SURELY YOU'RE JOKING, MR. FEYNMAN!

ADVENTURES OF A CURIOUS CHARACTER

RICHARD P. FEYNMAN

THE OUTFRAGEOUS EXPLOITS OF THE WORLD'S MOST OUTSPOKEN NOBEL PRIZEWINNING SCIENTIST

15 WEEKS ON THE NEW YORK TIMES BESTSELLER LIST
the end of the meal, I said to the waitress, “Kohi-o motte kite nadasai.” She bowed and walked away.

My friend Marshak did a double take: “What? What?”

“I talk Japanese,” I said.

“Oh, you faker! You’re always kidding around, Feynman.”

“What are you talkin’ about?” I said, in a serious tone.

“OK,” he said. “What did you ask?”

“I asked her to bring us coffee.”

Marshak didn’t believe me. “I’ll make a bet with you,” he said. “If she brings us coffee...”

The waitress appeared with our coffee, and Marshak lost his bet.

It turned out I was the only guy who had learned some Japanese—even Wheeler, who had told everybody they ought to learn Japanese, hadn’t learned any—and I couldn’t stand it any more. I had read about the Japanese-style hotels, which were supposed to be very different from the hotel we were staying in. The next morning I called the Japanese guy who was organizing everything up to my room. “I would like to stay in a Japanese-style hotel.”

“I am afraid that it is impossible, Professor Feynman.”

I had read that the Japanese are very polite, but very obstinate: You have to keep working on them. So I decided to be as obstinate as they, and equally polite. It was a battle of minds: It took thirty minutes, back and forth.

“Why do you want to go to a Japanese-style hotel?”

“Because in this hotel, I don’t feel like I’m in Japan.”

“Japanese-style hotels are no good. You have to sleep on the floor.”

“That’s what I want; I want to see how it is.”

“And there are no chairs—you sit on the floor at the table.”

“It’s OK. That will be delightful. That’s what I’m looking for.”

Finally he owns up to what the situation is: “If you’re in another hotel, the bus will have to make an extra stop on its way to the meeting.”

“No, no!” I say. “In the morning, I’ll come to this hotel, and get on the bus here.”

“Well, then, OK. That’s fine.” That’s all there was to it—except it took half an hour to get to the real problem.

He’s walking over to the telephone to make a call to the other hotel when suddenly he stops; everything is blocked up again. It takes another fifteen minutes to discover that this time it’s the mail. If there are any messages from the meeting, they already have it arranged where to deliver them.

“It’s OK,” I say. “When I come in the morning to get the bus, I’ll look for any messages for me here at this hotel.”

“All right. That’s fine.” He gets on the telephone and at last we’re on our way to the Japanese-style hotel.

As soon as I got there, I knew it was worth it: It was so lovely! There was a place at the front where you take your shoes off, then a girl dressed in the traditional outfit—the obi—with sandals comes shuffling out, and takes your stuff; you follow her down a hallway which has mats on the floor, past sliding doors made of paper, and she’s going cht-cht-cht-cht with little steps. It was all very wonderful!

We went into my room and the guy who arranged everything got all the way down, prostrated, and touched his nose to the floor; she got down and touched her nose to the floor. I felt very awkward. Should I touch my nose to the floor, too?

They said greetings to each other, he accepted the room for me, and went out. It was a really wonderful room. There were all the regular, standard things that you know of now, but it was all new to me. There was a little alcove with a painting in it, a vase with pussywillows nicely arranged, a table along the floor with a cushion nearby, and at the end of the room were two sliding doors which opened onto a garden.

The lady who was supposed to take care of me was a middle-aged woman. She helped me undress and gave me a yukata, a simple blue and white robe, to wear at the hotel.

I pushed open the doors and admired the lovely garden, and sat down at the table to do a little work.

I wasn’t there more than fifteen or twenty minutes when something caught my eye. I looked up, out towards the garden, and I saw, sitting at the entrance to the door, draped in the corner, a very beautiful young Japanese woman, in a most lovely outfit.

