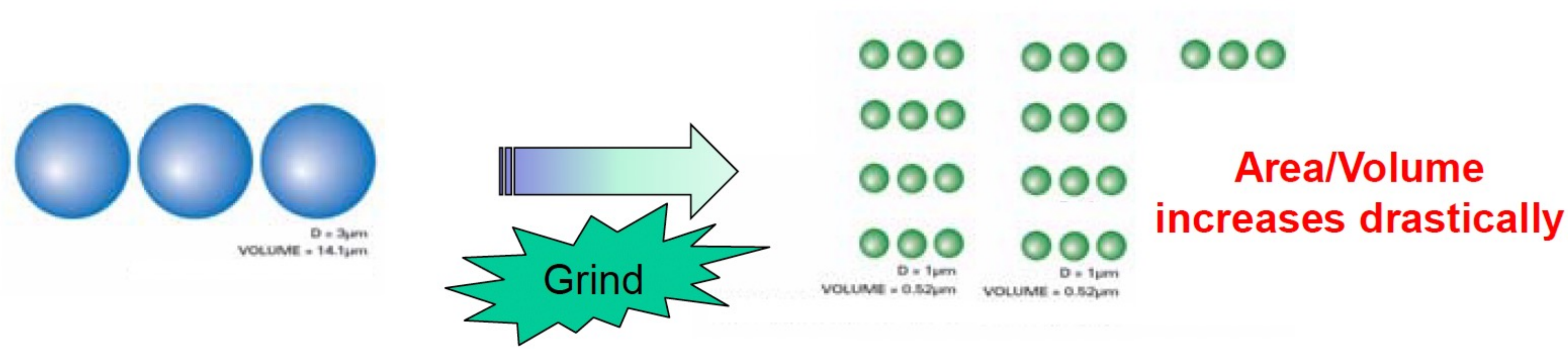
Number-Average (surface average) diameter $\quad \bar{d}_{NA}^2 = \frac{A_S}{\pi N}$

What makes a colloidal system different?

- **Surface area**

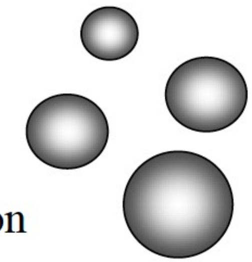
Number and area of spheres obtained by dividing a sphere of $r = 1$ cm into smaller spheres

Radius of sphere	No of spheres	Area/sphere, m^2	Total area, m^2
1 cm	1	1.26×10^{-3}	1.26×10^{-3}
1 µm	10^{12}	1.26×10^{-11}	1.26×10^{1}
100 nm	10^{15}	1.26×10^{-13}	1.26×10^{2}
10 nm	10^{18}	1.26×10^{-15}	1.26×10^{3}



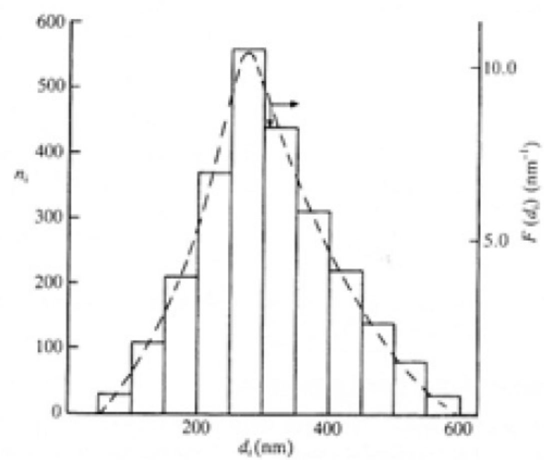
What makes a colloidal system different?

- **Size distribution – two most common ones are:**



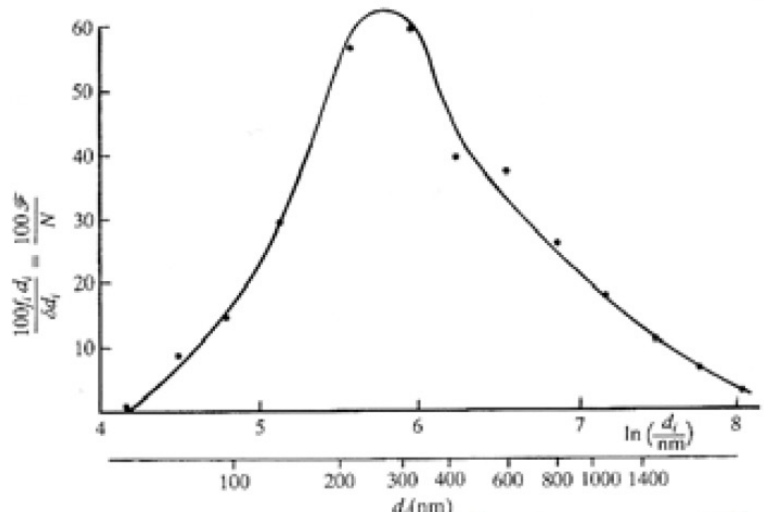
the parameter σ is its standard deviation. The variance of the distribution is σ^2

Normal distribution



$$f_{norm}(d) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{d-\bar{d}}{\sigma}\right)^2\right]$$

Log-Normal distribution

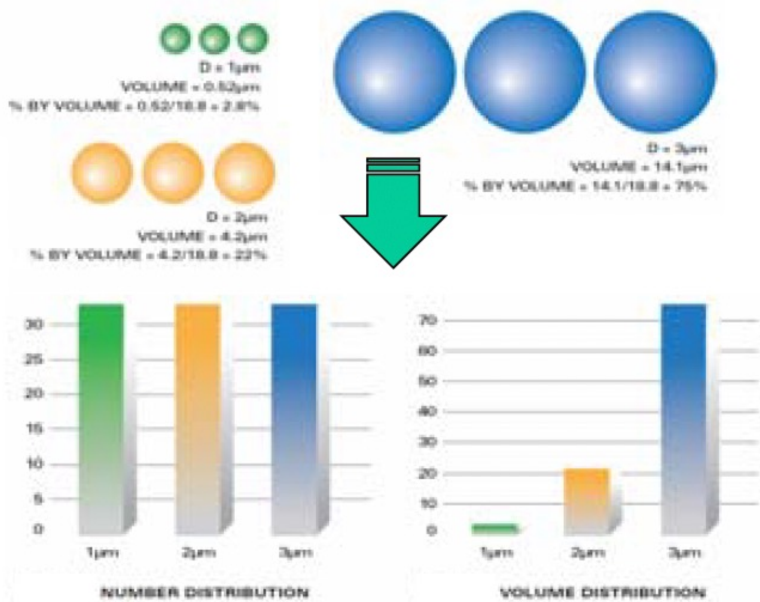


$$f_{norm}(\ln d) = \frac{1}{\ln\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2}\left(\frac{\ln d - \ln\bar{d}}{\ln\sigma}\right)^2\right]$$

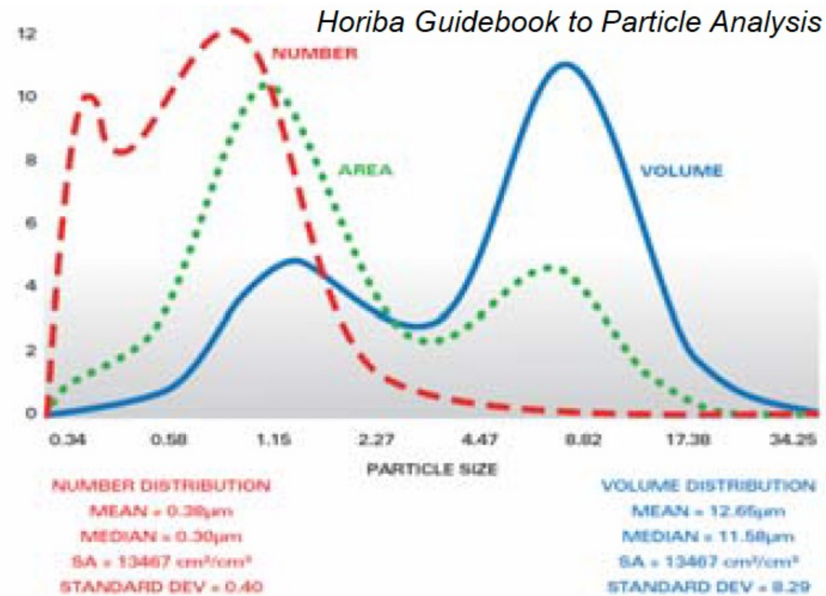
Large fraction of small particles, results from some practical processes

Note the difference in polydisperse particle distributions by number, area and volume

- Visualization of 9 particle "sample"



- Example of a real particle sample



$$A_S = \sum_i n_i \pi d_i^2 \quad \rightarrow \quad \pi \bar{d}_{NA}^2 = \frac{A_S}{N} \quad \rightarrow \quad \bar{d}_{NA} = \sqrt{\frac{A_S}{\pi N}} \quad \not\leftrightarrow \quad \bar{d} = \frac{1}{N}\sum_i n_i d_i$$

Total surface area (A_S)

Number-Average (surface average) mean diameter ($\bar{d}_{NA}$)

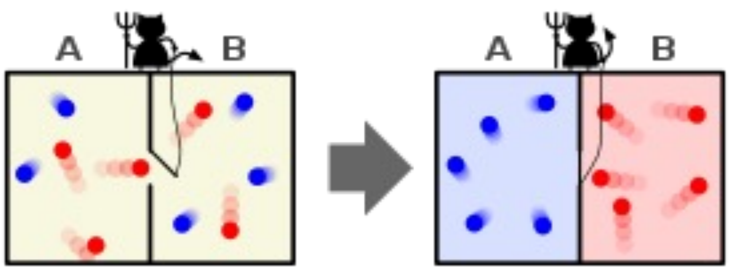
Not the same as the size average diameter unless dispersion is monodisperse

Stability in solution

- One of the hallmarks (or benefits) of having a colloidal particle system is that they can be stably dispersed in another medium, which allow them to take on many properties of the medium.
- For example: mobility (locomotion, cell transport in blood vessel); energy harvesting from thermal fluctuation (maxwell’s demon, active colloids, pollen)

Maxwell’s demon

- In the thought experiment, a demon controls a small massless door between two chambers of gas. As individual gas molecules (or atoms) approach the door, the demon quickly opens and closes the door to allow only fast-moving molecules to pass through in one direction, and only slow-moving molecules to pass through in the other. Because the kinetic temperature of a gas depends on the velocities of its constituent molecules, the demon's actions cause one chamber to warm up and the other to cool down. This would decrease the total entropy of the system, without applying any work, thereby violating the second law of thermodynamics.



https://en.wikipedia.org/wiki/Maxwell%27s_demon

Criticisms - Landauer's principle

- The essence of the physical argument is to show, by calculation, that any demon must "generate" more entropy segregating the molecules than it could ever eliminate by the method described. That is, it would take more thermodynamic work to gauge the speed of the molecules and selectively allow them to pass through the opening between A and B than the amount of energy gained by the difference of temperature caused by doing so.
- Leó Szilárd pointed out that **a real-life Maxwell's demon would need to have some means of measuring molecular speed, and that the act of acquiring information would require an expenditure of energy**. Since the demon and the gas are interacting, we must consider the total entropy of the gas and the demon combined. The expenditure of energy by the demon will cause an increase in the entropy of the demon, which will be larger than the lowering of the entropy of the gas.

Criticisms

- Ralph Landauer realized that **some measuring processes need not increase thermodynamic entropy as long as they were thermodynamically reversible**. He suggested these "reversible" measurements could be used to sort the molecules, violating the Second Law. However, due to the connection between entropy in thermodynamics and information theory, this also meant that the recorded measurement must not be erased. In other words, **to determine whether to let a molecule through, the demon must acquire information about the state of the molecule and either discard it or store it**. Discarding it leads to immediate increase in entropy but the demon cannot store it indefinitely.
- however well prepared, eventually the demon will run out of information storage space and must begin to erase the information it has previously gathered. **Erasing information is a thermodynamically irreversible process that increases the entropy of a system**.

Information entropy

- The defining expression for entropy in the theory of statistical mechanics established by Ludwig Boltzmann and J. Willard Gibbs in the 1870s, is of the form:

$$S = -k_{\mathrm{B}} \sum_i p_i \ln p_i$$

where p_i is the probability of the microstate *i* taken from an equilibrium ensemble, and k_B is the Boltzmann's constant.

https://en.wikipedia.org/wiki/Entropy_in_thermodynamics_and_information_theory

Information entropy

- The defining expression for entropy in the theory of information established by Claude E. Shannon in 1948 is of the form:

$$H = -\sum_i p_i \log_b p_i$$

where p_i is the probability of the message m_i taken from the message space M, and b is the base of the logarithm used.

Information entropy

- If all the microstates are equiprobable (a microcanonical ensemble), the statistical thermodynamic entropy reduces to the form, as given by Boltzmann,

$$S = k_{\mathrm{B}} \ln W$$

- where W is the number of microstates that corresponds to the macroscopic thermodynamic state. Therefore S depends on temperature.

Information entropy

- If all the messages are equiprobable, the information entropy reduces to the Hartley entropy

$$H = \log_b |M|$$

where $|M|$ is the cardinality of the message space *M*.

In mathematics, the **cardinality** of a set is a measure of the number of elements of the set. For example, the set $A = \{2, 4, 6\}$ contains 3 elements, and therefore A has a cardinality of 3.

