Basic Forces and Dynamics of Colloids

Reference text:

The Structure and Rheology of Complex Fluids, Ronald G. Larson Colloidal Systems, Darrell Velegol Slides from Orlin Velev Instead of deriving each concepts one by one which can often be quite boring and make people miss the big-picture, let's go through recent history and solve a mystery of modern colloidal science together...



Colloidal motors

• 2004 Ayusman Sen, Tom Mallouk and colleagues

Catalytic Nanomotors: Autonomous Movement of Striped Nanorods

Walter F. Paxton, Kevin C. Kistler, Christine C. Olmeda, Ayusman Sen, Sarah K. St. Angelo, Yanyan Cao, Thomas E. Mallouk, Paul E. Lammert, and Vincent H. Crespi

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https://pubs.acs.org/doi/10.1021/ja047697z

Colloidal motors

- Rod-shaped particles, 370 nm in diameter and consisting of 1 μm long Pt and Au segments.
- When the rods were placed in a 3.7% aqueous solution of hydrogen peroxide, something unexpected happened: The rods began to move spontaneously!
- In fact, they moved roughly 8 um/s four body lengths per second approximately how fast a world class athlete runs the 1500 m race.

 $2 \ \mu m$ long Pt/Au rods in 2.5% hydrogen peroxide



2 µm long Pt/Au rods in pure water

Au/Pt/Au rods in 2.5% hydrogen peroxide

Colloidal motors

 A control experiment using three-striped (Au/Pt/Au) rods --- which catalyze the decomposition of H2O2 at a similar rate --- established that the asymmetric Pt/Au geometry was necessary for rapid axial movement.



Table 1. Diffusion Coefficients (in $\mu m^2/s$) for 2 μm Long Platinum/Gold Rods

| sampling interval (seconds) | | | | | | | | |
|-------------------------------------|------|------|------|------|------|------|------|--|
| experiment | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 1.0 | 15 | |
| Au in H ₂ O ^a | | | | | | | 0.41 | |
| Pt/Au in H_2O | 0.43 | 0.41 | 0.40 | 0.40 | 0.39 | 0.42 | | |
| Pt/Au in $H_2O_2^b$ | 4.13 | 6.61 | 9.41 | 11.6 | 13.8 | 23.7 | | |

| H ₂ O ₂ (wt. %) | speed (µm/s) ^b |
|---------------------------------------|---------------------------|
| 4.9 | 7.7 ± 0.9 |
| 3.3 | 7.9 ± 0.7 |
| 1.6 | 5.6 ± 0.6 |
| 0.33 | 4.9 ± 0.3 |
| 0.031 | 3.9 ± 0.5 |
| pure water | 3.7 ± 0.3 |

^a From ref 11.^b In 3.3% hydrogen peroxide.

How are these colloidal motors made?

• 1999, Michael Natan and Tom Mallouk

ADVANCED MATERIALS

Communication 🛛 🔂 Full Access

Orthogonal Self-Assembly on Colloidal Gold-Platinum Nanorods

Benjamin R. Martin, Daniel J. Dermody, Brian D. Reiss, Mingming Fang, L. Andrew Lyon, Michael J. Natan, Thomas E. Mallouk

First published: 18 August 1999 | https://doi.org/10.1002/(SICI)1521-4095(199908)11:12<1021::AID-ADMA1021>3.0.CO;2-S | Citations: 439

https://onlinelibrary.wiley.com/doi/10.1002/(S ICI)1521-4095(199908)11:12%3C1021::AID-ADMA1021%3E3.0.CO;2-S

How are these colloidal motors made?

Alumina membrane



Evaporate Ag on membrane
Electroplate Ag on Ag film





Electroplate Au, Pt, etc.



Electroplate Ag in pores

1) Dissolve Ag in HNO₃ 2) Dissolve alumina in NaOH



Scheme 1. Electrochemical synthesis of metal rods.



Fig. 1. Bright-field optical micrograph at 1000× magnification of: a) 1 C Au/ 8 C Pt / 2 C Au rods, b) 2 C Au rods, c) 8 C Pt rods.

• "Jet propulsion" mechanisms, in which oxygen generated at platinum impels the rod through a pressure increase or by momentum recoil of bursting bubbles, as in the Whitesides system, would propel a rod away from its platinum end.



100 µm

AT Liu[†], JF Yang[†] et al. Faraday Discussions 227, 213

Catalytic Pt motors

• 2002 George Whitesides



Communication 6 Free Access

Autonomous Movement and Self-Assembly

Rustem F. Ismagilov Dr., Alexander Schwartz Dr., Ned Bowden, George M. Whitesides Prof. 🔀

First published: 14 February 2002 | https://doi.org/10.1002/1521-3773(20020215)41:4<652::AID-ANIE652>3.0.CO;2-U | Citations: 469

https://onlinelibrary.wiley.com/doi/10.1002/1 521-3773(20020215)41:4%3C652::AID-ANIE652%3E3.0.CO;2-U

Catalytic Pt motors

 Whitesides and co-workers have used the catalytic decomposition of hydrogen peroxide to propel cm/mmscale objects on a water surface. In that case, movement could be attributed to the recoil force of the oxygen (O₂) bubbles released from the Pt catalyst, which was situated on only one side of the "transom" of the "boat."



Figure 1

A) Schematic of a self-propelling object. A thin plate (circa 1–2 mm thick and 9 mm in diameter) was fabricated from PDMS in a desired shape, and specified faces were rendered hydrophilic by oxidation in a plasma formed in air. A 2×2 mm² piece of porous glass filter (covered with platinum by an electron beam evaporation) was mounted on the PDMS piece with a stainless steel pin. B) A diagram illustrating self-assembly by capillary interactions.

- Ayusman et al. found that movement occurred in the opposite direction, namely toward the platinum end of the rod. Moreover, macroscopic bubbles did not nucleate selectively at the Pt ends of the rods in the reaction, and the motion of the rods did not appear to be connected with the release of bubbles from either end.
- **Diffusiophoretic transport models** of colloidal particles in a gradient of neutral solute (i.e., oxygen molecules) also predicts movement away from its platinum end with a velocity orders of magnitude slower than that observed experimentally.

Diffusiophoresis

• 1989, John Quinn



Journal of Colloid and Interface Science Volume 130, Issue 1, June 1989, Pages 69-87



Diffusion-induced banding of colloid particles via diffusiophoresis: 1. Electrolytes

Peter O Staffeld¹, John A Quinn

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104 USA

Received 30 March 1988, Accepted 2 August 1988, Available online 21 July 2004.

https://www.sciencedirect.com/science/article /pii/0021979789900799?pes=vor

- With micron-size objects, interfacial forces can easily be larger than inertial forces.
- Interfacial tension also plays an important role in so-called "camphor motors," in which small particles of camphor move at the **air-water interface** by slowly dissolving and spreading a hydrophobic "wake" behind them.