I had read a lot about the customs of Japan, and I had an idea of why she was sent to my room. I thought, “This might be very interesting!”

She knew a little English. “Would you like to see the garden?” she asked.

I put on the shoes that went with the yukata I was wearing, and we went out into the garden. She took my arm and showed me everything.
L = R
When, Why, and How Does Like Like Like?

Electrostatic Attraction between Similarly Charged Species

(The DLVO theory?)
Coulomb law:

Plus (minus) repels plus (minus) and plus attracts minus,

(Like dislikes like and unlikes like each other)

if the pair exists alone.
Macroions and small ions in dissociating agent

Macroions
(charge $-Z_p$, radius $a$)

Salt ions

Counterions
\[ -Z_p - Z_p \]

Diagram:

- \( R \)
- \( a \)
- \( b \)
- \( Z_p^2/R^2 \)

Text:

\[ \approx Z_p^2/R^2 - Z_p/Z_p/Z_p^{2/R^2} - Z_p/Z_p^{2/R^2} = Z_p^2(1/R^2 - 1/r_{la}^2) < 0 \]

Counterion number \( \sim Z_p \)

\( R \gg r_{la}, r_{lb}, r_{lla}, r_{llb} \)

\( Z_p \uparrow: \) the attraction \( \uparrow \)
• Considering any one ion, we shall find on an average more dissimilar than similar ions in its surroundings, an immediate consequence of the electrostatic forces effective between the ions.

(Between likes) attraction arises because the repulsion of the likes and attraction of unlikes will tend to bring unlikes closer together and push likes farther apart.

Feynman Lecture on Physics, Chapt. 2
Experimental Findings of the Like-Like-Like Attraction

- Materials and techniques:
  - ionic latex particles
  - (microscopy, X-ray scattering, neutron scattering, dynamic/static light scattering)
  - polyelectrolytes, proteins, ionic dendrimers, ionic micelles, nanoparticles
  - (scattering)
  - counterion: mostly monovalent ions ($H^+$, $Na^+$)

Particle-Particle Interaction
Particle-Plane (Interface) Interaction
Intramacroion Interaction
Important Experimental Observations

(1) Formation of 3D-ordered structure at low salt conditions

(2) Solute distribution is NOT homogeneous.

- Non-space-filling structure
  - Coexistence of ordered and Brownian particles
- Void formation
Dilute Dispersions of Colloidal Particles

Colloidal particles as large as wavelength of visible light can directly be seen by (ultra-)microscope

R. Zsigmondy, Ann. Phys. 10, 1 (1903)

Seeing is believing / Believing is seeing
Ordered structure

Binary images of ordered structure with lattice imperfections. Sample: latex ($a$: 123 nm, $\sigma_a$: 1.9 $\mu$C cm$^{-2}$), $\phi$: $5 \times 10^{-3}$

2D-Fourier images
colloidal crystal

bcc and fcc are formed at low and high particle concentrations, respectively.

(real time) video-recording of particle distribution and motion on a horizontal plane 10 μm away from container wall

Particles are free from the wall effect and can move three-dimensionally (Einstein).
Movie
Trajectory in Two-State Structure

green: $t = 0$, yellow: $t = 11/15$ s

(1) Number density crystal > liquid
(2) No wall between crystal and liquid
(3) out-of-focus plane movement 15 out of 50

Latex particles ($a$: 150 nm, $\sigma_a$: 1.3 $\mu$C cm$^{-2}$), $\phi$: 0.02, at rm.
Inner structure as studied by confocal laser scanning microscope

Void filled with medium without particles

Brownian particles

**Fig. 1.** Confocal laser scanning micrographic image of random particle distribution. Latex, N1000 (diameter, 0.98 μm; charge density, 12.4 μC/cm²); latex concentration, 2%; dispersant, D₂O·H₂O. The latex particles are seen as white dots. The image shows the particle distribution in a horizontal focus plane.