The cardinality of a set may also be called its size

Information entropy

- in the words of G. N. Lewis writing about chemical entropy in 1930, "**Gain in entropy always means loss of information, and nothing more**".
- in the discrete case using base two logarithms, the reduced Gibbs entropy is equal to the average of the minimum number of yes–no questions needed to be answered in order to fully specify the microstate.

Information entropy

- If there are N moles, kilograms, volumes, or particles of the unit substance, **the relationship between h (in bits per unit substance) and physical extensive entropy** in nats is:

$$S = k_{\mathrm{B}} \ln(2) N h$$

- where ln(2) is the conversion factor from base 2 of Shannon entropy to the natural base e of physical entropy.
- **N h is the amount of information in bits needed to describe the state of a physical system with entropy S**.

Landauer's principle

- the **minimum energy E required (and therefore heat Q generated) by an ideally efficient memory change or logic operation by irreversibly erasing or merging N h bits of information** will be S times the temperature which is

$$E = Q = Tk_{\mathrm{B}} \ln(2) Nh$$

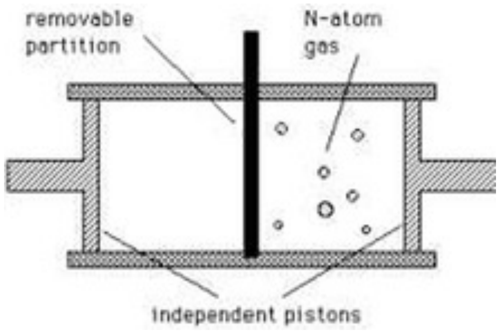
- where h is in informational bits and E and Q are in physical Joules. This has been experimentally confirmed.

https://www.nature.com/articles/nature10872

Landauer's principle

- any information that has a physical representation must somehow be embedded in the statistical mechanical degrees of freedom of a physical system.
- the entropy of the environment is increased by gaining an appropriate quantity of heat (specifically $kT \ln 2$) for every 1 bit of randomness erased.

Szilárd's engine



- Consider Maxwell's set-up, but with only a single gas particle in a box. If the supernatural demon knows which half of the box the particle is in (equivalent to a single bit of information), it can close a shutter between the two halves of the box, close a piston unopposed into the empty half of the box, and then extract **kT ln 2** joules of useful work if the shutter is opened again. The particle can then be left to isothermally expand back to its original equilibrium occupied volume.
- This was experimentally demonstrated using a Brownian particle.
- **This is also why computing (or information manipulation) will always cost energy.**

https://www.nature.com/articles/nphys1821

Stability in solution

- **Thermodynamically stable?**

- **Lyophillic**: "Solvent loving" (for water = "hydrophillic").
  - Thermodynamically stable
  - Spontaneous dispersion process

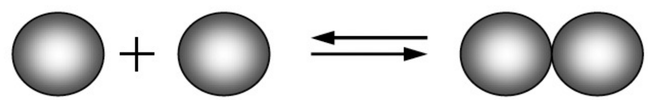
$$\Delta G_{dispersing} = \Delta H - T\,\Delta S < 0$$

- **Lyophobic**: "Solvent hating" (for water = "hydrophobic").
  - Thermodynamically unstable (but may be kinetically stable)
  - Dispersion process consumes external energy

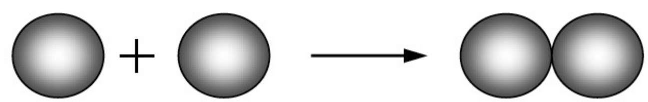
$$\Delta G_{dispersing} = \Delta H - T\,\Delta S > 0$$

Stability in solution

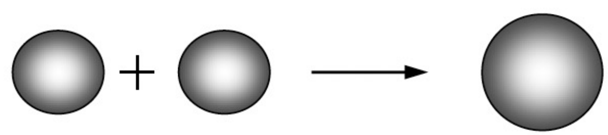
- **Kinetic stability**
  - **Flocculation (reversible)**



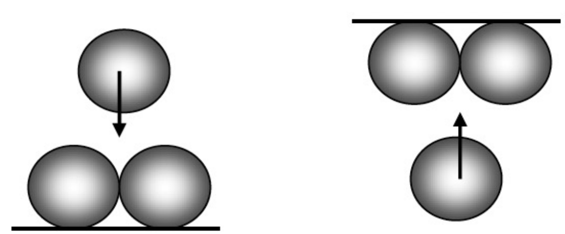
  - **Aggregation (irreversible)**



  - **Coalescence (emulsions), breakdown (foams)**

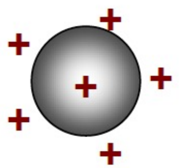


  - **Sedimentation or creaming**



How do we characterize dispersions?

- **Surface charge**

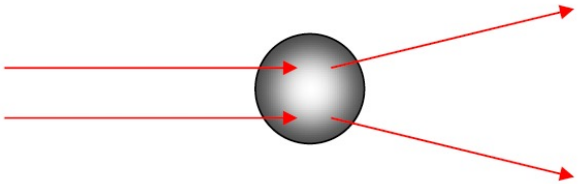


- **Surface properties**

- **Osmotic pressure**

$$\pi = R\,T\,C_p\,(1 + B_{22}\,C_p + \ldots)$$

- **Interaction with light and other radiation**



Osmotic Pressure

- Jacobus van't Hoff found a quantitative relationship between osmotic pressure and solute concentration, expressed in the following equation:

$$\Pi = icRT$$

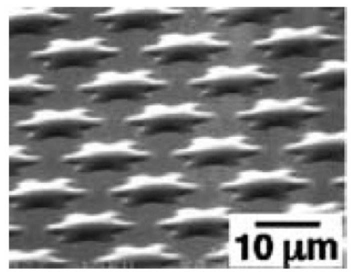
where Π is osmotic pressure, i is the dimensionless van 't Hoff index, c is the molar concentration of solute, R is the ideal gas constant, and T is the absolute temperature

- This formula applies when the solute concentration is sufficiently low that the solution can be treated as an ideal solution. Note the similarity of this formula to the ideal gas law.
- For more concentrated solutions the van 't Hoff equation can be extended as a power series in solute concentration.

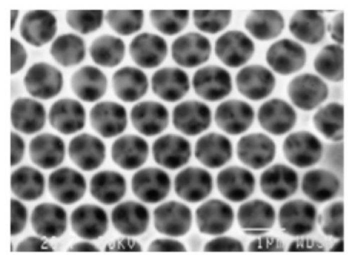
Particles and Particle Systems in Nanotechnology

Recent technological developments have provided an unprecedented degree of control ...

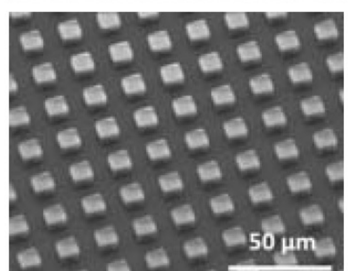
- Surface properties



- Structure



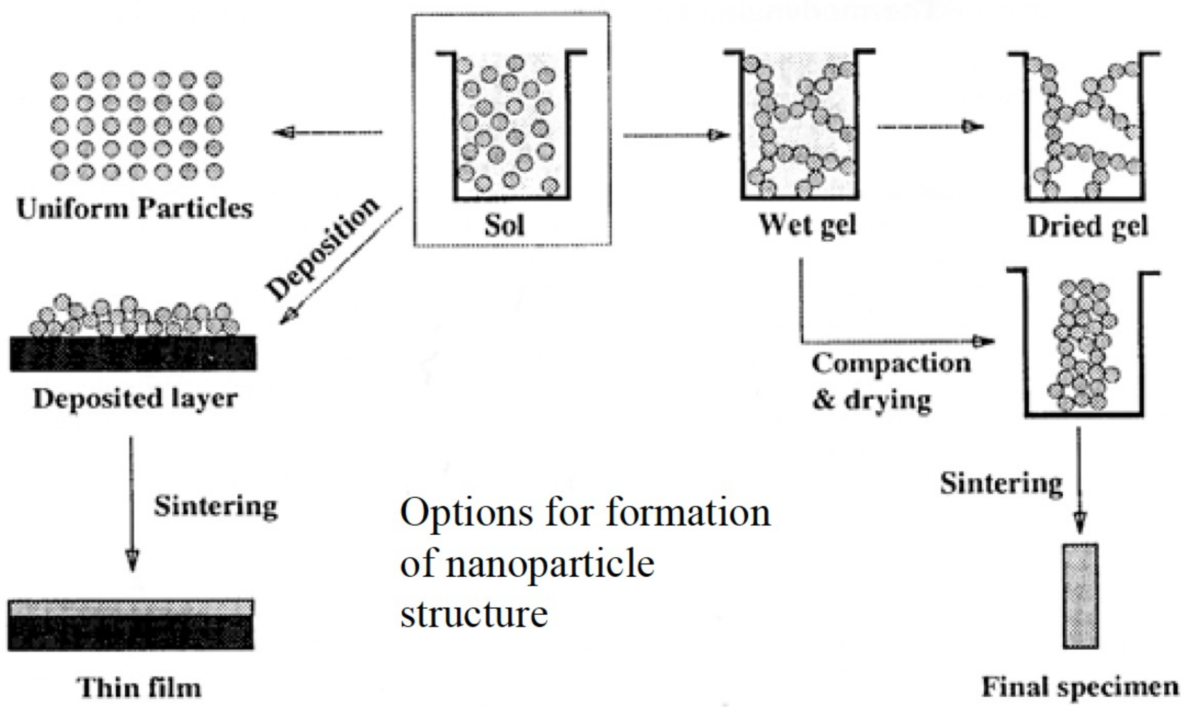
- Size and shape



... which opens new technology frontiers discussed in the later part of this course

Particles and Particle Systems in Nanotechnology

- **Control of the interactions**



Options for formation of nanoparticle structure

The least understood and developed nanotechnology tool

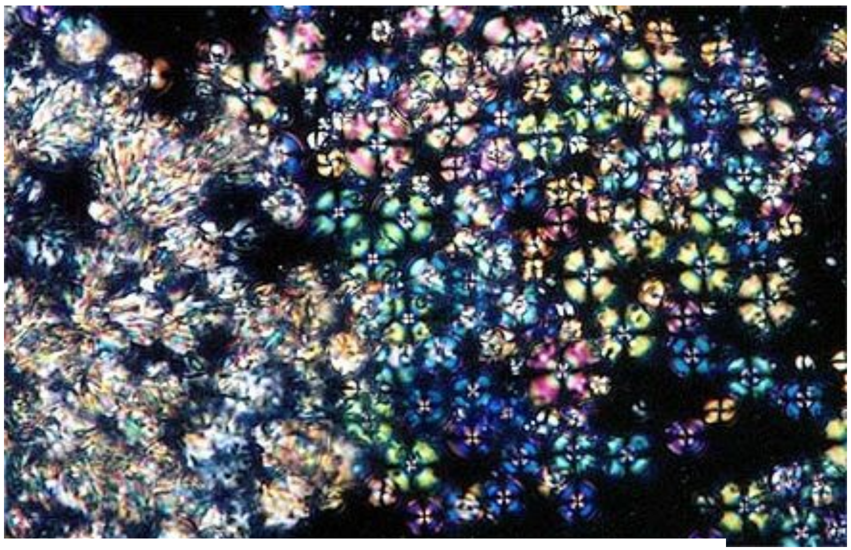
Let me give you some more "mundane" example in everyday life…

Liquid crystals

- Many computers, such as laptops, have flat-panel screens or displays that contain liquid crystals.
- Liquid crystals are composed of small semirigid molecules that are elliptical or oblong in shape and spontaneously orient, forming anisotropic fluids.
- The direction of the preferred orientation in a liquid crystal can be switched by application of an electric field, and since the optical properties (such as birefringence) are strongly orientation-dependent, the liquid crystal acts as an optical switch.
- The speed of switching in a liquid crystal is controlled by its viscous and elastic properties, as well as by its dielectric susceptibility. Displays can also be made in which the liquid crystal is emulsified as roughly 1-μm droplets in a polymer gel.

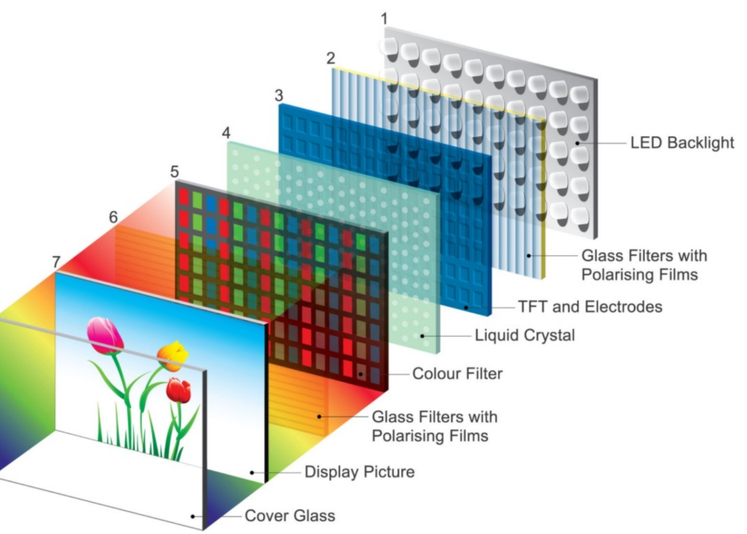
Liquid Crystals

Nematic

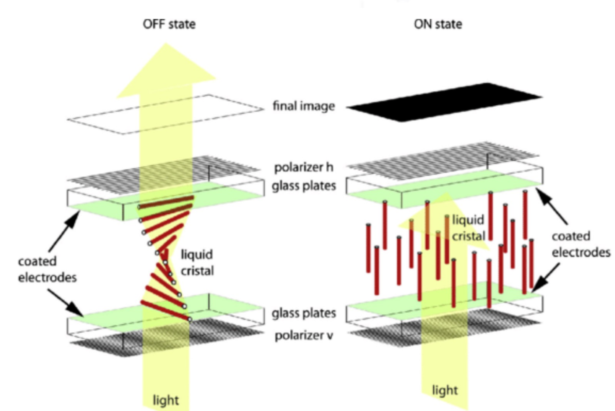


Smectic A

Smectic C



https://en.wikipedia.org/wiki/Liquid_crystal#:~:text=Liquid%20crystals%20(LCs)%20are%20a,in%20a%20crystal%2Dlike%20way.