Camphor motors

• 2002, Satoshi Nakata

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Intermittent Motion of a Camphene Disk at the Center of a Cell

Satoshi Nakata, Yukie Doi, and Yuko Hayashima

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Cite this: J. Phys. Chem. B 2002, 106, 44, 11681–11684
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https://pubs.acs.org/doi/10.1021/jp021675m





- The possibility of an **interfacial tension gradient**, which may be imposed by either a **temperature** or **solute gradient**, offers another alternative.
- Both temperature and chemical gradients are present in our system due to the exothermic decomposition of hydrogen peroxide. Because the platinum end is the source of these gradients, they are continually re-established as a rod moves through solution so long as hydrogen peroxide is present.
- We can calculate the interfacial tension force created by the solute gradient by solving the **convection-diffusion equation** in the frame of the moving rod.
- Oxygen is a nonpolar molecule that cannot act as a hydrogen bond donor, and it thus disrupts the hydrogen bonding network of liquid water.
- We make the simplification that the liquid-solid interfacial tension gradient is directly proportional to the gradient in the mole fraction of oxygen in the solution.

$$\frac{\partial C}{\partial t} = -v \cdot \nabla C + D \nabla^2 C$$

The uniform flux of oxygen S (i.e., the surface area-normalized oxygen generation rate) into the fluid along the Pt surface and zero flux along the Au surface provide boundary conditions.

• the scaling of the rod velocity with different parameters:



Figure 6 Effect of ethanol on axial velocity, v_z , where v_z is plotted versus the product of oxygen evolution rate per rod and solution surface tension (i.e., $S \cdot \gamma$). Included is a data point for rods moving in pure water, where the oxygen evolution rate is taken to be zero.

- The hypothesis was that a gradient of surface tension was driving the movement of the rods, not altogether different from how a camphor boat moves.
- But then the PhD students added a thin layer of dielectric material between the platinum and gold, and they found – somewhat surprisingly – that the movement of the rods stopped.
- the decomposition **must be happening electrochemically**, and that the reaction required that electrons transport through the metallic phase.
- At this time, Darrell Velegol and colleagues had discovered auto-electrophoresis driven flow between Au and Ag.
- Auto-electrophoresis: the electric field that arose due to the electrochemical decomposition of H2O2 was driving the particles through the aqueous solution electrokinetically.

Overall:
$$2H_2O_2 \rightarrow 2H_2O + O_2$$
 (1)

Anode:
$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$$
 (2)

Cathode: $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ (3)

Auto-electrophoresis

• 2005, Darrel Velegol, Tom Mallouk, Ayusman Sen

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Catalytic Micropumps: Microscopic Convective Fluid Flow and Pattern Formation

Timothy R. Kline, Walter F. Paxton, Yang Wang, Darrell Velegol, Thomas E. Mallouk, and Ayusman Sen

View Author Information \sim

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https://pubs.acs.org/doi/10.1021/ja056069u https://pubs.acs.org/doi/10.1021/jp064393l

Auto-electrophoresis



Protons (H+) generated by oxidation of H2O2 migrate from the anode (gold) to cathode (silver, center), generating electroosmotic flow (from anode (+) to cathode (-)).

Positively charged particles





r = R

Negatively charged particles



Figure 2 Protons (H⁺) generated by oxidation of H_2O_2 migrate from the anode (gold) to cathode (silver, center), generating electroosmotic flow. This flow creates a convection roll that sweeps tracer particles inward along the gold surface. The convection roll extends from r = a (near the silver) to r = R. Positively charged tracer particles (see inset) experience an additional electrophoretic force in the direction of the silver island. Negatively charged particles (inset) experience an electrophoretic force in the opposite direction, which results in circular patterns around the silver islands. Gold rods, which experience only a small outward electrophoretic force, are swept inward by the dominant electroosmotic flow and circulate in a tight convection roll near the silver island.

r = a

Electroosmotic flow







https://en.wikipedia.org/wiki/Electro-osmosis

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

Auto-electrophoresis as a propulsion mechanism

• 2005, Nicolas Mano and Adam Heller

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Bioelectrochemical Propulsion

Nicolas Mano and Adam Heller

View Author Information \sim

Cite this: J. Am. Chem. Soc. 2005, 127, 33, 11574-Article Views Altmetric Citations Share Add to Export 11575 3186 254 10 RIS Publication Date: July 28, 2005 V https://doi.org/10.1021/ja053937e LEARN ABOUT THESE METRICS Copyright © 2005 American Chemical Society Request reuse permissions Subscribed

Locomotion by the reaction of glucose and oxygen has not been previously reported.

https://pubs.acs.org/doi/10.1021/ja053937e

Auto-electrophoresis as a propulsion mechanism

- a carbon fiber is propelled rapidly at the water-O₂ interface when built with a terminal glucose oxidizing microanode and an O₂ reducing microcathode. The flow of current through the fiber is accompanied by transport of ions, which is so fast at the interface, where the viscous drag is small, that it carries the fiber at ~1 cm s⁻¹.
- In the direct bioelectrochemical to mechanical power conversion process of this communication, conductive carbon fibers, of 0.5–1 cm length and 7 μ m diameter, were autonomously propelled by the glucose–oxygen reaction at 37 °C and at pH 7 under 1 atm O₂.
- One of their end-segments was coated with a bioelectrocatalyst for the oxidation of glucose, redox polymer wired glucose oxidase (GOx). Their opposite end-segment was coated with a bioelectrocatalyst for the four-electron reduction of O₂ to water, redox polymer wired bilirubin oxidase (BOD).

```
Anode reaction \beta-D-glucose \rightarrow \delta-glucono-1,5-lactone + 2 H<sup>+</sup> + 2 e<sup>-</sup>
```

```
Cathode reaction \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O
```





Scheme 1. The Self-Propelled Bioelectrochemical Motor^a

^{*a*} (A) The two ends of a carbon fiber are made hydrophilic by exposure to a 1 Torr O₂ plasma. (B) One end of the fiber is modified with the electrostatic adduct of glucose oxidase (GOx) and redox polymer *I*. The other end is modified with an electrostatic adduct of bilirubin oxidase (BOD) and redox polymer *II*. When the fiber is dipped in a pH 7 buffer solution containing 10 mM glucose, electrons flow along the path glucose \rightarrow GOx \rightarrow *I* \rightarrow carbon fiber \rightarrow *II* \rightarrow BOD \rightarrow O₂, and the fiber is propelled at the solution-O₂ interface by the ion flow accompanying the flow of electrons. (C) When an insulator is introduced between the two electrocatalytic fiber ends, the fiber does not move.

This current was balanced by a stream of ions, hydrated protons, flowing at/or near the gas-solution interface from the anode to the cathode, propelling the fibers.

Protons and their associated water molecules flow from the anode to the cathode in this pH gradient, their stream carrying the floating fibers.

Heterodoublets of Ag-Au colloidal particles

- Darrell Velegol had developed a simple technique for producing doublets of particles from single spheres, a method they called Stimulate-Quench-Fuse (SQF) assembly.
- They wondered if we could make colloidal motors in this case, heterodoublets of goldparticles and silver particles (Figure 1-1) in a simple, scalable manner.



Figure 1-1. Gold-silver heterodoublet. This fieldemission scanning electron micrograph (FESEM) shows the diameter of each particle to be about 1 μ m. The gold particle (right) has a slightly different surface structure than the silver particle.

How to make Au nanoparticles?