**Fig. 2.** Void structures as seen by confocal laser scanning microscope at various times and distances from the glass-dispersion interface. The experimental conditions are the same as in Fig. 1. Direct micrographs were image-processed by an image data analyzer SEM-IPS (Carl Zeiss, Oberkochen, Germany) to obtain stronger contrast. Photographing conditions were adjusted between pictures so as to attain better contrast between particles and background. This caused distortions (for example, in the particle size) in the final images. The scale given applies to all nine pictures.
3D-CLSM images of voids

Sample: latex ($\alpha$:60 nm, $\sigma_a$: 4.8$\mu$C cm$^{-2}$), $\phi$:10$^{-3}$, medium: H$_2$O-D$_2$O ($\rho$: 1.05 g cm$^{-3}$)

The 3D images (for 160x160x64$\mu$m$^3$) are reconstructed from 40 LSM images, each 1.6 $\mu$m apart, observed by shifting the focus plane from 3 to 67 $\mu$m.
Dielectric Constant Dependence of the Interparticle Spacing in Crystal

\(\varepsilon \downarrow, 2D_{\text{exp}} \downarrow\)

(Z_p is not sensitive to \(\varepsilon\))

Ise et al. Langmuir, 6, 296 (1990)

\[ + \text{or} - \frac{Z_p^2}{\varepsilon R^2} \]
Polyoxomolybdate (POM) in water

Na$_{15}$[Mo(VI)$_{126}$Mo(V)$_{28}$O$_{462}$H$_{14}$(H$_2$O)$_{70}$]·~400H$_2$O

{Mo$_{154}$}

wheel-shaped (2$a$: 3.6 nm)

No hydrophobic moiety

Blue and light blue: Mo
Red: O

Hollow vescicle from POM wheels

DLS and SLS

\[ M_W : 2.54 \times 10^7 \]
\[ (= 1165 \text{ POM}) \]

\[ R_h : 45 \text{ nm} \]
\[ R_G : 45 \text{ nm} \]

Homogeneous sphere
\[ R_G = 0.77 \ R_H \]

2\(D_0\): 150 nm at 0.01 mg cm\(^{-3}\)

2\(D_{\text{exp}}\) = 5 nm

2\(D_{\text{exp}}\) < < 2\(D_0\)
Poly(alkyl-p-phenylene) sulfonates in water

M. Bockstaller et al., Macromolecules 34, 6359 (2001)
Structure formation of PPPS cylindrical micelles

Ellipsoidal cluster with internal lyotropic order

Long and short Axes: 300 and 120 nm at $c = 10^{-1}$

Triangular lattice

Nematic phase
Particle-Plane (Interface) Interaction
Interaction between (anionic) interface and (anionic) particles

Sample: latex ($a$:280 nm, $\sigma_a$: $-5.5 \mu$C cm$^{-2}$), $\phi$: $6.5 \times 10^{-4}$

$\zeta$ potential of glass surface:
$-70 \sim -90$ mV

$N(z)$: particle number in area $37 \times 31 \mu$m$^2$ counted by CLSM

Average particle number from $\phi$:
$20 \sim 30$
Observation

(1) Concentration effect at low $C_s$ and in a $z$-range (5 – 60 $\mu$m)

(2) The effect disappears at $10^{-4}$ M. (electrostatic effect)

(3) The effect is enhanced with increasing charge density of particles.
Concentration effect and charge number

$N_5, N_b$: particle numbers at $z = 5 \, \mu m$ and $60 \, \mu m$

Particle charges
(4) The effect becomes larger with increasing charge number of the interface.