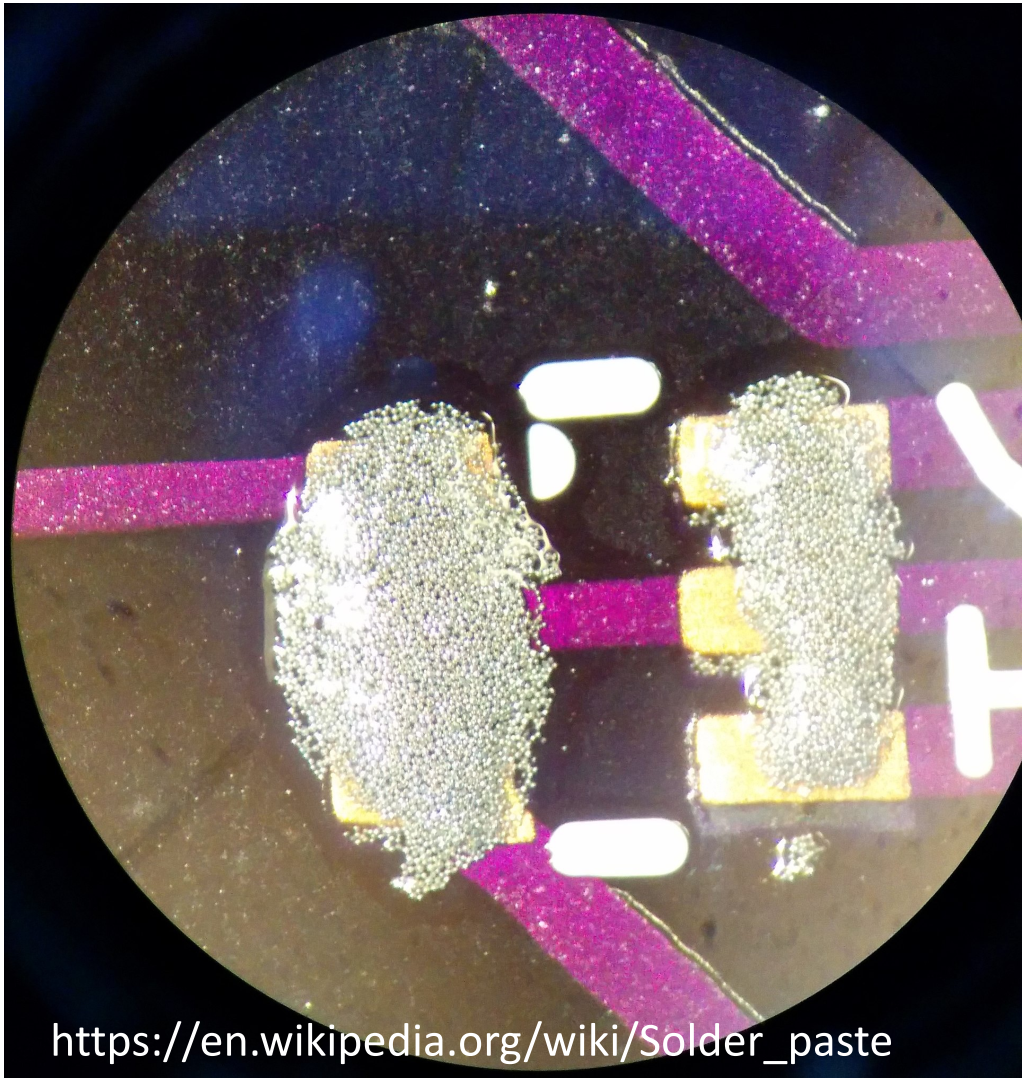
Liquid Crystals

- The simplest liquid crystal phase is the nematic. In a **nematic** phase, calamitic organic molecules lack a crystalline positional order, but do self-align with their long axes roughly parallel. The molecules are free to flow and their center of mass positions are randomly distributed as in a liquid, but their orientation is constrained to form a long-range directional order.
- The **smectic** phases, which are found at lower temperatures than the nematic, form well-defined layers that can slide over one another in a manner similar to that of soap.
- The **smectic A phase** has molecules organized into layers. In the **smectic C phase**, the molecules are tilted inside the layers.

Solder particles

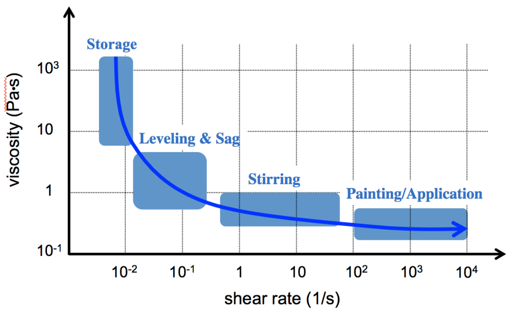
- When electronic devices are mounted onto circuit boards, their conducting leads must be soldered into place. A convenient way to do so is to first lay down small spots, or "pads," of solder paste onto the circuit board by screen printing.
- The components can then be placed onto the boards, with wire leads immersed into the solder-paste pads; the **50-μm lead solder balls** in the paste are melted by heating, which allows them to flow together to provide a conductive bond between the wire leads and the circuit board.
- Coalescence of the molten solder balls is promoted by the **acid in the viscous suspending medium, or "flux,"** which dissolves oxidized lead from the surfaces of the solder balls.
- As a result of environmental legislation, most solders today, including solder pastes, are made of lead-free alloys

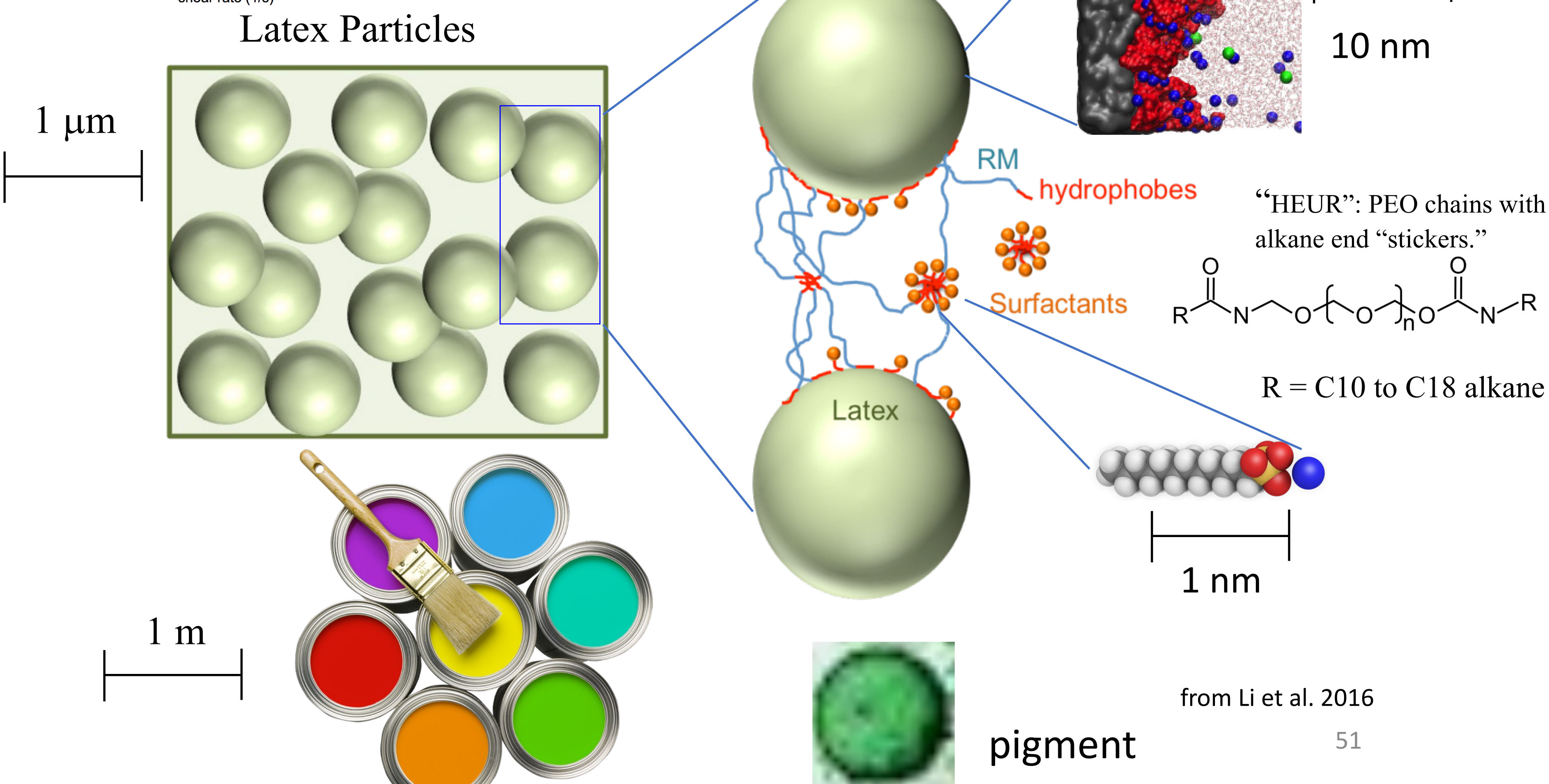
Solder particles



Latex Paint

PMMA particles (latex), end-modified water-soluble polymers, surfactant





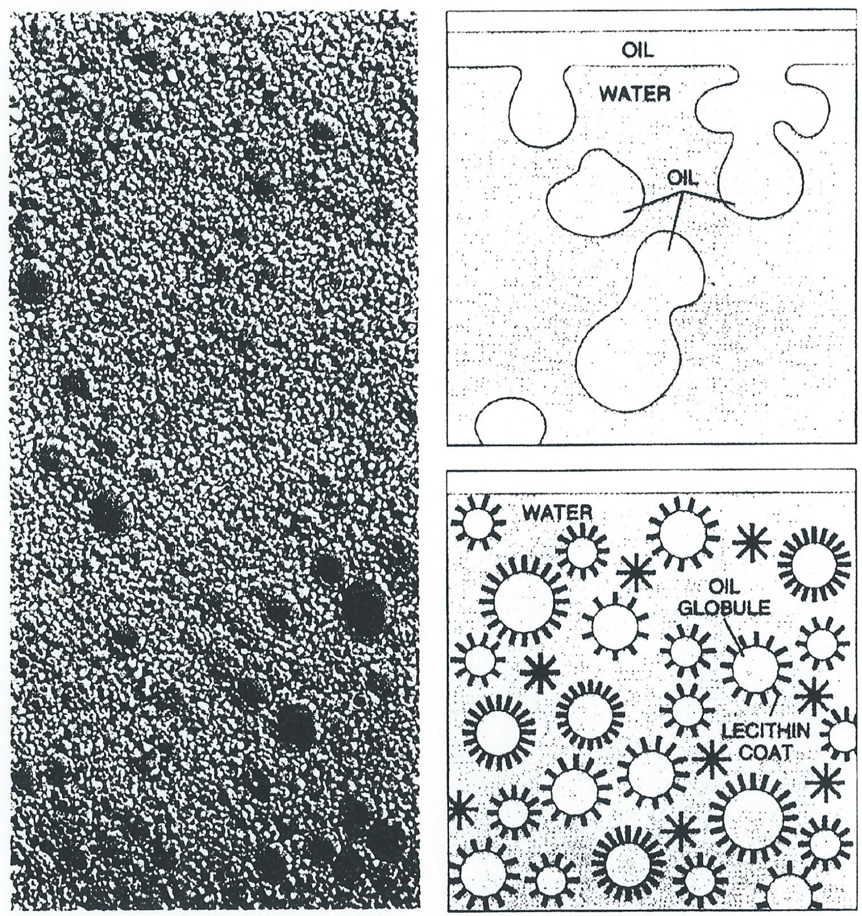
from Li et al. 2016

Foods

- Mayonnaise: **droplets of vegetable oil in the vinegar or lemon juice are stabilized by lecithin, which is a natural surfactant contained in egg yolk**.
- Mayonnaise is an emulsion; that is, it contains one liquid dispersed in another.
- Mayonnaise holds its shape against gravity, but flows smoothly under slight forces --- it has a **yield stress**, a stress below which it will not flow.
- **The magnitude of the yield stress is controlled by the size of the droplets** (around 10 µm for good mayo) and by the **surface tension of the droplet surfaces**.