• 1998, Egon Matijevic



Colloids and Surfaces A: Physicochemical and Engineering Aspects Volume 146, Issues 1–3, 15 January 1999, Pages 139-152



Tailoring the particle size of monodispersed colloidal gold 🖈

DanV. Goia¹, Egon Matijević 🝳 🖂

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https://doi.org/10.1016/S0927-7757(98)00790-0 🫪

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Nanoparticles in Liquids

Prof. Michael Faraday

1856



https://www.rigb.org/explore-science/explore/collection/michael-faradays-gold-colloids



1856, Basement laboratory at the Royal Institution

Gold Nanoparticles from M. Faraday

When Michael Faraday was 65 years old, he prepared pure colloidal gold using phosphorus to reduce gold chloride.





Colloidal gold - 107X

[145]

X. THE BAKERIAN LECTURE.—Experimental Relations of Gold (and other Metals) to Light. By MICHAEL FARADAY, Esq., D.C.L., F.R.S., Fullerian Prof. Chem. Royal Institution, Foreign Associate of the Acad. Sciences, Paris, Ord. Boruss. pour le Mérite, Eq., Memb. Royal and Imp. Acadd. of Sciences, Petersburgh, Florence, Copenhagen, Berlin, Göttingen, Modena, Stockholm, Munich, Bruxelles, Vienna, Bologna, Commander of the Legion of Honour, &c. &c.

Received November 15, 1856,-Read February 5, 1857.

THAT wonderful production of the human mind, the undulatory theory of light, with the phenomena for which it strives to account, seems to me, who am only an experimentalist, to stand midway between what we may conceive to be the coarser mechanical actions of matter, with their explanatory philosophy, and that other branch which includes, or should include, the physical idea of forces acting at a distance; and admitting for the time the existence of the ether, I have often struggled to perceive how far that medium might account for or mingle in with such actions, generally; and to what extent experimental trials might be devised which, with their results and consequences, might contradict, confirm, enlarge, or modify the idea we form of it, always with the hope that the corrected or instructed idea would approach more and more to the truth of nature, and in the fulness of time coincide with it.

The phenomena of light itself are, however, the best and closest tests at present of the undulatory theory; and if that theory is hereafter to extend to and include other actions, the most effectual means of enabling it to do so will be to render its application to its own special phenomena clear and sufficient. At present the most instructed persons are, I suppose, very far from perceiving the full and close coincidence between all the facts of light and the physical account of them which the theory supplies. If perfect, the theory would be able to give a reason for every physical affection of light; whilst it does not do so, the affections are in turn fitted to develope the theory, to extend and enlarge it if true, or if in error to correct it or replace it by a better. Hence my plea for the possible utility of experiments and considerations such as those I am about to advance.

Light has a relation to the matter which it meets with in its course, and is affected by it, being reflected, deflected, transmitted, refracted, absorbed, &c. by particles very minute in their dimensions. The theory supposes the light to consist of undulations, which, though they are in one sense continually progressive, are at the same time, as regards the particles of the ether, to and fro transversely. The number of progressive alternations or waves in an inch is considered as known, being from 37,600 to 59,880, and the number which passes to the eye in a second of time is known also, being from MDCCCLVII. X

M. Faraday, The Bakerian Lecture: Experimental Relations of Gold (and Other Metals) to Light, Philos. Trans. R. Soc. Lond., 147 (1857) 145-181.

P. P. Edwards, J. M. Thomas, Gold in a Metallic Divided State— From Faraday to Present-Day Nanoscience, *Angew. Chem.* **2007**, 46, 5480.

How to make Au nanoparticles?

 The present paper describes a versatile precipitation method capable to generate mono-dispersed, spherical gold particles using aqueous solutions of gold chloride and iso-ascorbic acid as the reducing agent.

 $2[AuCl_{x}(OH)_{4-x}]^{-} + 3C_{6}H_{8}O_{6} \rightarrow 2Au^{0} + 3C_{6}H_{6}O_{6} + 6H^{+} + 2xCl^{-} + 2(4-x)OH^{-}$

| Table 1. Preparation and composition of gold complex solutions ^a | | | | | | Table 2. Selected properties of dispersions of gold particles obtained with solutions | | | | | | | | | | |
|---|--------------------|--------------------|------------------|-------|--------------------|---|--------------------|--|-----------|------------------------|-------|-------------------------|--------------------------|---------------------------------|-----------------------|---------|
| Sample | HCl | NaOH | Free | Free | Final | Final | рН | Gold | listed in | n Table 1 ^a | | | | | | |
| | added ^b | added ^c | HCl ^d | NaOH | [HCl] | [OH ⁻] | (H_0) | complex | Sample | Induction | Final | Ionic | Particle | Crystallite | $D_{\rm p}/d_{\rm c}$ | Carbon |
| | (mol) | (mol) | (mol) | (mol) | (mol | (mol | | | | period (s) | рН | strength ^d | diameter, D _p | size <i>d</i> _c (nm) | <u>^</u> | content |
| | | | | | dm ⁻³) | dm ⁻³) | | | | | | (mol dm ⁻³) | (µm) | | | (ppm) |
| 1 | 0.275 | - | 0.35 | - | 3.5 | - | -1.23 ^f | HAuCl ₄ ·7HCl | 1 | 8 | с | 1.25 | 4.6 | 29 | 160 | 2700 |
| 2 | 0.025 | - | 0.10 | - | 1.0 | - | -0.21 ^f | HAuCl ₄ ·2HCl | 2 | 2 | с | 0.625 | 2.2 | 27 | 120 | 2800 |
| 3 | - | 0.026 | 0.05 | - | 0.5 | - | 0.2 ^f | HAuCl ₄ ·HCl | 2 | 5 | | 0.025 | 5.2 | 21 | 120 | 2800 |
| 4 | _ | 0.076 | 0 | _ | 0 | _ | 3.3 | HAuCl ₄ | 3 | 2 | С | 0.625 | 2.7 | 24 | 112 | 2850 |
| 5 | _ | 0.126 | - | _ | _ | _ | 6.2 | AuCl ₃ (OH)⁻ | 4 | 3 | 0.5 | 0.625 | 3.3 | 25 | 130 | 2700 |
| 6 | - | 0.176 | - | - | _ | - | 7.1 | AuCl ₂ (OH) ₂ ⁻ | 5 | <1.0 | 1.0 | 0.625 | 0.9 | 24 | 38 | 2900 |
| _g | - | 0.226 | - | _ | - | - | 8.1 | AuCl(OH) ₃ ^{-f} | 6 | b | 1.3 | 0.625 | 0.2 | 22 | 8.8 | 3100 |
| 7 | - | 0.276 | - | _ | | 0.083 ^e | 12.9 | Au(OH) ₄ ⁻ | 7 | b | 9.6 | 0.875 | 0.09 | 16 | 5.6 | 4000 |



How to make Ag nanoparticles?

• 2003, Krassimir Velikov and Alfons van Blaaderen RETURN TO ISSUE | < PREV RESEARCH ARTICLE NEXT >

Synthesis and Characterization of Large Colloidal Silver Particles

Krassimir P. Velikov, Gabby E. Zegers, and Alfons van Blaaderen

View Author Information \sim

Cite this: Langmuir 2003, 19, 4, 1384–1389
Publication Date: January 18, 2003 ~
https://doi-org.proxy.lib.umich.edu/10.1021/la026610p
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https://pubs.acs.org/doi/10.1021/la026610p

Particle Synthesis. Silver ions were reduced to metal silver by ascorbic acid ($C_6H_8O_6$), which has a sufficiently lower redox potential, ^{21,50} according to the following reaction:

 $\mathrm{C_6H_8O_6} + 2\mathrm{Ag^+} {\rightarrow} 2\mathrm{Ag^0} + \mathrm{C_6H_6O_6} + 2\mathrm{H^+}$

Matijevic et al. proposed a particle growth model for a similar synthesis of gold particles. ⁵¹ The nucleation burst takes place when the concentration of metal atoms reaches a critical supersaturation. In the first step, the nuclei formed grow to nanosized primary particles by diffusion capture of the remaining atoms. In the second step, depending on the reaction conditions, the primary particles aggregate, leading to the formation of larger spherical aggregates accompanied with narrowing of the size distribution.⁵¹ The precipitation was carried out at different pH values, different concentrations of the protective colloid, and different concentrations of silver and ascorbic acid (Table 1).