(5) The observation is in disagreement with double layer interaction theory.
Concentration effect and interface charge number

(A) Δ: Glass surface modified by coupling polystyrene sulfonate with silanol groups (ζ: -94 mV). ○: unmodified (ζ: -70 mV)
(B) □: modified with polyacrylamide (ζ: -4 mV). ○: unmodified (-24 mV)

| charge number | ↑, concentration effect ↑. |
DLVO theory:

Poisson equation

\[ \Delta \psi = - \left( \frac{4 \pi \rho}{\varepsilon} \right) \]

Boltzmann distribution

\[ n_i = n \exp \left( -e \frac{\psi}{k_B T} \right) \]

surface charge number \( \sigma \)

\[ \sigma = - \int_0^\infty \rho \, dr \]
Neutron reflection study on the interface-micelle interaction


Sample: $C_{14}D_{29}N(CD_{3})_{3}Br/H_{2}O$

$\phi$

0.6

0.1

0.07

Av. $\phi$: 0.05
• Interpretation

Repulsion-only assumption

(Anionic) particles are pushed from the (anionic) interior toward interfaces, causing higher concentrations near the interfaces.

If so, higher charges of the interface should decrease the particle number by repulsion.

(opposite to the observation)
Counterion-mediated attraction between anionic interface and anionic particles

Triple-ion is more favored than ion-pair and free ion.

At a given charge density and for infinite interface, particle-interface attraction is stronger particle-particle attraction.
Intramacroion Interaction
flexible ionic polymer chain
Viscosity of non-ionic polymer solutions

\[ \frac{\eta_{sp}}{c} = [\eta] + k' [\eta]^2 c \]

Reduced viscosity increases with concn.

\[ [\eta] = KM^\alpha (\text{MHS}) \]

\[ \alpha \]

- sphere: 0
- random coil: 0.5 ~ 0.8
- rod: 2
Ionic polymers

R. M. Fuoss, Discuss. Faraday Soc. 11, 125, 1951

Sample: Butyl bromide-quarternized polyvinyl pyridine

Curve 1: water, 2: Fuoss plot, 3: $10^{-3}$M KBr, 4: $3.35 \times 10^{-3}$ M KBr

Reduced viscosity ($\eta_{sp}/c$) simply decreases with increasing concentration under salt-free condition.
Fuoss’ plot

\[ \eta_{sp}/c = A/(1 + B \ c^{1/2}) + D \]

\[ 1/ (\eta_{sp}/c - D) = 1/A + Bc^{1/2}/A \]

\[ c \to 0, \quad [\eta] = (A + D) \]

Un-neutralized polymethacrylic acid: \( \alpha = 0.82 \)

100%-neutralized PMA: \( \alpha = 1.87 \)

random coil \( \to \) rod (\( c = 0 \))
Full dissociation

Stronger dissociation and repulsion (elongation)

Partial dissociation

$\eta_{sp}/c$

$c$
(1) Full dissociation: acceptable at infinite dilution.

Is the ionic concentration inside macroion domain so low? No!

- anion-anion distance in 10 M NaCl: ~0.62 nm
- COOH-COOH distance for PAA: ~0.25 nm

“ionic concentration” in PAA domain:
roughly $10 \times \left(\frac{0.62}{0.25}\right)^3 = 152$ M
(2) Sharp decrease of $\eta_{sp}/c$
also for latex particles and spherical gels

polystyrene-based telechelic polymers with one ionizable group at the chain end (No intra-molecular interaction)

Reduced viscosity against polymer concentration for mono halato-telechelic ionomer (♦) in DMF as well as for unquaternized polymer (■).
(3) A maximum in $\eta_{sp}/c$-c plots


**Figure 2.** Reduced viscosity plotted against concentration for aqueous and saline solutions of sodium polystyrene sulphonate. $\bigcirc$, Conductivity water; $\square$, $5 \times 10^{-5}$ M NaCl; $\triangle$, $7 \times 10^{-4}$ M NaCl; $\blacksquare$, $8 \times 10^{-3}$ M NaCl.

**Figure 3.** Reduced viscosity plotted against concentration for solutions of fractionated sodium polystyrene sulphonate. Fractions obtained: $\bigcirc$, by HCl precipitation, in water; $\triangle$, by NaI precipitation, in water; $\blacksquare$, by NaI precipitation, in $4 \times 10^{-5}$ M NaCl; $\square$, by NaI precipitation, in $4 \times 10^{-3}$ M NaCl.
NaPSS in water after shear rate correction at 25°C

○: $M_W$: $1.7 \times 10^6$
Deg. of sulfonation: 0.88

▲: $1.1 \times 10^6$, DS: 0.8!