Mayonnaise

mayonnaise micrograph



from RG Larson

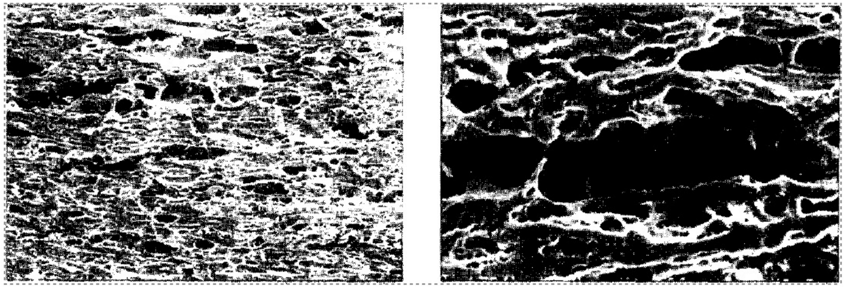
Ice cream

- Another even more delicious complex fluid is ice cream, which is a partially frozen emulsion of cream, milk, sugar, and flavoring and is foamed with 40-50% by volume air.
- A quick way to make ice cream is to pour an equal volume of liquid nitrogen into the ice cream ingredients while stirring with a wooden spoon (why wooden spoon?). The liquid nitrogen both cools and foams the ingredients. The quick cooling keeps ice crystals small and the texture smooth.

Mustard

- Mayonnaise and ice cream both have a yield stress, which is produced in these foods by droplets and air bubbles that must deform if flow is to occur. Another food with a yield stress is **mustard; it is neither an emulsion nor a foam, but a suspension or paste**, containing particles 30 μm or so in diameter that attract each other and form a weak network.
- Mustard is made by simply grinding mustard seeds, together with vinegar, salt, spices, and water, into a mash.

Cheese and gelatin



Sharkasi and Kilara, MRS Bulletin, July 1994, p.47

- Cheese is made from milk, which is itself a complex fluid containing micelles (small 0.04- to 0.3-μm spheres) of the protein casein.
- By adding a weak acid and the appropriate enzyme (rennet), the micelles are destroyed and the proteins then gel, or congeal together to form a solid mass, or curd, which separates from the remaining liquid.
- See electron micrographs of mozzarella cheese, in which stretching the curd orients the protein fibers.
- Ordinary gelatin is also a gel, produced from a biological protein called collagen mixed with a high volume fraction of water.

Kombucha

https://www.youtube.com/watch?v=NtkuZ0b5c6A&ab_channel=JourneytotheMicrocosmos
(0:45 – 6:00)

Kombucha

- Kombucha is produced by symbiotic fermentation of sugared tea using a symbiotic culture of bacteria and yeast (SCOBY). The microbial populations in a SCOBY vary. The yeast component generally includes *Saccharomyces cerevisiae*, along with other species; the bacterial component almost always includes *Gluconacetobacter xylinus* to oxidize yeast-produced alcohols to acetic acid (and other acids).

Kombucha

- **Yeast produce invertase as a public good that enables both yeast and bacteria to metabolize sugars**. Bacteria produce a surface biofilm which may act as a public good providing protection from invaders, storage for resources, and greater access to oxygen for microbes embedded within it. **The ethanol and acid produced during the fermentative process (by yeast and bacteria, respectively) may also help to protect the system from invasion by microbial competitors from the environment.** Thus, kombucha can serve as a model system for addressing important questions about the evolution of cooperation and conflict in diverse multispecies systems.

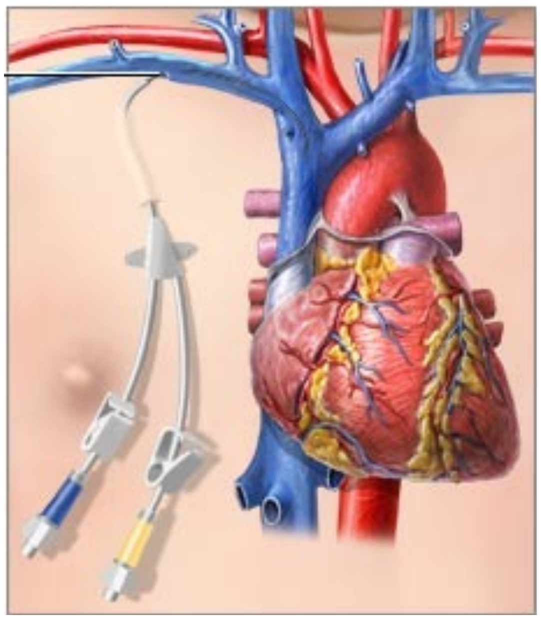
doi: 10.7717/peerj.7565

biofilms: bacterial colonies

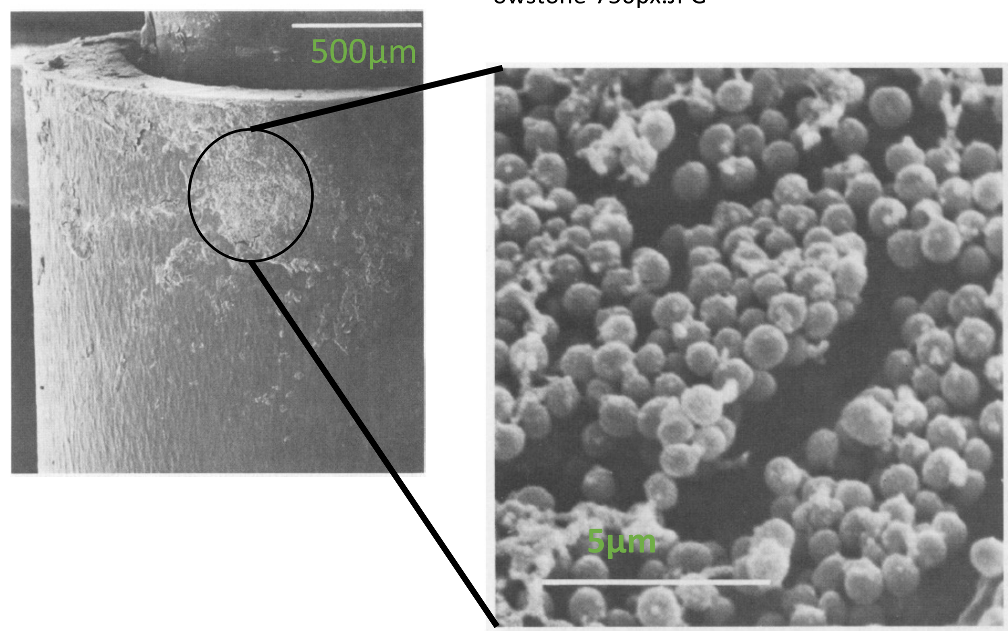
- 17 million biofilm infections and 550,000 deaths per year in US[1]
- Infections frequently from biofilm formation on medical devices

biofilm at Yellowstone Park

https://en.wikipedia.org/wiki/Biofilm#/media/File:Bacteria_mats_near_Grand_Prismatic_Spring_in_Yellowstone-750px.JPG



Central venous catheter[2]

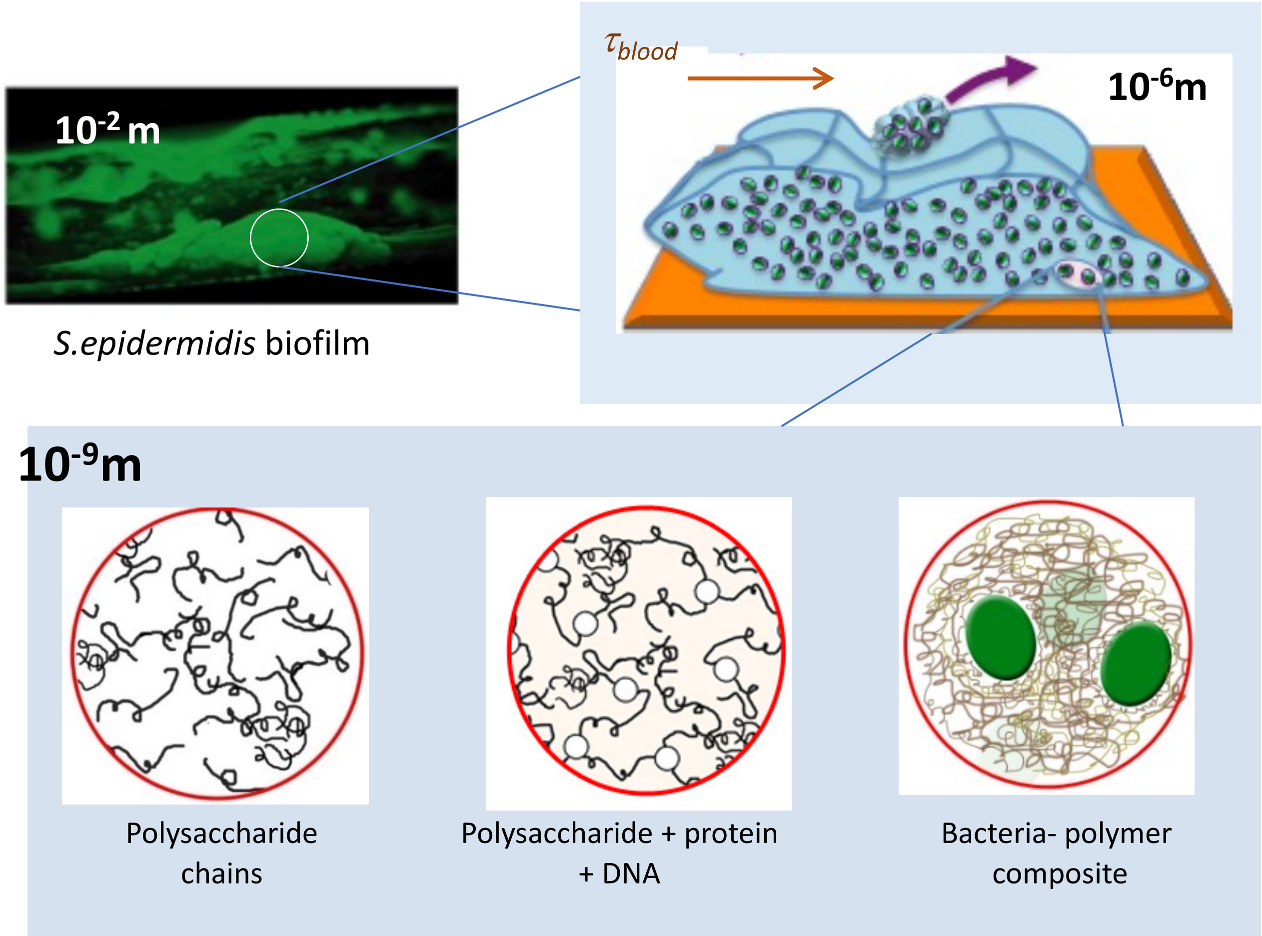


SEM of biofilm on catheter[3]

[1]Wolcott et al., *Journal of Wound Care*, (2010).
[2]http://www.umm.edu/imagepages/19861.htm
[3]Marrie, Costerton, *J. Clin. Microbiol*., (1984).

from MJ Solomon

Biofilm Structure and its Extrapolymeric Substance (EPS)



<u>EPS promotes</u> [1,2]

- biofilm formation
- resistance to antibiotics
- resistance to blood shear and biofilm viscous and elastic modulus

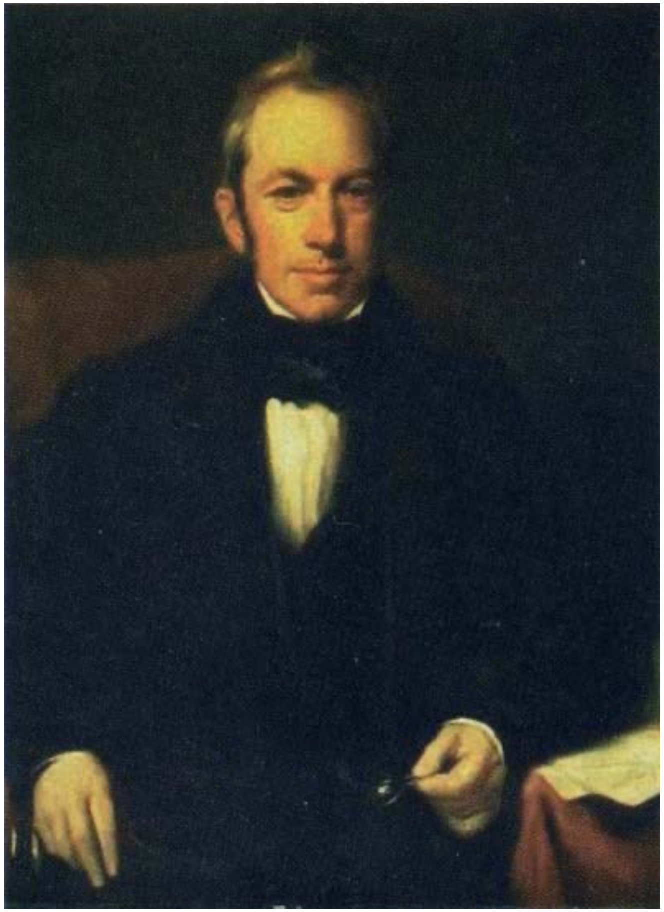
from MJ Solomon

[1] Wilking,J., et al., *MRS Bulletin* (2011)
[2] Flemming, H-C., et al *Nat. Rev. Microbiol.* 8 (2010)