Table 1. Radius (R) and Polydispersity (δ) of Silver Particles Obtained at Different Experimental Conditions As Determined by TEM

| sample | [AgNO ₃] (mol/L) | [C ₆ H ₈ O ₆] (mol/L) | ratio [acid]/[Ag] | gum arabic wt % | <i>R</i> (nm) | δ (%) |
|--------|------------------------------|---|-------------------|-----------------|---------------|-------|
| 15 | 0.083 | 0.333 | 4 | 0.7 | 223 | 67 |
| 11 | 0.083 | 0.167 | 2 | 0.7 | 894 | 24 |
| 9 | 0.083 | 0.333 | 4 | 0.35 | 429 | 33 |
| 12 | 0.083 | 0.167 | 2 | 0.35 | 1149 | 16 |
| 14 | 0.167 | 0.666 | 4 | 0.7 | 796 | 29 |
| 16 | 0.167 | 0.333 | 2 | 0.7 | 525 | 39 |
| 13 | 0.167 | 0.666 | 4 | 0.35 | 943 | 35 |
| 10 | 0.167 | 0.333 | 2 | 0.35 | 588 | 31 |



Figure 1 Scanning electron micrographs (SEM) of monodisperse silver particles obtained under different experimental conditions, radii (*R*), and relative widths of the size distribution (δ): (a) *R* = 197 nm, δ = 13%; (b) *R* = 284 nm, δ = 17%; (c) *R* = 383 nm, δ = 13%; (d) *R* = 418 nm, δ = 12%. The scale bars are 2 µm. The insets show a blowup of the particle surface. The scale bars in the insets are 200 nm.

Colloidal forces. Particle aggregation depends on these forces.

 Say that we have synthesized our gold and silver colloidal particles. How do we go from single spherical particles of gold and silver, to heterodoublets of gold and silver (Figure 1-1)?



Figure 1-1. Gold-silver heterodoublet. This fieldemission scanning electron micrograph (FESEM) shows the diameter of each particle to be about 1 μ m. The gold particle (right) has a slightly different surface structure than the silver particle.

Colloidal forces

- The structure of matter at the length scales greater than the atomic is governed by electromagnetic forces.
- At the temperatures of interest to us, around 200-500 K, molecules composed of covalently bonded atoms can be regarded as indivisible units, and the electromagnetic forces that we need consider are those that the molecules exert on one another.

Colloidal forces

 The force F between two such molecules is often described using a potential function W (r), which for spherical molecules separated by a distance r is given by

$$F = -\frac{dW}{dr}$$

 A potential function can also be used to describe the force between a pair of colloidal particles. The electromagnetic forces that contribute to W (r) can be grouped into several categories, namely excluded volume (or steric), van der Waals, electrostatic, hydrogen bonding, and hydrophobic.
Excluded-volume interactions

- When molecules or atoms are brought closer and closer together, their electron clouds eventually overlap, producing a very strong repulsion that increases so steeply with decreasing intermolecular distance that it easily overpowers all other forces.
- This excluded-volume force is largely responsible for determining the short-range structure of liquids and the crystallographic order of solids composed of small molecules, or of densely packed hard colloidal particles.
- We briefly consider the **excluded-volume forces** for the simplest cases, **hard spherical particles**.

Hard Sphere Phase Diagram

Figure 2.1 The hard-sphere phase diagram. Below volume fraction $\phi < \phi_1 = 0.494$, the suspension is a disordered fluid. Between $\phi_1 = 0.494$ and $\phi_2 = 0.545$, there is coexistence of this disordered phase with a colloidal crystalline phase with FCC (or HCP) order; the colloidal crystalline phase is the equilibrium one up to the maximum close-packing limit of $\phi_{cp} = 0.74$. Nonequilibrium colloidal "glassy" behavior can also occur between $\phi_g = 0.58$ and the limit of random close packing at $\phi_{rcp} = 0.64$. (From Poon and Pusey, fig. 5, with kind permission of Kluwer Academic Publishers, Copyright 1995.)

Fluid Crystal 000 Fluid + Crystal (vol. fr.) Ø 0 0.545 0.494 0.74 Glass ¢ cp φ1 Ф2 **•** rcp ~ 0.64 **\$**g ~ 0.58

videos from Solomon group

(c) The hexagonal structure of the fcc lattice: Three hexagonal layers are stacked while being shifted against each other (type A-B-C-A-B-C).





hexagonal structure

Fig. 1 - How close-packed structures of spheres can be constructed: In a first layer the spheres are arranged in a hexagonal pattern, each sphere being surrounded by six others (A). Then a second layer with the same structure is added. But this layer is slightly shifted and hence just filling the gaps of the first layer (B). In a third step another equivalent layer is added filling the gaps just as before but now there are two opportunities: Either this layer lies exactly above the first one (A) or it is shifted with respect to both A and B and thus has its own position C.

 In both of these packings, each sphere has 12 identically spaced nearest neighbors; the only difference between FCC and HCP is in the stacking sequence of the layers of spheres.

https://www.physics-in-a-nutshell.com/article/11/close-packed-structures-fcc-and-hcp

What is the pair correlation function g(r)?

- This is related to the probability of finding the center of a particle a given distance from the center of another particle.
- For short distances, this is related to how the particles are packed together. For example, consider hard spheres (like marbles). The spheres can't overlap, so the closest distance two centers can be is equal to the diameter of the spheres. However, several spheres can be touching one sphere; then a few more can form a layer around them, and so on.



https://physics.emory.edu/faculty/weeks/idl/gofr.html

Depletion force

When both large colloidal particles and small depletants are in a suspension, there is a region which surrounds every large colloidal particle that is unavailable for the centers of the depletants to occupy. This steric restriction is due to the colloid-depletant hard-sphere potential.^{[7][8]} The volume of the excluded region is

$$V_{
m E}=rac{\piig(D+dig)^3}{3}$$

where D is the diameter of the large spheres and d is the diameter of the small spheres.

When the large spheres get close enough, the excluded volumes surrounding the spheres intersect. The overlapping volumes result in a reduced excluded volume, that is, an increase in the total free volume available to small spheres.^{[1][4]} The reduced excluded volume, $V'_{\rm E}$ can be written

$$V_{
m E}^{\prime}=V_{
m E}-rac{2\pi l^2}{3}iggl[rac{3\left(D+d
ight)}{2}-liggr]$$

where l = (D + d)/2 - h/2 is half the width of the lens-shaped region of overlap volume formed by spherical caps.