□: $6.7 \times 10^5$, DS: 0.73,

●: $3.7 \times 10^5$, DS: 0.85

J. Yamanaka et al, JACS, 112, 587 (1990)
Molecular weight dependence of $[\eta]$ of NaPSS at 25 C

○: observed
●: Kirkwood-Auer theory

Line A: $\alpha$: 1.6
Line B: 1.2

$\alpha \neq 2$
rod model is not valid?
Experimental data against rod-model

Butler (1957), sedimentation coefficient end-to-end distance $< (1/2)$ of contour length

Krause (1989), SLS

Amis (2001), SANS radius of gyration $R_{G,c} <<$ rod model
Why does the DLVO theory give only the repulsion?

Analysis by Fowler–Guggenheim, McQuarrie of the D-H Theory

\[ \frac{\beta \Delta F^{el}}{V} = -\frac{\kappa^3}{12\pi} \quad \text{at} \quad \kappa a \to 0 \]

\[ \kappa^2 = \frac{4\pi\beta}{\epsilon V} \sum q_i^2 c_i \]

\[ \beta = \frac{1}{k_B T} \]

\[ \mu_i^{el} = \left( \frac{\partial \Delta F^{el}}{\partial N_i} \right)_{T,V} \]

\[ \Delta G^{el} = \sum_i N_i \mu_i^{el} \]

\[ \beta \Delta G^{el} = \frac{-\kappa^3}{8\pi} \]

\[ \frac{\beta \Delta G^{el}}{V} = \frac{\beta \Delta F^{el}}{V} + \beta p^{el} \]

\[ \beta p^{el} = -\frac{\kappa^3}{24\pi} \quad \text{(negative)} \]

Generally, \( \Delta G^{el} \neq \Delta F^{el} \) due to the interaction.
In the DLVO theory, $\Delta G_{el} = \Delta F_{el}$

(because of incompressibility of solvent, $\Delta V_{el} = 0$)

The osmotic term is NOT considered.

$p_{el}$ is assumed to be zero.
The natural function for the determination of equilibrium is the Gibbs free energy, because experiments are performed at constant pressure and temperature.
Pair-Potentials by Sogami

Helmholtz free energy

\[ U^F = \frac{Z^2 e^2}{\varepsilon} \frac{1}{r} \exp(-\kappa r) \]  (Pure repulsion)

Gibbs free energy

\[ U^G = \frac{Z^2 e^2}{\varepsilon} \left[ \frac{1 + k \text{coth}(ka)}{r} - \frac{1}{2} \kappa \right] \exp(-\kappa r) \]

Origin of attraction

Overbeek’s criticism


“Sogami theory… contains errors and, when the errors are corrected, $\Delta G^e = \Delta F^e$, and attraction disappears.”
Derivation of $\Delta G^{el}$ from $\Delta F^{el}$

$[\partial \Delta F^{el}/\partial N_i]_{V,T}$  $\mu_i$  solvent, solutes  $\Delta G^{el} = \Sigma N_i \mu_i$

$(\partial \Delta F^{el}(T, V, N_i) / \partial N_0)_{V,T}$

$(\partial \Delta F^{el}(T, v_0N_0, N_i) / \partial N_0)_{V,T}$

0  (D-H theory)  $-k^2$

$V = v_0 N_0$
\[ (\partial \Delta F^e_l(T, V, N_i)/\partial N_i)_{V,T} \]
\[ \approx (\partial \Delta F^e_l(T, v_0N_o, N_i)/\partial N_i)_{V,T} \]
\[ + K^2 \]

Summing up the solvent and solute contributions,
\[ \Delta G^e_l = \Delta F^e_l. \]

If Overbeek’s substitution were correct, not only the Sogami potential but also the D-H theory is wrong.
“Interparticle interaction is purely repulsive in a mean field approach (repulsion-only assumption)”

Not axiomatically correct.