Microparticles in Liquids

Prof. Robert Brown

1827



What Happens if there is no Brownian Motion

Before vibration

After vibration

“Brazil nut effect”

https://www.youtube.com/watch?v=ktA9CjbvDRo

The importance of diversity of inclusion

Before vibration

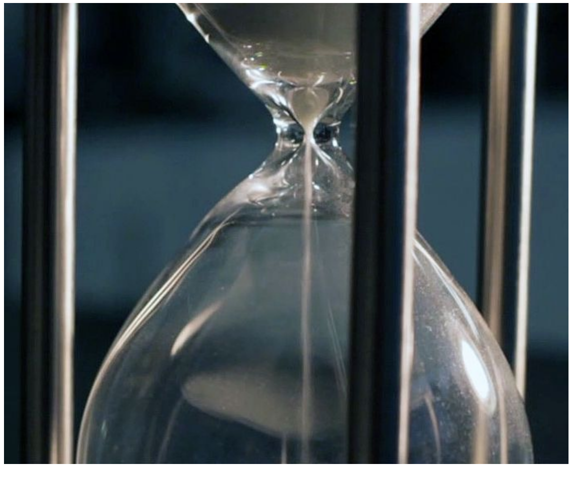
After vibration

"Brazil nut effect"

https://www.youtube.com/watch?v=ktA9CjbvDRo

Granular materials

- From far away, **flowing sand resembles a liquid**, streaming down the center of an hourglass like water from a faucet. But up close, one can make out **individual grains** that slide against each other, **forming a mound** at the base that holds its shape, much **like a solid**.



https://news.mit.edu/2012/sand-modeling-0406

Granular materials

- Sand's curious behavior — part fluid, part solid — has made it difficult for researchers to predict how it and other granular materials flow under various conditions. A precise model for granular flow would be particularly useful in optimizing processes such as pharmaceutical manufacturing and grain production, where tiny pills and grains pour through industrial chutes and silos in mass quantities.
- Granular material is the second-most-handled material in industry, second only to water.
- understanding how granular materials flow could also help predict geological phenomena such as landslides and avalanches and help engineers come up with new ways to generate better traction in sand

Modeling granular materials

- it’s extremely difficult to predict how grains behave collectively: While kernels of corn are solid, they behave more like a liquid when flowing through a silo. Simulating the flow of grains in silos, and in other geometries, has proven a tricky, centuries-old problem for scientists.
- made a key adjustment to an existing set of equations that are normally used to describe the way liquids flow. To predict, for example, how water flows through a funnel, these equations essentially divide the volume of water into a fine grid, predicting how the whole volume will flow based on how water molecules behave in a single box of the grid.

https://news.mit.edu/2013/research-update-sand-modeling-0325

Modeling granular materials

- a **continuum model** — essentially means “blurring out” individual grains or molecules.
- Such models work well for fluids like water, which is easily divisible into particles that are almost infinitesimally small. However, grains of sand are much larger than water molecules — **the size of an individual grain can significantly affect the accuracy of a continuum model**.
- For example, a model can precisely estimate how water molecules flow in a cup, mainly because the size of a molecule is so much smaller than the cup itself. For the same relative scale in the flow of sand grains, the sand’s container would have to be the size of San Francisco.

Size matters

- But why exactly does size matter? When modeling water flow, molecules are so small that their effects stay within their respective cubes. As a result, a model that averages the behavior of every cube in a grid, and assumes each cube is a separate entity, gives a fairly accurate flow estimate. However, in granular flow, much **larger grains such as sand can cause “bleed over” into neighboring cubes**, creating cascade effects that are not accounted for in existing models.

Size matters

- There's more chatter between neighbors. The basic mechanical properties of a cube of grains become influenced by the movement of neighboring cubes.
- in granular flow, size matters: Because grains are not vanishingly small compared to their environment — they are much larger than water molecules — their size affects how neighboring grains move, making it impossible to generalize the flow of one tiny box of grains to an entire silo. Recognizing this, researchers added **a new "nonlocal" term to the equations to account for grain size**.

Motion-induced quicksand

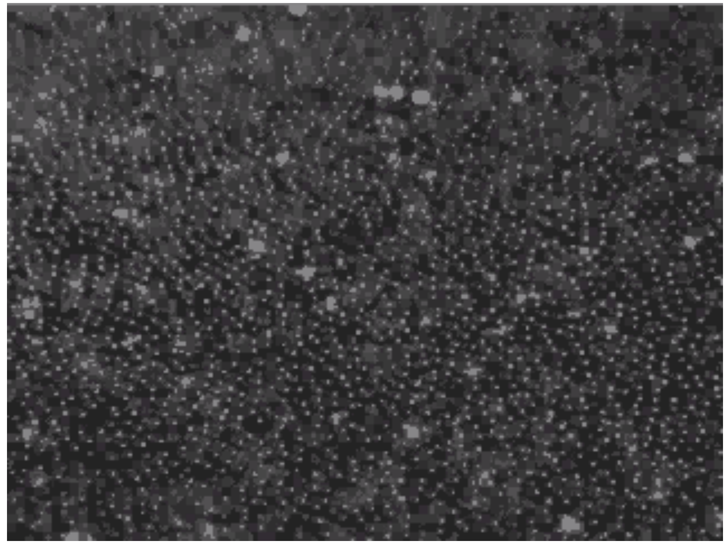
- a scenario in which the movement of sand in one location changes the character of sand at a distance.
- for example, if you're walking in the desert and there's a sand dune landslide far away, you will start to sink, very slowly. It's very wacky behavior.

https://news.mit.edu/2014/motion-induced-quicksand-1117

DOI:10.1103/PhysRevLett.113.178001

Motion-induced quicksand

- “annular Couette cell” — a geometry resembling the bowl of a food processor, with a rotating ring in its base. In experiments, researchers have filled a Couette cell with sand, and attempted to push a rod horizontally through the sand.
- In a stationary Couette cell, the rod will not budge without a significant application of force. If, however, the cell’s inner ring is rotating, the rod will move through the sand with even the slightest push — even where the sand doesn’t appear to be moving.



- By spinning the turntable at the bottom of the bucket, the turntable "liquifies" the entire granular assembly, even the material very far from it. It has converted a granular solid (a material that has no trouble supporting the weight of the ball) to a granular fluid in which any object denser than the granular pile will sink. The ball is acting like a force probe, showing that the response of the grains has switched from solid to fluid.

Motion-induced quicksand

- **secondary rheology**, where motion at a primary location affects movement at a secondary, removed region.
- if a constant force is applied to the probe, then **spinning the inner ring twice as fast will cause the probe to creep twice as fast**

Motion-induced quicksand

- a general mechanism that researchers have held regarding granular flow, termed a “**force chain network**.” According to this theory, there exist tiny forces between individual grains that connect the whole of a network. Any perturbation, or movement in the material, can ripple through the network, causing forces between particles to “flicker”. Such flickering may not be strong enough to move particles, but may **weaken bonds between grains, allowing objects to move through the material as if it were liquid**.

Motion-induced quicksand

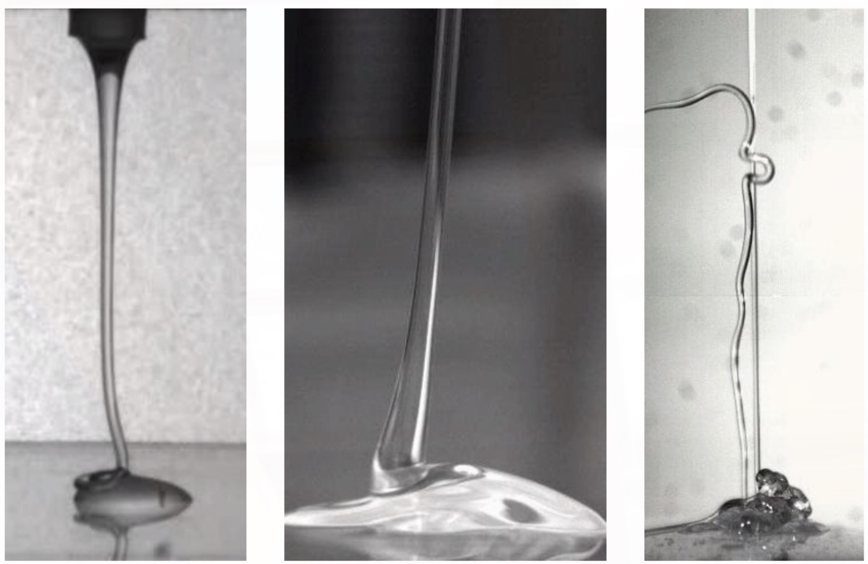
- Because particles at the wall are connected to particles far away thru the force chain network, by jiggling around over here, you're making the forces fluctuate thru the material.
- While **quicksand** — **a soupy mix of sand and water — may look like a solid, the water in it essentially lubricates the frictional contacts between grains** such that when someone steps in it, they sink. In the case of **dry granular media**, it's perturbations through the force chain network, not water, that are in essence **lubricating the contacts between grains**.

You need to log in using your umich.edu account in order to access this poll

Lecture 2 Poll: Non-Newtonian Fluids

How many of the following four substances are Non-Newtonian Fluids? Honey, Blood, Snake-venom, Oobleck (cornstarch and water).

- A. 1
- B. 2
- C. 3
- D. 4



https://nnf.mit.edu/home/billboard/topic-1#:~:text=Honey%20is%20a%20purely%20viscous,complexity%20by%20studying%20viscoelastic%20jets.&text=A.,silicone%20oil%2C%20a%20Newtonian%20liquid.

Long URL https://forms.gle/Lc4w1escYjnTAZeb9

Short URL https://shorturl.at/ezCGL

Shear-thickening fluids

- This starch-water mixture behaves similarly to quicksand. Under gentle force, the sand grains slide past one another because they are lubricated by water. Sudden pressure displaces the water from the gaps and forces the solid components together, dramatically increasing the resistance. As with quicksand, starch molecules are separated by a layer of water. And when strong forces bring them into contact, the mixture coalesces.
- Could an oobleck-like substance fill highway potholes and temporarily harden as a car drives over it? Or perhaps the slurry could pad the lining of bulletproof vests, morphing briefly into an added shield against sudden impacts.

https://news.mit.edu/2019/oobleck-behavior-predict-cornstarch-1006

Shear-thickening fluids

- Granular material in oobleck is much finer than sand: A single particle of cornstarch is about 1 to 10 microns wide and about one-hundredth the size of a grain of sand. Kamrin says particles at such a small scale experience effects that larger particles such as sand do not. For instance, because cornstarch particles are so small, they can be influenced by temperature, and by electric charges that build up between particles, causing them to slightly repel against each other.

Shear-thickening fluids

- As long as you squish slowly, the grains will repel, keeping a layer of fluid between them, and just slide past each other, like a fluid.
- But if you do anything too fast, you'll overcome that little repulsion, the particles will touch, there will be friction, and it'll act as a solid.
- the more the underlying particles make frictional, as opposed to lubricated, contact. If it is slowly and gently deformed, oobleck is less viscous, with particles that are more evenly distributed and that repel against each other, like a liquid.

https://www.pnas.org/doi/abs/10.1073/pnas.1908065116

Liquid armor

http://www.youtube.com/watch?v=rYIWfn2Jz2g
(1:00 – 5:00)

http://nvate.com/4233/liquid-armor/

http://rpg.drivethrustuff.com/product/25395/Dept-7-Technology-Update-Liquid-Armor?it=1

Newtonian Fluids

https://www.rheosense.com/applications/viscosity/newtonian-non-newtonian#:~:text=A%20common%20example%20of%20shear,as%20the%20shear%20rate%20increases.

- Newtonian fluids are named after Sir Issac Newton (1642 - 1726) who described the flow behavior of fluids with a simple linear relation between shear stress [mPa] and shear rate [1/s]. This relationship is now known as Newton's Law of Viscosity, where the proportionality constant η is the viscosity [mPa-s] of the fluid:

$$\underbrace{\tau}_{\text{Shear Stress}} = \underbrace{\eta}_{\text{Viscosity}} \times \underbrace{\dot{\gamma}}_{\text{Shear Rate}}$$

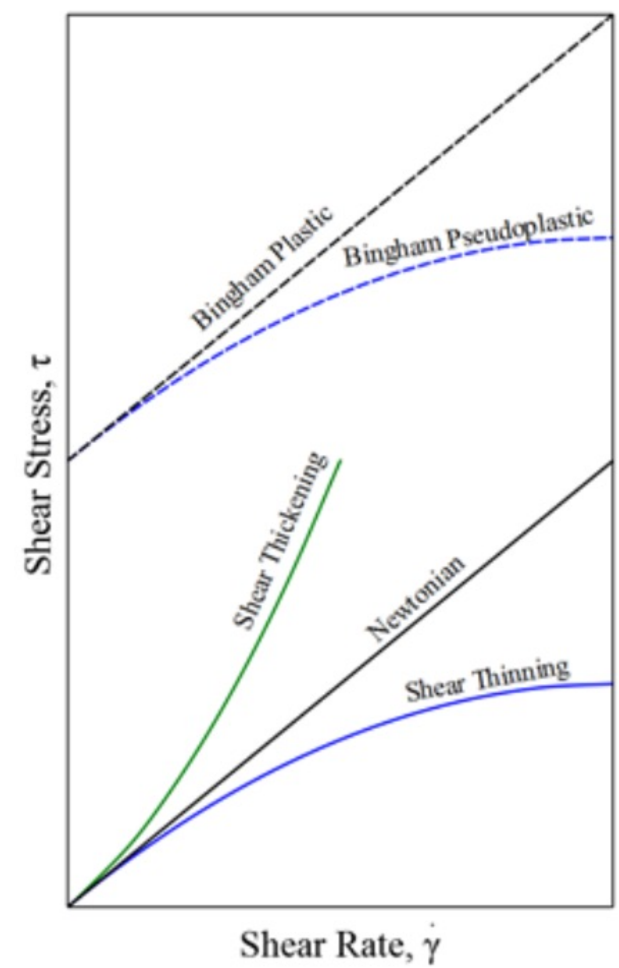


Figure 1. Shear stress as a function of shear rate for several kinds of fluids

Newtonian Fluids

- Some examples of Newtonian fluids include water, organic solvents, and honey. For those fluids viscosity is only dependent on temperature. This means that the viscosity of Newtonian fluids will remain a constant (see Figure 2) no matter how fast they are forced to flow through a pipe or channel (i.e. viscosity is independent of the rate of shear).