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



Excluded volumes of hard spheres overlap resulting in an increase in the total volume available to depletants. This increases the entropy of the system and lowers the Helmholtz free energy

Colloidal forces



Figure 1-1. Gold-silver heterodoublet. This fieldemission scanning electron micrograph (FESEM) shows the diameter of each particle to be about 1 µm. The gold particle (right) has a slightly different surface structure than the silver particle.

- One route is to use a very simple, quick method like Stimulate-Quench-Fuse assembly.
- In this method we intentionally change solution conditions to encourage aggregation of the particles.
- 2006, Darrell Velegol

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Fabrication of Colloidal Doublets by a Salting Out-Quenching-Fusing Technique

Allison M. Yake, Rocco A. Panella, Charles E. Snyder, and Darrell Velegol

View Author Information \sim

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https://pubs.acs.org/doi/10.1021/la061339n

van der Waals (VDW) forces

- Why would particles clump together? Answer: van der Waals (VDW) forces.
- The mechanism of attraction is quantum mechanical in nature: The electrons within all atoms continually do their "quantum mechanical dance", and so at any instant of time, slightly more electrons exist in one region of an atom or colloidal particle than another. Temporary electric dipoles result on every particle, and although they might be small, they are not zero. In turn, these temporary dipoles will induce dipoles in neighboring atoms or particles. The temporary dipole interacts with the induced dipole to give an attractive force.
- VDW forces always exist between atoms, and they are always attractive, at least at the atomic level.

van der Waals (VDW) forces

• A simple equation for estimating the VDW attractive energy (Φ_{VDW}) between two spherical particles of radius (a), separated by a distance (δ), is

$$\Phi_{VDW} = -\frac{Aa}{12\delta}$$

- The Hamaker constant (A) hides all of the complicated quantum mechanics.
- Typical values are $A = 1.4 \times 10^{-20}$ J for two **polystyrene surfaces interacting across water**, and for **gold in water** or vacuum $A = 20 \times 10^{-20}$ J.
- Almost always A > 0, meaning that the VDW energy is negative, which by definition is attractive.
- The gravitational potential energy of an object with mass (*m*) at a height (*h*) is $\Phi_{grav} = mgh$. Just like the gravitational force is $F_g = -d \Phi_{grav}/dh = -mg$, the **VDW force** is

$$F_{VDW} = -\frac{d\Phi_{VDW}}{d\delta} = -\frac{Aa}{12\delta^2}$$

Lecture 4 Poll: vdW Energy
$$\Phi_{VDW} = -\frac{Aa}{12\delta}$$

- Estimate the VDW energy between two polystyrene particles suspended in water, if they have the same diameter $2a = 1.5 \mu m$ and are separated by a gap $\delta = 25 nm$ between their closest points. Recall $A = 1.4 \times 10^{-20}$ J for two polystyrene surfaces interacting across water.
- A. -3.5×10⁻²³ J
- B. -3.5×10⁻²⁰ J
- C. -3.5×10⁻¹⁷ J
- D. -3.5×10⁻¹⁴ J

Long URL <u>https://forms.gle/dx18gxWCXybYnk4a6</u>

Short URL https://shorturl.at/sFIK0



🛛 Сору

Estimate the VDW energy between two polystyrene particles suspended in water, if they have the same diameter $2a = 1.5 \mu m$ and are separated by a gap $\delta = 25 nm$ between their closest points.

12 responses



Answer: B

answer: $\Phi_{VDW} = -3.5 \times 10^{-20}$ J. Negative energies are attractive, by definition. To compare this with a "molecular energy scale", we use kT, since from statistical mechanics we know that every particle has an average kinetic energy of kT/2 in each direction. The Boltzmann constant $k = 1.38065 \times 10^{-23}$ J/K (the gas constant divided by Avogadro's number), and so if we choose a temperature of T = 290 K, then kT = 4.00×10^{-21} J. This means that $\Phi_{VDW} = -3.5 \times 10^{-20}$ J = -8.75 kT. This is a small but significant energy that will cause aggregation of the particles, unless a repulsive energy also exists. Sometimes we list Hamaker constants in terms of kT's, as in saying that the Hamaker constant in this problem is $A = 1.4 \times 10^{-20} J = 3.5 kT$.

- If VDW forces are always attractive, then what can provide the repulsive force to keep particles from aggregating? Usually one of two types of forces is used to provide the repulsion: electrostatic or steric.
- For electrostatic forces, we know that like charges repel and opposite charges attract, and we see a similar trend between particles.
- The key difference between electrostatic forces in a vacuum and electrostatic forces in aqueous solution is the electrical double layer (EDL).

Electrical Double Layer (EDL)

- Almost any surface immersed in water becomes charged, for example by dissociated surface carboxyl groups on polymer colloids, or adsorbed ions on gold particles, or dissociated silanol groups on silica particles.
- The surface charges have a given surface charge density (ρ_s) that has a typical value of 1 μC/cm². A single charge group has the charge of a proton *e* = 1.6022×10⁻¹⁹ C, and so 1 μC/cm² corresponds to having one univalent charge group every 16 nm², or charge groups with an average spacing of 4 nm.

- These charge groups give rise to an electrical potential at the surface, given in volts. Sometimes this is called the surface potential, and if the potential is measured using electrophoresis, it is called the "zeta potential".
- In solution the surface potential decays to a bulk value of zero – electroneutrality – more quickly than Coulomb's law would suggest. Why?

 The combination of the fixed charges on the particle surface and the diffuse charges in the thin layer around the particle is called the "electrical double layer"

The thickness of the electrical double layer is characterized by the "Debye screening length" (κ^{-1} or $\lambda_{\rm D}$), which is often called simply the "Debye length".



Table 1-2. Debye length (κ^{-1} , in nm) at various concentrations of aqueous solution for T = 293 K. Typical 1:1 salts are KCl or NaCl; a 2:1 salt is CaCl₂. The Debye length decreases with the square root of the ionic strength, and increases with the square root of temperature. So for instance to find the Debye length of a 23 mM KCl solution at T = 300 K, we might start with the Debye length for a 1:1 salt at 1 mM, which is 9.65 nm, then multiply by two factors (300 K / 293 K)^{0.5} × (1 mM / 23 mM)^{0.5} = 0.211 to get 2.04 nm.

| conc (mM) | 1:1 (KCl) | 2:1 (CaCl ₂) | 3:1 (AlCl ₃) | 2:2 (CaSO ₄) | 3:2 [Al ₂ (SO ₄) ₃] | 3:3 (AIPO ₄) |
|--------------|--------------|-----------------------------|-----------------------------|-----------------------------|---|-----------------------------|
| 0.001 | 305 | 176 | 125 | 153 | 78.8 | 102 |
| 0.003 | 176 | 102 | 71.9 | 88.1 | 45.5 | 58.7 |
| 0.01 | 96.5 | 55.7 | 39.4 | 48.2 | 24.9 | 32.2 |
| 0.03 | 55.7 | 32.2 | 22.7 | 27.9 | 14.4 | 18.6 |
| 0.1 | 30.5 | 17.6 | 12.5 | 15.3 | 7.88 | 10.2 |
| 0.3 | 17.6 | 10.2 | 7.19 | 8.81 | 4.55 | 5.87 |
| 1 | 9.65 | 5.57 | 3.94 | 4.82 | 2.49 | 3.22 |
| 3 | 5.57 | 3.22 | 2.27 | 2.79 | 1.44 | 1.86 |
| 10 | 3.05 | 1.76 | 1.25 | 1.53 | 0.788 | 1.02 |
| 30 | 1.76 | 1.02 | 0.719 | 0.881 | 0.455 | 0.587 |
| 100 | 0.965 | 0.557 | 0.394 | 0.482 | 0.249 | 0.322 |
| 300 | 0.557 | 0.322 | 0.227 | 0.279 | 0.144 | 0.186 |
| 1000 | 0.305 | 0.176 | 0.125 | 0.153 | 0.0788 | 0.102 |