It happens to originate from $\Delta G^{el} = \Delta F^{el}$. 
MC simulation with the Sogami potential

\[ U^G(r) = \left[ \sinh(\kappa a) \frac{Z_n e}{\kappa a} \right]^2 \frac{1}{2\varepsilon} \frac{A}{r - \kappa} \exp(-\kappa r) \]

\[ A = 2 + 2\kappa \text{coth}(\kappa a) \]

\[ \kappa^2 = \left[ \frac{4\pi e^2}{\varepsilon k_B T} \right] [n_p Z_n + C_s] \]

\[ R_m = \left[ A + \{ A (A + 4) \}^{1/2} \right] / 2\kappa \]

MC simulation; \( N: 432, a: 55 \text{ nm} \), parameters: \( \phi, \sigma_n \) and \( C_s \).

radial distribution function \( g(r) \) and mean square displacement \( \langle r^2 \rangle \)

bcc-fcc and solid-liquid transitions

\[ C_s: 0, \ \sigma_n: 0.15 \, \mu\text{C cm}^{-2} \]
\[ \phi: a, 0.1, b, 0.14, c, 0.2, d, 0.3 \]

Transition point \( \phi: 0.14 \sim 0.20 \)

Sirota 0.15 \sim 0.20 for \( a: 45.5 \, \text{nm} \)

\[ C_s: 4 \, \mu\text{M}, \ \sigma_n: 0.2 \, \mu\text{C cm}^{-2} \]
\[ \phi: a, 0.01, b, 0.015, c, 0.02, d, 0.03 \]

Melting: 0.015 \sim 0.02
Solid-void/liquid transition with varying $\sigma_n$ (A) and $C_s$ (B)

$C_s: 0$, $\phi: 0.03$

$\sigma_n: 0.35$, $\phi: 0.03$

Insets: projection of particle coordinates

In the MC cell

(No void from the MC with DLVO potential)
Why was the DLVO theory “successful”?
The DLVO scheme is advocated by ignoring historical findings.

Inhomogeneous charge distribution (AFM)

Hectic rotational motion → smearing of inhomogeneity
Why was the DLVO theory “successful”?

1. Mostly low charge density samples are studied, so that $\Delta G^{el}$ is almost equal to $\Delta F^{el}$.
2. Charge number is estimated by $\zeta$ potential, which is not well-defined.
3. Hamaker constant is regarded as adjustable parameter.
4. The two-body theory is applied for many-body phenomena, or high concentrations.
5. The counterconcept is not disproved.
<table>
<thead>
<tr>
<th>author</th>
<th>$\sigma_n$</th>
<th>radius</th>
<th>Reference</th>
<th>Note</th>
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<td>320</td>
<td>5</td>
<td>d</td>
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<td>Grier</td>
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<td>Category B (Attraction was detected.)</td>
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<tr>
<td>Ito</td>
<td>1.33</td>
<td>250</td>
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Why was the DLVO theory “successful”?

1. Mostly low charge density samples are studied, so that $\Delta G^{el}$ is almost equal to $\Delta F^{el}$.
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Definition of $\zeta$ potential

There is no direct measure of the distance of the slipping plane from the surface... It is impossible to relate $\zeta$ directly to $\psi_a$