$$\underbrace{\tau}_{\text{Shear Stress}} = \underbrace{\eta}_{\text{Viscosity}} \times \underbrace{\dot{\gamma}}_{\text{Shear Rate}}$$

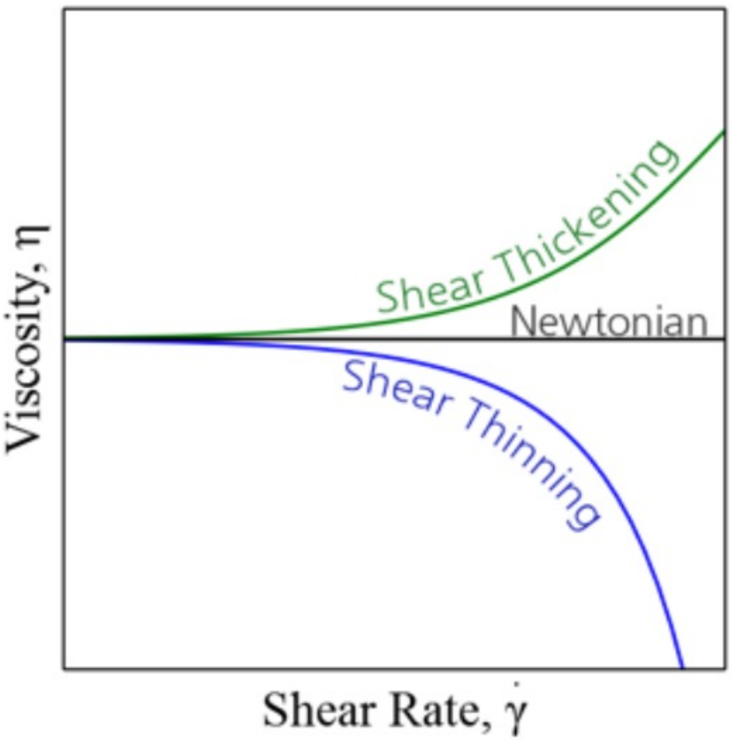


Figure 2. Viscosity of Newtonian, Shear Thinning and Shear Thickening fluids as a function of shear rate.

Non-Newtonian Fluids

- An exception to the rule is Bingham plastics, which are fluids that require a minimum stress to be applied before they flow. These are strictly non-Newtonian, but once the flow starts they behave essentially as Newtonian fluids (i.e. shear stress is linear with shear rate). A great example of this kind of behavior is mayonnaise.

$$\underbrace{\tau}_{\text{Shear Stress}} = \underbrace{\eta}_{\text{Viscosity}} \times \underbrace{\dot{\gamma}}_{\text{Shear Rate}}$$

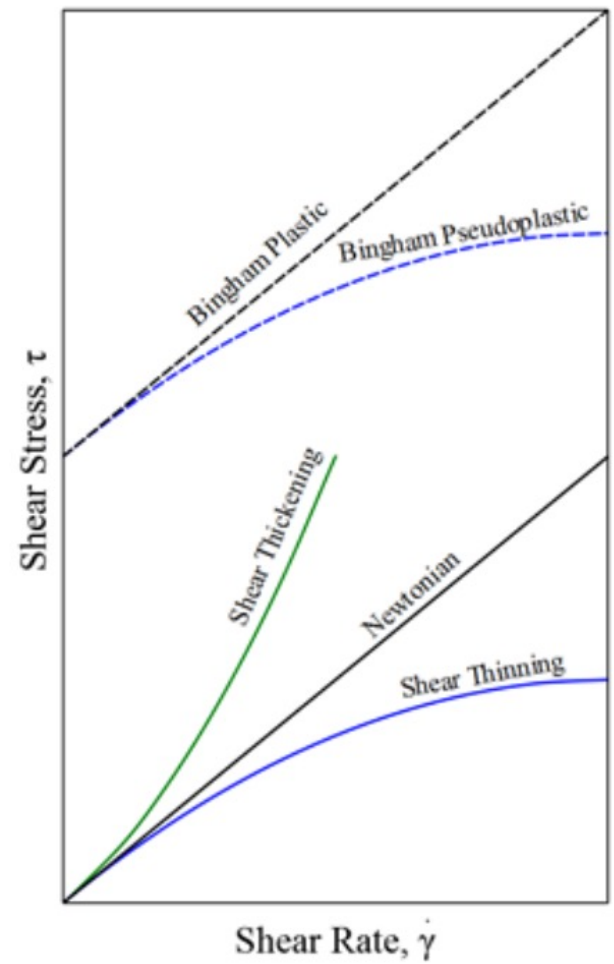


Figure 1. Shear stress as a function of shear rate for several kinds of fluids

Non-Newtonian Fluids

- Newtonian fluids are normally comprised of small isotropic (symmetric in shape and properties) molecules that are not oriented by flow.
- In reality most fluids are non-Newtonian, which means that their viscosity is dependent on shear rate (Shear Thinning or Thickening) or the deformation history.

$$\underbrace{\tau}_{\text{Shear Stress}} = \underbrace{\eta}_{\text{Viscosity}} \times \underbrace{\dot{\gamma}}_{\text{Shear Rate}}$$

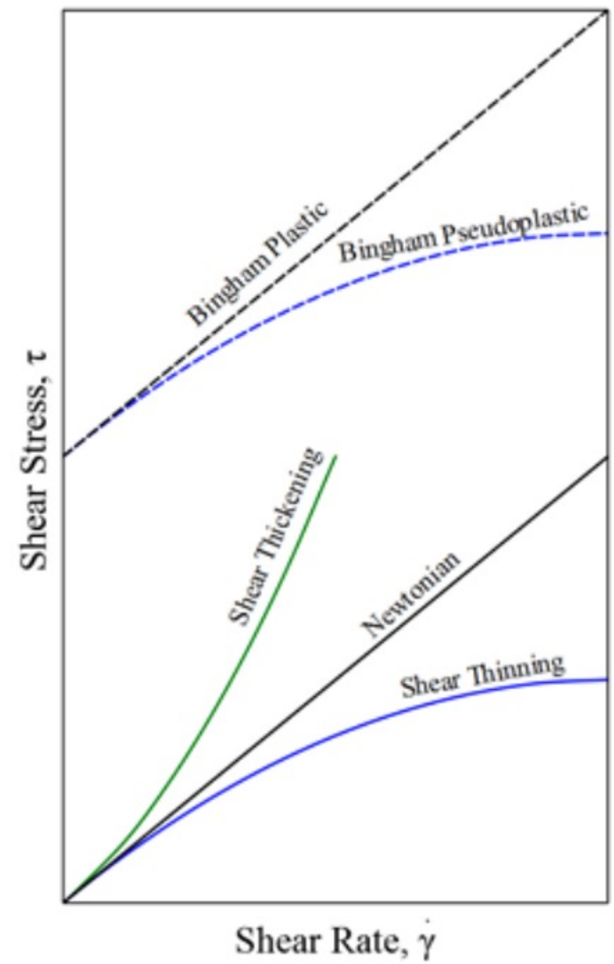


Figure 1. Shear stress as a function of shear rate for several kinds of fluids

Non-Newtonian fluids

- Cornstarch and water
- https://www.youtube.com/watch?v=2mYHGn_Pd5M&ab_channel=ScienceMandotcom
- https://www.youtube.com/watch?v=mYTerCbDUzE&ab_channel=TheUniversityofChicago

Shear-thinning fluids

MARCH 12, 2021 | 4 MIN READ

Ketchup Is Not Just a Condiment: It Is Also a Non-Newtonian Fluid

Everybody's favorite red sauce may be thin or thick, depending on how it is handled

BY H. JOACHIM SCHLICHTING

- a thin strip of ketchup should be applied to a hot dog so that it does not end up all over your clothes—even when you are cramming it into your mouth. Yet ketchup should not be sticky either: with each bite, the sauce should melt in your mouth and not require any chewing to be savored.
- https://www.youtube.com/watch?v=FrLh1GILomc&ab_channel=America%27sTestKitchen

https://www.scientificamerican.com/article/ketchup-is-not-just-a-condiment-it-is-also-a-non-newtonian-fluid/#:~:text=In%20the%20case%20of%20%E2%80%9Cnon,the%20form%20of%20a%20thickener.

Shear-thinning fluids

- In physical terms, ketchup undergoes stress via shaking, spreading or eating. The bottom part of the mass, which is viscous at rest, sits on a solid base and is held there by adhesion or other forces, while the upper layers are situated in a parallel direction. In “Newtonian” fluids, viscosity is independent of the pressure being applied to the fluid per unit of area. In the case of “non-Newtonian” fluids such as ketchup, the situation is different: a stronger force reduces the viscosity.

Shear-thinning fluids

- This behavior, known as shear thinning, is caused by polymers that are added to the sauce (a concoction of tomato paste, sugar and other ingredients) in the form of a thickener. Polymers are microscopic complex molecules composed of long chains of atoms, which become entangled and release energy into their surroundings. In this state, the polymer is quite pulpy and viscous. Applying sufficiently large shear force, however, provides the energy needed to stretch the polymer molecules out and align them lengthwise. The chains now easily slide past one another, and macroscopically, the result is reduced viscosity.

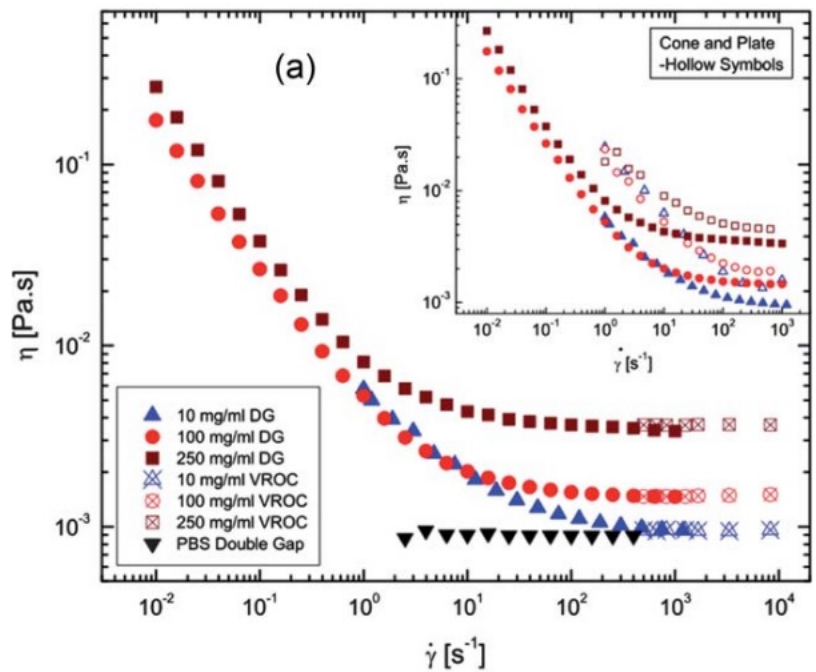
Shear-thinning fluids

- Once the shear forces have subsided, and the ketchup is allowed to settle, the polymer molecules become entangled again and release energy. This process takes a bit of time, which explains why the sauce does not immediately resolidify after the shaking and shearing.
- Everyday life offers other examples of shear-thinning substances such as shampoo. A small amount of shampoo flows very slowly into the palm of your hand, giving you time to lift it to your head and rub it into your hair. There is hardly any resistance because the shear force of lathering thins out the fluid.

DOI: 10.1039/c0sm01312a

Shear-thinning fluids

- Shear thinning fluids, also known as pseudo-plastics, are ubiquitous in biological processes. Why should blood be shear-thinning?
- Blood. Bovine Serum Albumin (BSA)
- Snake Venom: Once moving, the shear-thinning properties of the venom decrease the venom's viscosity, increasing its flow rate down the fang and into the snake's prey.