• The electrical potential decays away from a flat surface at a rate given roughly by the **Debye-Huckel equation**:

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

Surface potential

Distance from the surface

 Typical magnitudes of the surface potential (Ψ) are 10 to 150 mV, and can be negative or positive. Since these potentials arise due to the surface charges, the relationship between the surface charge density (units C/m²) and the surface potential is:

$$\rho_s = \varepsilon \kappa \psi_0$$

Electrical permittivity

• Between two particles of radius (*a*), the electrostatic energy (Φ_{ES}) resulting from the electrical potentials on a particle separated by a distance of closest approach (δ) is approximated by

$$\Phi_{ES} = 2\pi \varepsilon a \psi_0^2 e^{-\kappa \delta}$$

Electrical permittivity

Fluids with higher dielectric constants give larger electrostatic interactions energies, not only since ε appears in equation above, but also since particles tend to become more highly charged – and therefore have a larger magnitude of surface potential – in these fluids. **Table 1-3**. Static (zero frequency) electrical permittivities for several liquids. The permittivity of vacuum is $\varepsilon_0 = 8.8542 \times 10^{-12} \text{ C}^2/\text{N-m}^2$. For most liquids the electrical permittivity (ε) is represented by a multiple of ε_0 called the "dielectric constant" and a "relative permittivity" (ε_r). For example, at 20 C water has $\varepsilon_r = 80.1$, and so the permittivity of water at 20 C is $80.1\varepsilon_0 = 7.09 \times 10^{-10} \text{ C}^2/\text{N-m}^2$. The static dielectric constant depends weakly on temperature.¹²

| fluid | $\varepsilon_{\rm r}$ at $T =$ | $\varepsilon_{\rm r}$ at $T =$ | dielectric constant (Er) |
|-------------|--------------------------------|--------------------------------|---|
| | 20 C | 25 C | at T (C) |
| acetone | 21.2 | 20.7 | $\varepsilon_r = 21.2 \exp[-0.00472(T-20)]$ |
| ammonia | 17.4 | 16.9 | $\varepsilon_r = 17.4 - 0.090(T - 20)$ |
| benzene | 2.284 | 2.274 | $\varepsilon_r = 2.284 - 0.0020(T - 20)$ |
| cyclohexane | 2.023 | 2.015 | $\varepsilon_r = 2.023 - 0.0016(T - 20)$ |
| ethanol | 25.1 | 24.3 | $\varepsilon_r = 25.1 \exp[-0.006217(T-20)]$ |
| methanol | 33.62 | 32.63 | $\varepsilon_r = 33.62 \exp[-0.00599(T-20)]$ |
| water | 80.37 | 78.54 | $\varepsilon_r = 80.37 \exp[-0.004605(T-20)]$ |

DLVO energy

 As a first approximation to the total energy between the particles, we can simply add the electrostatic and VDW energies to give the well-known "Derjaguin-Landau-Verwey-Overbeek" (DVLO) energy between the two particles.

$$\boldsymbol{\Phi} \approx \boldsymbol{\Phi}_{DLVO} = \boldsymbol{\Phi}_{ES} + \boldsymbol{\Phi}_{VDW} \approx 2\pi \epsilon a \psi_0^2 e^{-\kappa \delta} - \frac{Aa}{12\delta}$$

etween colloidal particles

other forces between colloidal particles can be significant: hydrophobic forces, depletion forces, etc.

the expressions for the electrostatic and VDW energies written here are approximate

DLVO energy -- exercise

Estimate the electrostatic energy, the van der Waals attractive energy, and the total energy between two polystyrene particles suspended in water, if they have the same diameter $2a = 1.5 \mu m$ and are separated by a gap $\delta = 25$ nm between their closest points. The surface potential of the particles is $\psi_0 = -35$ mV, and the solution is 10 mM KCl at a temperature T = 20 C. The Hamaker constant A for a PS-water-PS system is approximately 1.4×10^{-20} J.

DLVO energy -- exercise

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answer: $\Phi_{ES} = +1.13 \times 10^{-21} J = +0.28 kT$. Previously we found that $\Phi_{VDW} = -35.0 \times 10^{-21} J = -8.656 kT$. $\Phi_{DLVO} = -33.9 \times 10^{-21} J = -8.38 kT$.

Would the particles aggregate?

DLVO energy -- exercise

Estimate the electrostatic energy, the van der Waals attractive energy, and the total energy between two polystyrene particles suspended in water, if they have the same diameter $2a = 1.5 \mu m$ and are separated by a gap $\delta = 25$ nm between their closest points. The surface potential of the particles is $\psi_0 = -35$ mV, and the solution is 10 mM KCl at a temperature T = 20 C. The Hamaker constant A for a PS-water-PS system is approximately 1.4×10^{-20} J.

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Would the particles aggregate?

This energy is attractive at this distance.

DLVO energy

- In maintaining **stability**, usually we consider the maximum energy barrier to aggregation (Φ_{max}).
- **Thermodynamics** indicate that aggregation will always prevail. Rather, stability is a question of **kinetics**, and in order to assess stability, we must learn about the **aggregation rate**.



Stability. Aggregation occurs by diffusion or shear.

- Getting back to our doublet story ... in order to fabricate colloidal doublets, we are using the **Stimulate-Quench-Fuse** method.
- The essential idea is to reduce the **electrostatic repulsion** between particles, enabling the **VDW attractive forces** to cause **aggregation**.
- Two methods that are used to reduce electrostatic repulsion are to lower the pH of the solution, which reduces the number of dissociated charge groups on the negative particles, or to increase the ionic strength of the solution, which also reduces electrostatic forces.



Figure 1-1. Gold-silver heterodoublet. This fieldemission scanning electron micrograph (FESEM) shows the diameter of each particle to be about 1 μ m. The gold particle (right) has a slightly different surface structure than the silver particle.

How quickly will the singlets aggregate into doublets?

Stability. Aggregation occurs by diffusion or shear.

- Particles can **aggregate** only when they **collide**.
- There are two common mechanisms for collision: diffusive collisions and shear-induced collisions.
- We will focus here on diffusive or "Brownian" aggregation.
- The Smoluchowski aggregation equation gives an estimate of the aggregation time (τ) for roughly half of the particles in suspension to aggregate:
 Fluid viscosity

$$\tau = \frac{\pi \eta a^3}{2kT\phi} W$$
Aggregation energy barrier
Volume fraction of particle
Stability ratio (W): $W = 1 + 0.25 \left[exp \left(\frac{\Phi_{max}}{kT} \right) - 1 \right]$

What causes diffusive aggregation?

 Diffusive aggregation results first when the interparticle repulsive forces are small enough so that they cannot prevent aggregation, and simultaneously when the process of "Brownian motion" causes particles to collide.