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( f^b )</th>
<th>( t_{2p} )</th>
<th>( Z_n )</th>
<th>( \sigma_n ) ( \mu \text{C cm}^{-2} )</th>
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<tr>
<td>(A) SS-36 (( a=65 \text{ nm} ), ( Z_a=1.5 \times 10^4 ), ( \sigma_a=4.6 \mu \text{C cm}^{-2} ), ( \zeta^c=-72\sim-137 \text{ mV} ))</td>
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<td>0.012</td>
<td>0.13 [0.09]</td>
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<td>(B) SS-39 (( a=175 \text{ nm} ), ( Z_a=2.6 \times 10^5 ), ( \sigma_a=10.6 \mu \text{C cm}^{-2} ), ( \zeta^c=-43\sim-49 \text{ mV} ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.015</td>
<td>0.08[0.01]</td>
<td>0.05</td>
<td>2.08\times10^4</td>
<td>0.85</td>
</tr>
<tr>
<td>0.049</td>
<td>0.07</td>
<td>0.07</td>
<td>1.82\times10^4</td>
<td>0.74</td>
</tr>
<tr>
<td>0.075</td>
<td>0.08</td>
<td>0.06</td>
<td>2.08\times10^4</td>
<td>0.85</td>
</tr>
<tr>
<td>(C) #1 (( a=38 \text{ nm} ), ( Z_a=7.2 \times 10^5 ), ( \sigma_a=650 \mu \text{C cm}^{-2} ), ( \zeta^c=-55\sim-83 \text{ mV} ))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0011</td>
<td>0.04[0.001]</td>
<td>0.05</td>
<td>2.9\times10^4</td>
<td>26</td>
</tr>
<tr>
<td>0.0018</td>
<td>0.04</td>
<td>0.07</td>
<td>2.9\times10^4</td>
<td>26</td>
</tr>
<tr>
<td>0.0023</td>
<td>0.04</td>
<td>0.10</td>
<td>2.9\times10^4</td>
<td>26</td>
</tr>
<tr>
<td>0.0041</td>
<td>0.03</td>
<td>0.09</td>
<td>2.2\times10^4</td>
<td>20</td>
</tr>
</tbody>
</table>

\(^a\) The samples (A) and (B) are copolymers of styrene and styrene sulfonate and are believed to have the charges on the particle surface. (C) is prepared by sulfonation of polystyrene spheres with \( \text{SO}_3 \), and the charges are inside of the sphere and on the surface. Thus the surface charge density per unit surface is not important.

\(^b\) The value in [ ] is due to Alexander et al.'s theory [6].

\(^c\) Obtained by using a theory of Wiersema et al.[7] from the mobility found by electrophoresis at \( \phi = 10^{-5} \).
Number of ionizable groups \((Z_a)\):

Conductometric titration

Number of net charge \((Z_n)\):

Conductance measurements

\[
K = n_p Z_n e \Lambda (H^+)/N_{av} + K_b
\]

\(K\): conductivity, \(n_p\): particle number, \(e\): electron charge, 
\(\Lambda\): specific conductivity, \(N_{av}\): Avogadro number, 
\(K_b\): conductivity of supporting medium
(Shaefer)
Results of transference experiments of acid-form latex

$f$ is smaller than 0.14 and decreases with increasing $\sigma_a$.

(cf. $f = 0.4 \sim 0.9$ for linear polyions)

$t_{2p}$ is smaller than 0.13 and tends to decrease with increasing $\sigma_a$.

(cf. $t_{2p} \sim 0.5$ for linear polyions)

No correlation between $\zeta$ and $\sigma_n$
<table>
<thead>
<tr>
<th>$Z_a$ / particle (conductance)</th>
<th>$\zeta$-potential (mV)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.5 \times 10^4$</td>
<td>- 72 $\sim$ - 137 (-53)$^b$</td>
</tr>
<tr>
<td>$2.6 \times 10^4$</td>
<td>- 43 $\sim$ - 49 (-51)</td>
</tr>
<tr>
<td>$7.2 \times 10^4$</td>
<td>- 55 $\sim$ - 83 (-88)</td>
</tr>
</tbody>
</table>

\[ u = 10^3 \kappa t_{2p}/cF = \varepsilon \zeta f(\kappa a, \zeta)/\pi \eta \]

b: microelectrophoresis at volume fraction of $10^{-5}$
Why was the DLVO theory “successful”?