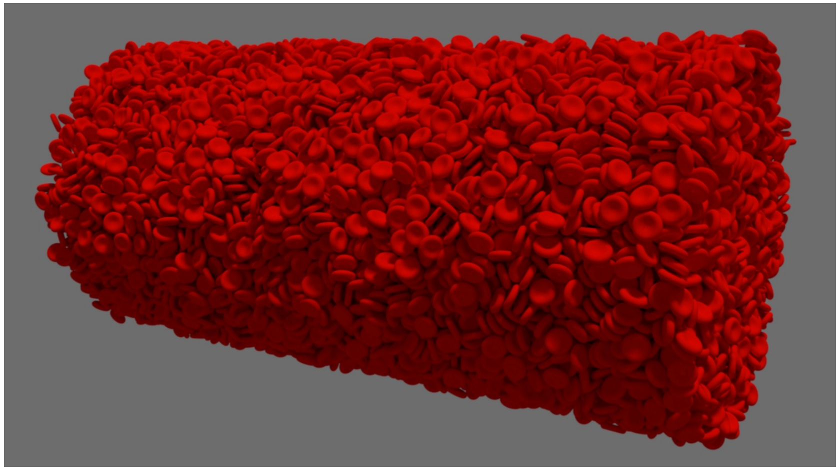


https://journals.aps.org/prl/abstract/10.1103/PhysRevLett.106.198103

Blood

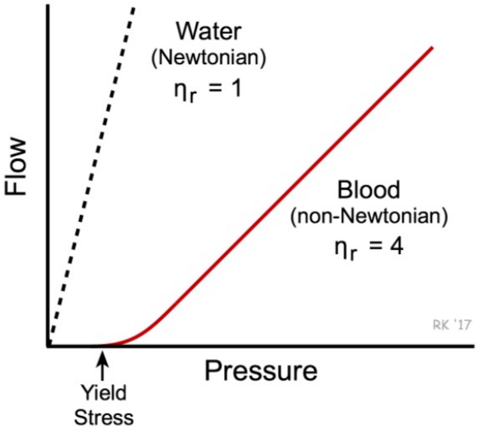
https://en.wikipedia.org/wiki/Blood

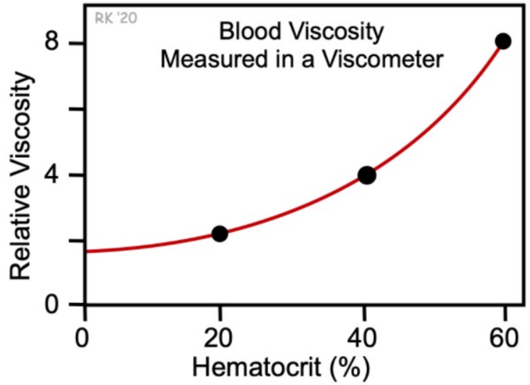
from Zavodszky et al. Front. Physiol. 2017



https://www.frontiersin.org/articles/10.3389/fphys.2017.00563/full

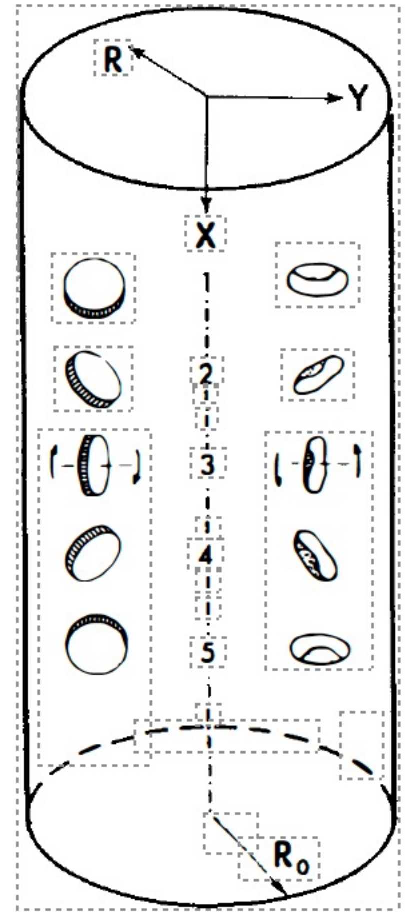
https://www.cvphysiology.com/Hemodynamics/H011#:~:text=In%20fact%2C%20plasma%20at%2037,platelets)%20further%20increases%20the%20viscosity.





Blood

- Blood is a suspension containing around 40% by volume blood cells, which are flexible puckered disks roughly 10 μm in diameter, suspended in clear plasma, which is itself a viscoelastic fluid containing interacting protein macromolecules.
- The viscoelastic properties of blood determine the pumping load on the heart, for example, and affect the performance of artificial heart valves.
- At modest shear rates, the flow and orientation properties of red blood cells are similar to those of rigid disks (see figure), while at higher shear rates their flow behavior resembles that of fluid droplets.
- At low shear rates, red blood cells often stack up up like poker chips into so-called rouleaux.

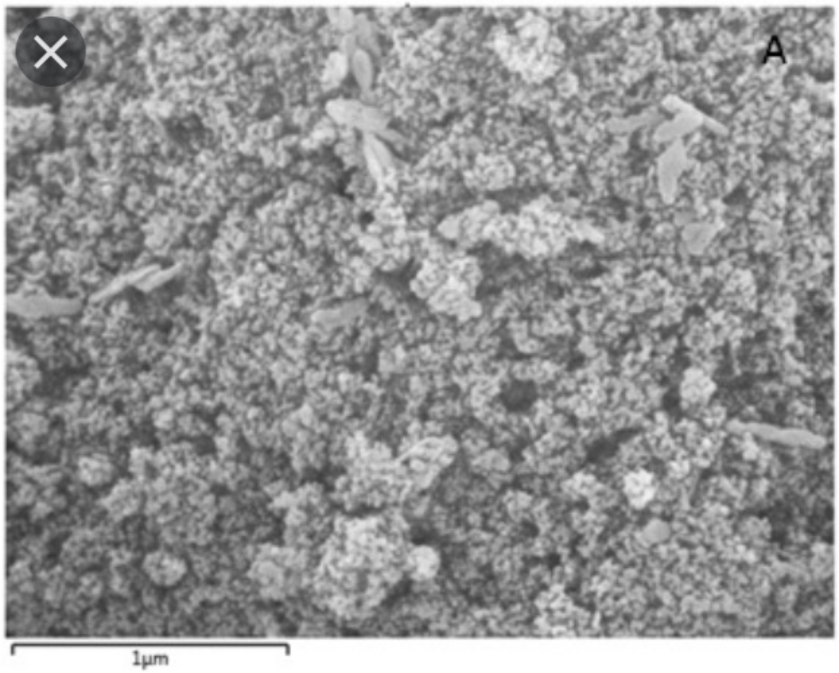


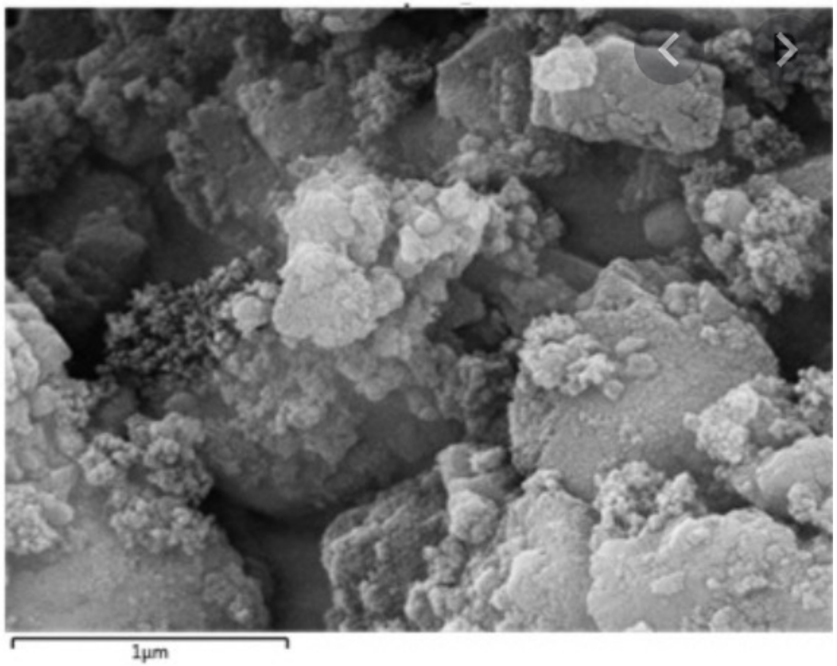
Personal Care Products

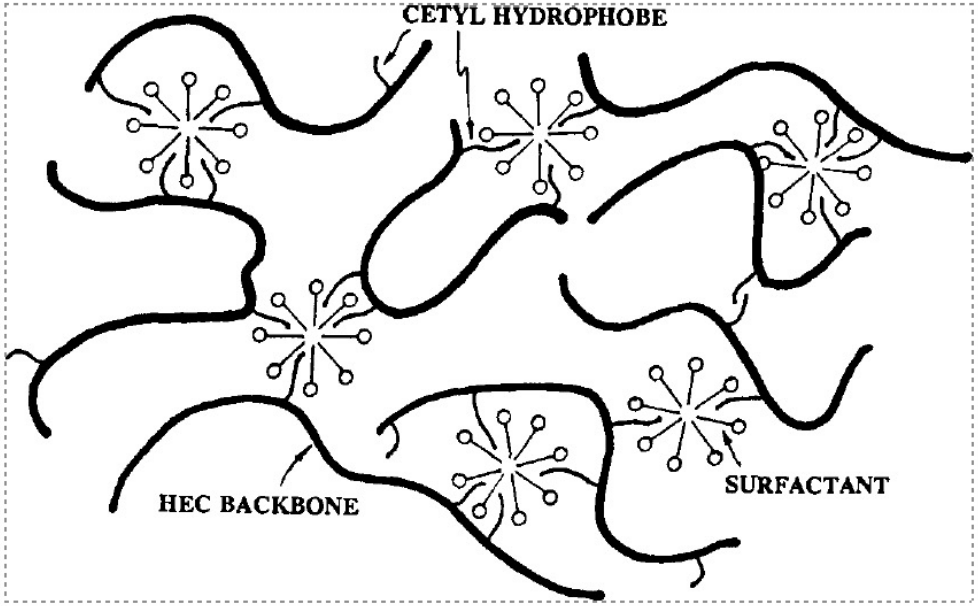
- Shampoo, nail polish, lipstick, deodorant, and toothpaste are all commonplace products whose rheology is carefully tuned for customer satisfaction.
- Toothpaste, for example, must flow out of the tube only when squeezed, must flow under modest force, and must stop flowing immediately after it has been applied to the brush so that it doesn't sink into the bristles.
- Thus, the ingredients of toothpaste include not only gentle abrasives such as silica powder, fluoride for combating tooth decay, and flavoring and foaming agents, but also polymers, such as carboxymethylcellulose, for control of rheology.

Toothpaste

https://www.researchgate.net/figure/SEM-micrographs-of-Colgate-Sensitive-toothpaste-A-pre-agitation-B-post-agitation_fig1_329555819

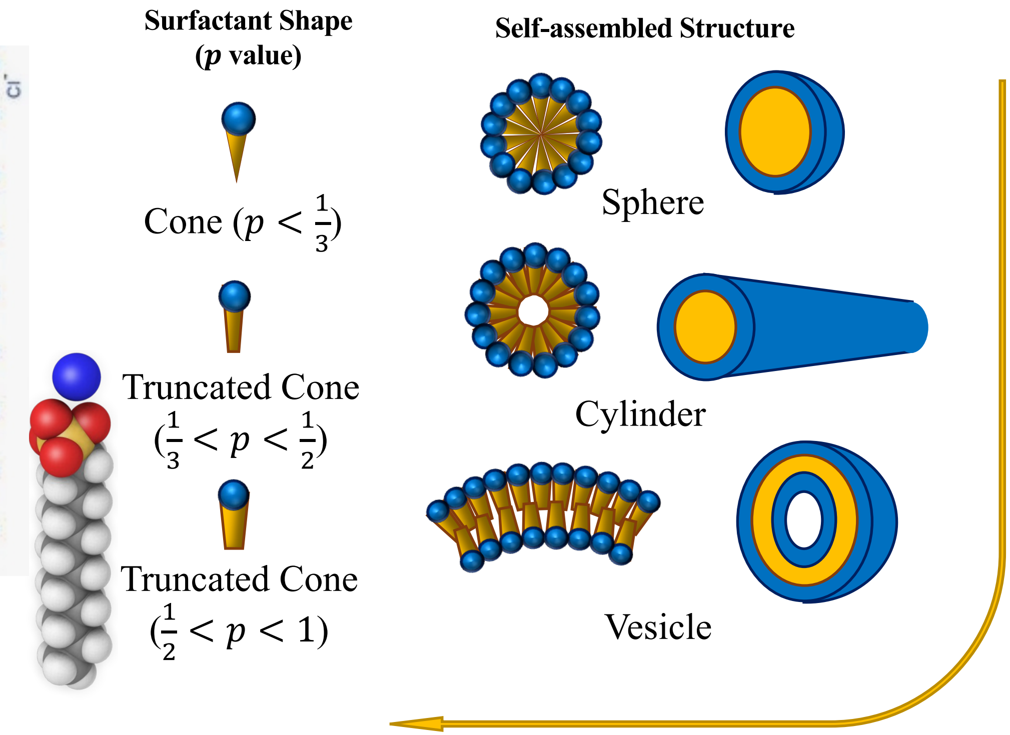






- Many shampoos and conditioners are designed to flow readily from the tube or bottle into one's hand while having enough "body" that they do not quickly drip.
- This is accomplished by careful control of the surfactant concentration as well as the addition of polymeric "thickeners" such as carbomers (very high molecular weight polyacrylic acid). Very thick "mousses" can be formulated using polymeric "associative thickeners," such as hydrophobically modified hydroxyethylcellulose.