Colloidal aggregation rate exercise

We have a suspension of 1.1 µm diameter gold spheres in water at 298 K. The volume fraction of particles is $\phi = 0.00033$. Estimate how long it will take for half the particles to aggregate, both in a) rapid aggregation $(\Phi_{max} = 0)$ and b) with electrostatic stabilization $(\Phi_{max} = +20 \text{ kT})$. The viscosity of water at 298 K is 0.00089 Pa-s.

Colloidal aggregation rate exercise

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answer: a) For rapid aggregation, W = 1 and so $\tau = 171$ s ≈ 3 min. The particles will aggregate on a time scale that we could watch in the lab; they would not aggregate too fast to see, say μ s, or too slow to see, say years. b) $W = 1.21 \times 10^8$ and $\tau = 659$ years. The particles are predicted not to aggregate on a commercial time scale of even 2 to 3 years. As a rule of thumb, particles with surface potentials $|\psi_{0}| > 50$ mV are stable.

https://www.compadre.org/informal/features/ featureSummary.cfm?FID=654

Brownian motion

- From classical statistics mechanics, we know that **every molecule in the system is moving randomly in all three dimensions**, with an average kinetic energy *kT*/2 in each direction, or **3***kT***/2 total**.
- The thermal energy (kT) is the Boltzmann constant (k = 1.38065×10⁻²³ J/K) multiplied by the absolute temperature (T).
- The average kinetic energy of a molecule is $m(v_x^2 + v_y^2 + v_z^2)/2 = 3kT/2$.
- smaller particles move faster



Average speed of a molecule undergoing random thermal motion

Find the root-mean-square (RMS) speed $\langle v^2 \rangle^{1/2} = \langle v \cdot v \rangle^{1/2}$ for a water molecule in a beaker of water, at T = 293 K. The mass of a water molecule is 18 g/mol = (0.018 kg/mol) / (6.022×10²³ / mol) = 2.989×10⁻²⁶ kg/molecule.

Average speed of a molecule undergoing random thermal motion

Find the root-mean-square (RMS) speed $\langle v^2 \rangle^{1/2} = \langle \mathbf{v} \cdot \mathbf{v} \rangle^{1/2}$ for a water molecule in a beaker of water, at T = 293 K. The mass of a water molecule is 18 g/mol = (0.018 kg/mol) / (6.022×10²³ / mol) = 2.989×10⁻²⁶ kg/molecule.

answer: $\langle v^2 \rangle^{1/2} = 637$ m/s. Sound travels at roughly 1500 m/s in water.

Brownian motion

- Our gold particles in this doublet fabrication, having a diameter of roughly 1 μm, are hit on all sides by the water molecules.
- First, the very rapid buffeting of the solvent molecules, which will in general not be exactly symmetric about the particle at any instant, produces an instantaneous force on the particle. Second, when the particle is given a force, it moves through the sea of water molecules, but it must move out all the molecules in front of it. This second process gives resistance to the particle movement, which dissipates the energy of the particle back into the solvent molecules in front of it.



Figure 1-1. Gold-silver heterodoublet. This fieldemission scanning electron micrograph (FESEM) shows the diameter of each particle to be about 1 μ m. The gold particle (right) has a slightly different surface structure than the silver particle.

Fluctuation-dissipation

The entire process is a "fluctuation-dissipation" process, with the fluctuation being the Brownian kick the particle receives, and the dissipation being the movement of the solvent molecules in front of it. The kicks give an average kinetic energy to the particle of 3kT/2. The fluid resistance force against the particle is given by Stokes law for a particle, which predicts the hydrodynamic resistance force (F_H) for a particle of radius (*a*) moving through a fluid of viscosity (η) at a velocity (U):

$$\mathbf{F}_{H}=-6\pi\eta a\mathbf{U}$$

• The analysis to find the Brownian motion of the gold particles is involved, and I will save the details for later lectures.

Fluctuation-dissipation

 a couple useful results for Brownian motion that we can use to make quick and accurate estimates

$$L^{2}_{RMS} = \left\langle \Delta x^{2} + \Delta y^{2} + \Delta z^{2} \right\rangle = \left\langle \Delta \mathbf{x} \cdot \Delta \mathbf{x} \right\rangle = 6Dt \quad \text{where} \quad D = \frac{kT}{6\pi\eta a}$$

- "root-mean-square" distance (L_{RMS}) that a particle will diffuse by Brownian motion in 3-dimensional space. For one dimension, the right hand side is simply one third as much, or 2Dt, and for two dimensions, 4Dt.
- The diffusion coefficient (D) is given by the Stokes-Einstein result on the right. Both the kT "kick factor" and the Stokes dissipation factor appear in the expression for D.

Diffusion of a colloidal particle example

What is the average (root-mean-square) distance a gold particle of diameter 0.9 μ m will diffuse in 3 dimensions in 1 minute? In 1 dimension? The temperature T = 298 K. The viscosity of water at 298 K is 0.00089 Pa-s.

Diffusion of a colloidal particle example

What is the average (root-mean-square) distance a gold particle of diameter 0.9 μ m will diffuse in 3 dimensions in 1 minute? In 1 dimension? The temperature T = 298 K. The viscosity of water at 298 K is 0.00089 Pa-s.

answer: $D = 5.45 \times 10^{-13} \text{ m}^2/\text{s}$, $L_{RMS,3D} = 14.0 \mu \text{m}$, $L_{RMS,1D} = 8.09 \mu \text{m}$.

Doublet Synthesis

- We are now armed with several simple and powerful results from colloidal physics, which enable us to design our process for **fabricating doublets**.
- Say we have **1.1 \mum diameter gold spheres** in water at 298 K, at a volume fraction of particles ϕ = **0.00033**. How do we form doublets?
- We first "stimulate" the aggregation by killing the electrostatic repulsive forces. We might suddenly change the pH – for our gold particles, which are for example stabilized by citric acid groups with a pKa of 3.1, we might change the pH to 1.5 or 2.0 – or we might suddenly change the ionic strength to say 500 mM KCl.
- Then as calculated before, we wait roughly 3 min.
- The final step is to **"quench" the aggregation**, by **restoring the electrostatic repulsion** between the particles. If we were using a low pH, we would add base to bring the pH back to 6.0 or so. If we were using a high ionic strength to kill the electrostatic repulsion, we would now dilute to 10 mM to restore the repulsive force.
Sorting. Colloidal assemblies must be sorted from mixtures.

- In the process of forming doublets, we are left with a large amount of "unreacted" singlets, as well as a small fraction of particles that went beyond doublets to form doublets, triplets, 4lets, and so on. After all, this is a random aggregation process.
- I will use the name "sedimentation" for the process of settling in a gravitational field (g), whether it is in the earth's gravitational field (1g) or in centrifugation (perhaps 1000s of g).

Particle motion – gravity sedimentation



 \leftarrow Suspensions are sometimes – but not always - sedimented

- F_{stokes}
- Gravitational force pulls down

$$F_{grav} = m_{particle} g = \frac{4}{3} \pi R^3 (\rho_{particle} - \rho_{media}) g$$

• Viscous friction resists downward motion

 $F_{Stokes} = 6 \pi \eta R u_{sed}$ \leftarrow Stokes formula – sphere of radius Rmoving in media of viscosity η

Combined formula
$$F_{grav} = F_{Stokes}$$

$$u_{sed} = \frac{2(\rho_{particle} - \rho_{media}) g R^2}{9 \eta}$$

Sorting. Colloidal assemblies must be sorted from mixtures.

- In the process of forming doublets, we are left with a large amount of "unreacted" singlets, as well as a small fraction of particles that went beyond doublets to form doublets, triplets, 4lets, and so on. After all, this is a random aggregation process.
- I will use the name "sedimentation" for the process of settling in a gravitational field (g), whether it is in the earth's gravitational field (1g) or in centrifugation (perhaps 1000s of g).
- An analysis of the fluid mechanics equations reveals that a sphere of density (ρ_p) settles in a fluid of density (ρ_f) and viscosity (η) during a sedimentation operation at a velocity (**U**) given by

$$\mathbf{U} = \frac{2a^2 \left(\rho_p - \rho_f\right)}{9\eta} \mathbf{g}$$

- If the particle is a doublet settling long-axis downward, the particle settles 1.55x as fast as a singlet, whereas if the long-axis is horizontal, the particle settles 1.41x as fast.
- Upon sorting the doublets, we end up with a suspension that appears as shown in Figure 1-4. This optical microscope image shows greater than 80% doublets, with only a few singlets. No high order aggregates appear.

Electrokinetics. Electric fields drive the fluid in the EDL.

- At this point we have our colloidal motor doublets.
- Will they in fact move like the Sen-Mallouk bimetallic nanorods?
- Through careful study it was found that the nanorods move by the mechanism of auto-electrophoresis.

8

Electrophoresis



potential)

- electrophoresis occurs when an applied electric field (E_∞) acts on the charges on the particle itself, as well as on the charges within the electrical double layer (EDL)
- The net result is that the electric field acts upon the charged fluid of the EDL which now behaves like a continuum of charged fluid with a volumetric charge density (ρ_e) causing it to move with a rather complex flow field field.

Electrophoresis exercise

Estimate how fast a 2.0 μ m diameter polystyrene sphere will move by electrophoresis through an aqueous solution of 0.1 M KCl at T = 293 K? The applied electric field is $\mathbf{E}_{\infty} = 3$ V/cm = 300 V/m. The zeta potential of the particle is $\zeta = +37$ mV, since it is amidine-functionalized. Compare this to speed to that of a pseudo-cubic hematite (α -Fe₂O₃) peanut-shaped particle with a length 1.8 μ m and a diameter 0.8 μ m, which at a particular pH also has $\zeta = +37$ mV.



Electrophoresis exercise

Estimate how fast a 2.0 μ m diameter polystyrene sphere will move by electrophoresis through an aqueous solution of 0.1 M KCl at T = 293 K? The applied electric field is $\mathbf{E}_{\infty} = 3$ V/cm = 300 V/m. The zeta potential of the particle is $\zeta = +37$ mV, since it is amidine-functionalized. Compare this to speed to that of a pseudo-cubic hematite (α -Fe₂O₃) peanut-shaped particle with a length 1.8 μ m and a diameter 0.8 μ m, which at a particular pH also has $\zeta = +37$ mV.

answer: Both move with $U = +7.9 \mu m/s$. This is a typical electrophoretic speed, given in $\mu m/s$. The size and shape of the particle do not affect the speed, when the thickness of the double layer is thin compared to the size of the particle (large κa). For a 1.0 μm radius particle in 100 mM KCl, $\kappa a = 1000$.

Auto-electrophoresis

- Electrophoresis is one type of electrokinetic phenomenon. There are others, such as diffusiophoresis, which we will explore in more detail.
- The colloidal motor doublets also move by an electrokinetic mechanism, called auto-electrophoresis.
- The silver-gold doublets are charged since they are in aqueous solution.
- The two metals catalyze the reaction of hydrogen peroxide in solution, and this reaction causes a spontaneous electric field to occur in the near vicinity of the particle.

Auto-electrophoresis

- At its surface the gold particle produces protons (H+) that diffuse and are convected toward the silver particle, where the protons are consumed in a reaction.
- The moving protons are what set up the electric field in the vicinity of the particle.
- This field acts on the charge groups on the particle and on the charge groups in the diffuse layer of the EDL around the particles.



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

Vol 464 25 March 2010 doi:10.1038/nature08906

COMMUNICATION

www.rsc.org/softmatter | Soft Matter

Vol 457 8 January 2009 doi:10.1038/nature07610

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

LETTERS

Measured long-range repulsive Casimir-Lifshitz forces

– J. N. Munday¹, Federico Capasso² & V. Adrian Parsegian³

Quantum fluctuations create intermolecular forces that pervade macroscopic bodies¹⁻³. 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.

Lock and key colloids

S. Sacanna¹, W. T. M. Irvine¹, P. M. Chaikin¹ & D. J. Pine¹

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*_n of a polymer

Literature and youtube presentations for Lecture 5

- Random group assignments
- <u>https://docs.google.com/spreadsheets/d/1EWhNB</u> <u>hl2nLaJGBrVEoSe4y0x5w41fPwD1HhYuJGUd9Y/edit</u> <u>#gid=267969935</u>

| Student | 2/6 | 2/13 | 2/20 | 2/27 | 3/12 | 3/19 | 3/26 | 4/2 | 4/9 | 4/16 |
|------------------------|-----|------|------|------|------|------|------|-----|-----|------|
| | А | А | Α | D | А | А | В | С | D | А |
| Mitchell Godek | D | С | D | В | D | В | Α | С | С | В |
| Jen Bradley | D | А | А | D | В | D | D | А | А | D |
| Amir Nazemi | В | D | D | С | В | А | С | D | D | С |
| Charlotte Zhao | D | D | В | В | А | С | Α | В | Α | А |
| | В | В | В | В | D | С | С | А | D | С |
| William Morgan | Α | С | А | В | С | А | D | В | С | В |
| Ankit Saraf | В | С | С | С | В | В | В | D | Α | D |
| Henry Thurber | Α | D | С | А | D | D | А | В | С | А |
| Ellie Anderson-Zych | С | А | С | В | А | С | D | А | D | D |
| Dushyanth Velugubantla | С | D | В | А | С | А | В | D | А | В |
| Gabrielle Grey | А | А | D | С | В | D | А | D | D | С |
| Weiyuan Fan | D | В | D | D | С | В | В | В | В | D |
| Aham Lee | С | В | А | С | А | В | D | А | В | А |
| Suraj Kannur | С | С | В | D | С | D | С | С | С | С |
| Nathan Bryant | С | D | А | А | D | В | А | С | С | В |
| Nhayeon Lee | В | В | С | С | С | С | D | С | В | С |
| Nathan Irgang | В | С | В | Α | А | С | В | D | В | D |
| Muchen Wang | А | В | С | А | D | D | С | А | А | А |
| Anna Klinger | D | А | D | D | В | А | С | В | В | В |

Key Video Presentation First Paper Presentation Second Paper Presentation

| Week 2 | | | | | | |
|--------|---------------------------------|--|--|--|--|--|
| Group | Paper Title | | | | | |
| Α | P2_Glotzer_NatMat_anisotropy_07 | | | | | |
| В | P3_kotov_science.1242477 | | | | | |
| С | P1_deGennes-RevModPhys.64.645 | | | | | |
| D | P4_whitesides-pq0802004769 | | | | | |