Surfactant-containing products

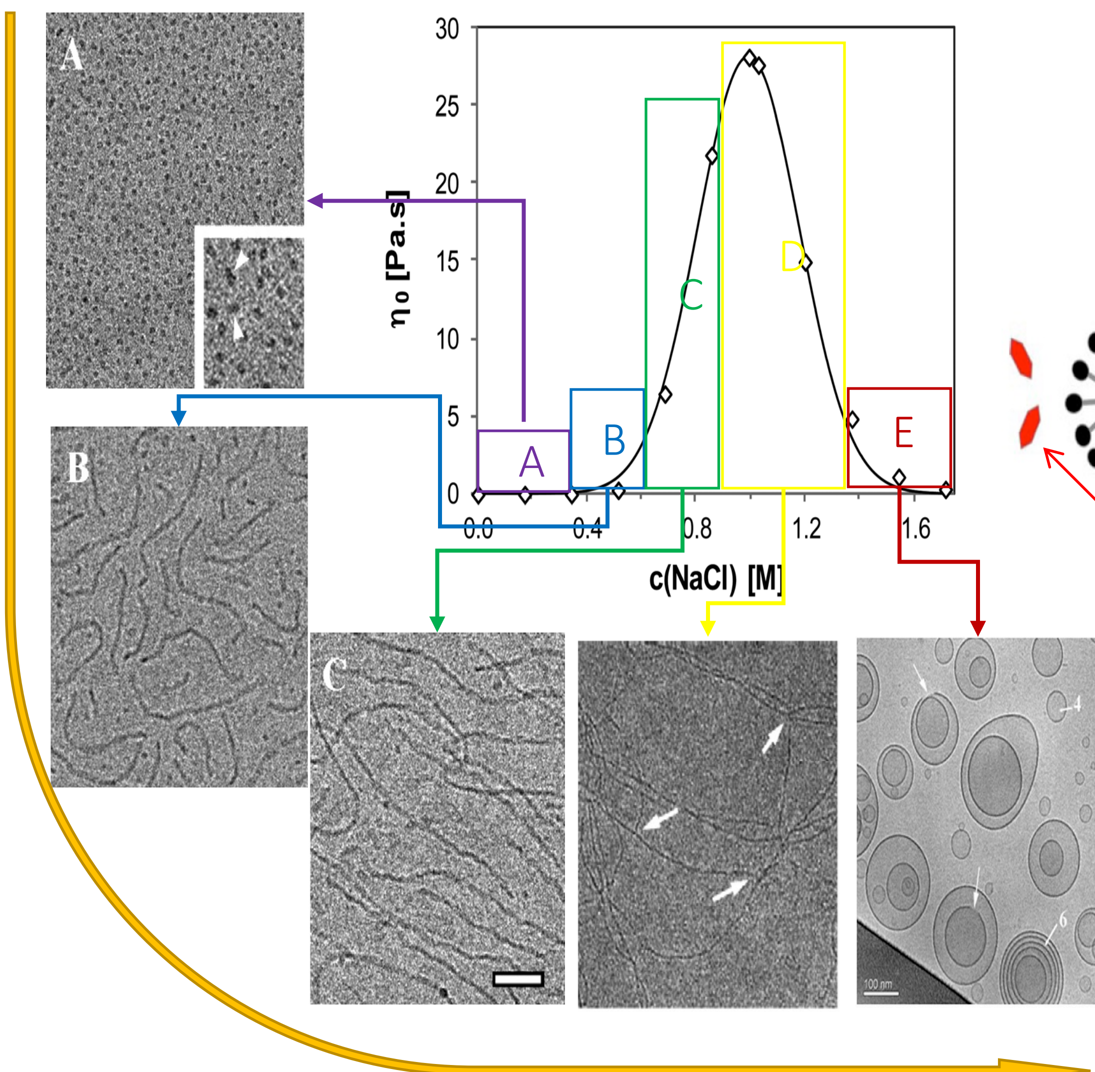


$$p = \frac{V}{l_c a_0}$$

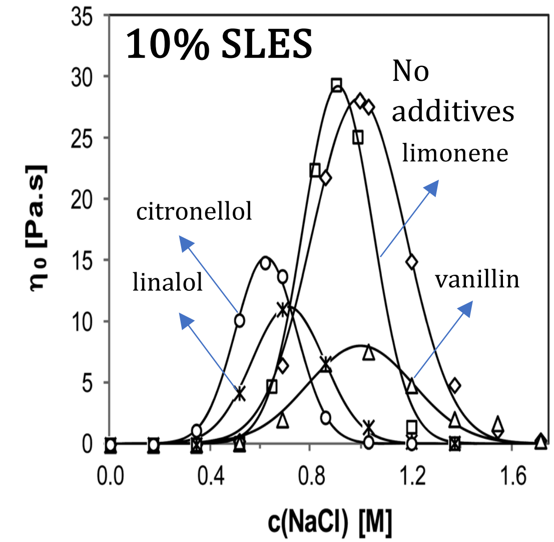
V: volume of tail; l_c: length of tail; a_0: area of head

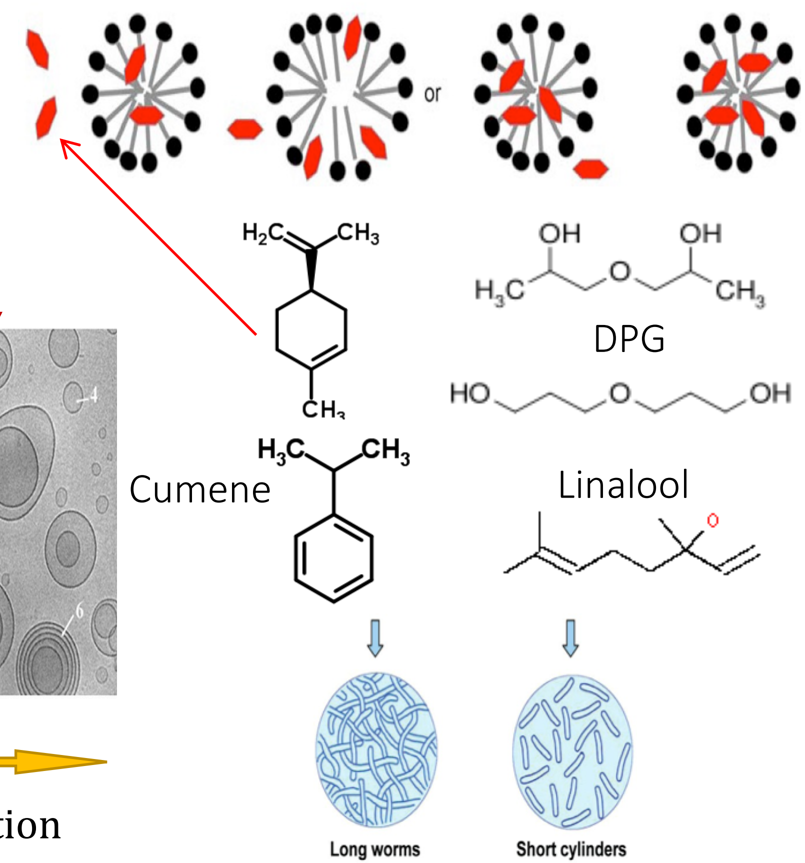
R. Nagarajan (1989): The Journal of Physical Chemistry;
A. Parker and W. Fieber (2013): Soft Matter

Micellar solutions: the salt curve



Increase surfactant/salt concentration

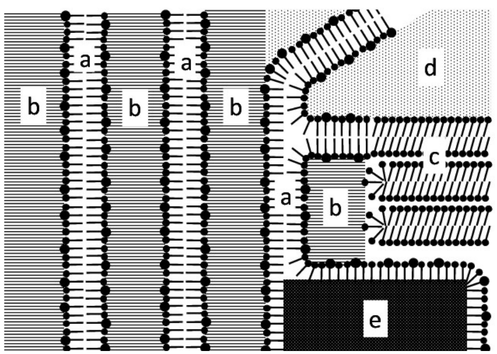


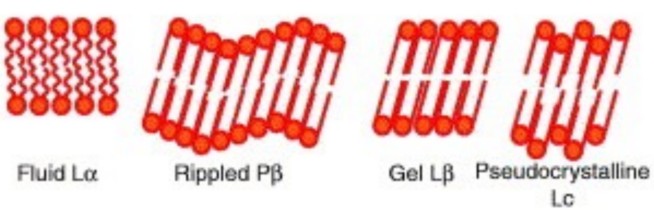


Cosmetic Emulsions: Hair Conditioners

Cosmetic oil-in-water emulsions form a class of materials often referred to as “lamellar gel networks”

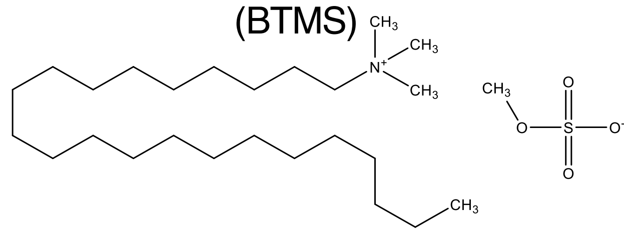
G. M. Eccleston, M. K. Behan-Martin, G. R. Jones, and E. Towns-Andrews, “Synchrotron X-ray investigations into the lamellar gel phase formed in pharmaceutical creams prepared with cetrimide and fatty alcohols,” *Int. J. Pharm.*, vol. 203, no. 1–2, pp. 127–139, 2000.



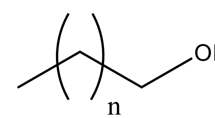


Excess Water (85-95%) + **Cationic Surfactant** + **Fatty Alcohol**

Behentrimonium methosulfate (BTMS)



Cetostearyl Alcohol (cetyl : stearyl = 1:2.5 by weight)



n = 14-16

Literature presentations for Lecture 4

letters to nature

A colloidal model system with an interaction tunable from hard sphere to soft and dipolar

Anand Yethiraj*† & Alfons van Blaaderen*

** Soft Condensed Matter, Debye Institute, Utrecht University, Padualaan 5, 3584CC Utrecht, and FOM Institute for Atomic and Molecular Physics, Kruislaan 407, 1098 SJ Amsterdam, The Netherlands*

Monodisperse colloidal suspensions of micrometre-sized spheres are playing an increasingly important role as model systems to study, in real space, a variety of phenomena in condensed matter

COMMUNICATION www.rsc.org/softmatter | Soft Matter

Tunable attractive and repulsive interactions between pH-responsive microgels

Jae Kyu Cho,[a] Zhiyong Meng,[b] L. Andrew Lyon[b] and Victor Breedveld[a]

Received 19th June 2009, Accepted 16th July 2009
First published as an Advance Article on the web 31st July 2009
DOI: 10.1039/b912105f

We report direct measurements of the pairwise interparticle potential between poly(*N*-isopropylacrylamide-*co*-acrylic acid) (pNIPAm-*co*- be explained relatively well by defining an effective volume fraction of particles and using hard-sphere-like interactions, the incorporation of

nature Vol 457 | 8 January 2009 | doi:10.1038/nature07610

LETTERS

Measured long-range repulsive Casimir–Lifshitz forces

J. N. Munday[1], Federico Capasso[2] & V. Adrian Parsegian[3]

Quantum fluctuations create intermolecular forces that pervade macroscopic bodies[1–3]. At molecular separations of a few nano- presented[15,21–24]. When working at small separations, however, the polarity and orientation of the molecules may influence the force.

Vol 464 | 25 March 2010 | doi:10.1038/nature08906

LE

Lock and key colloids

S. Sacanna[1], W. T. M. Irvine[1], P. M. Chaikin[1] & D. J. Pine[1]

New functional materials can in principle be created using colloids that self-assemble into a desired structure by means of a programmable recognition and binding scheme. This idea has been explored by attaching ‘programmed’ DNA strands to nanometre-[1–3] and depletant—to the system, causing depletion interactions[8,9] which have their origin in the entropy associated with the centre of mass of the polymers. That is, each colloidal particle is surrounded by an exclusion layer whose thickness is given by the radius r_p of a polymer

A	B	C	D	E	F	G	H	I	J	K
All Presentation Dates										
Student	**2/6**	**2/13**	**2/20**	**2/27**	**3/12**	**3/19**	**3/26**	**4/2**	**4/9**	**4/16**
Pranjal Khakse	A	A	A	D	A	A	B	C	D	A
Mitchell Godek	D	C	D	B	D	B	A	C	C	B
Jen Bradley	D	A	A	D	B	D	D	A	A	D
Amir Nazemi	B	D	D	C	B	A	C	D	D	C
Charlotte Zhao	D	D	B	B	A	C	A	B	A	A
Will Hobson-Rhoades	B	B	B	B	D	C	C	A	D	C
William Morgan	A	C	A	B	C	A	D	B	C	B
Ankit Saraf	B	C	C	C	B	B	B	D	A	D
Henry Thurber	A	D	C	A	D	D	A	B	C	A
Ellie Anderson-Zych	C	A	C	B	A	C	D	A	D	D
Dushyanth Velugubantla	C	D	B	A	C	A	B	D	A	B
Gabrielle Grey	A	A	D	C	B	D	A	D	D	C
Weiyuan Fan	D	B	D	D	C	B	B	B	B	D
Aham Lee	C	B	A	C	A	B	D	A	B	A
YATIN NARAYANAN	C	C	B	D	C	D	C	C	C	C
Nathan Bryant	C	D	A	A	D	B	A	C	C	B
Nhayeon Lee	B	B	C	C	C	C	D	C	B	C
Nathan Irgang	B	C	B	A	A	C	B	D	B	D
Muchen Wang	A	B	C	A	D	D	C	A	A	A
Anna Klinger	D	A	D	D	B	A	C	B	B	B

Group	Paper Title
A	P1_Yethiraj_AVB_soft_dipolar_Nature_2003
B	P2_Sacanna_et_al_Lock_and_Key_Colloids_Nature_2010
C	P3_Breedveld_deformable_microgels_Soft_Matter_2011
D	P4_Casimir_Lifshitz_force_Nature_2009

Literature and youtube presentations for Lecture 4

- Random group assignments
- https://docs.google.com/spreadsheets/d/1EWhNBhl2nLaJGBrVEoSe4y0x5w41fPwD1HhYuJGUd9Y/edit#gid=267969935