1. Mostly low charge density samples are studied, so that $\Delta G^{el}$ is almost equal to $\Delta F^{el}$.
2. Charge number is estimated by $\zeta$potential, which is not well-defined.
3. Hamaker constant is regarded as adjustable parameter.
4. The two-body theory is applied for many-body phenomena, or high concentrations.
5. The counterconcept is not disproved.
Highly concentrated dispersion
Dilute dispersion

Clustering

Free particle

voids
Why was the DLVO theory “successful”?

1. Mostly low charge density samples are studied, so that $\Delta G^{el}$ is almost equal to $\Delta F^{el}$.

2. Charge number is estimated by ζpotential, which is not well-defined.

3. Hamaker constant is regarded as adjustable parameter.

4. The two-body theory is applied for many-body phenomena, or high concentrations.

5. The counterconcept is not disproved.
Logical requirement:

Proposition A and its counterproposition B

If A should be proven correct,
B must be proven wrong.

In the repulsion/attraction arguments,
attraction has never been tested.
("Inconvenient truth" is ignored.)
repulsion cannot be claimed to be correct.
Experiments were carried out under conditions where the attraction happened to be negligible. (e.g., low charge particles)
Cockroach experiment

Forward, march!

This experiment proves conclusively that cockroaches hear with legs

M. Eigen, R. Winkler, Das Spiel: Naturgesetze steuern den Zufall, Kap. 17
SAXS curves of polyvinylpyrrolidone (PVP) and its mixtures with polystyrene sulfonate (PSS)

1 & 2: [PVP] = 0.04 & 0.08gml$^{-3}$, 3:[PSS] = 0.04, 4: [PVP & PSS] = 0.02 + 0.04, 5:[PVP & PSS] = 0.04 + 0.04
Counterion valency

Prevailing view (from computer simulation)

(Linse et al. Phys.Rev.E 63, 020401(R) ’01)

Attraction is possible for multi-valent counterions, but not for mono-valent counterions.

Attraction appears at short distances.
SAXS and SANS study of ionic dendrimers


Schematic diagram of a third generation (3G) PAMAM dendrimer with an EDA core. The 2-d structure is idealized.
SAXS curves from ionic dendrimer solutions

Mono-valent counterions: Structure formation with the same Bragg spacing

Bi-valent counterions ($\text{SO}_4^{2-}$): No structure formation

$(G7, \text{weight fraction } w = 0.05)$
Structure factor for G7 dendrimer

Assuming $f_M(K)$ for a sphere, $F(K)$ is derived by

$$I(K) = F(K) f_M(K)$$

As $w$ increases, $2D_{\text{exp}}$ decreases.
Number of ionizable groups ($Z_a$): 
Conductometric titration

Number of net charge ($Z_n$): 
Conductance measurements

\[ K = n_p Z_n e \Lambda (H^+)/N_{av} + K_b \]

$K$: conductivity, $n_p$: particle number, $e$: electron charge, 
$\Lambda$: specific conductivity, $N_{av}$: Avogadro number, 
$K_b$: conductivity of supporting medium 
(Shaefer)
Table 3.2. Charge number of a cationic dendrimer at a degree of neutralization of 0.6

<table>
<thead>
<tr>
<th></th>
<th>$a$ (nm)$^a$</th>
<th>$Z_{nd}^d$</th>
<th>$\sigma_n$ ($\mu$C cm$^{-2}$)$^e$</th>
<th>$\sigma_a$ ($\mu$C cm$^{-2}$)$^f$</th>
<th>$\sigma_n/\sigma_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water$^b$</td>
<td>Acids$^c$</td>
<td>Cl$^{-}$ SO$_4^{2-}$</td>
<td>Cl$^{-}$ SO$_4^{2-}$</td>
<td>Cl$^{-}$ SO$_4^{2-}$</td>
</tr>
<tr>
<td>G4</td>
<td>2.1</td>
<td>2.3</td>
<td>18 5</td>
<td>4.4 1.1</td>
<td>9.5 0.46 0.12</td>
</tr>
<tr>
<td>G7</td>
<td>4.3</td>
<td>4.5</td>
<td>44 11</td>
<td>2.7 0.66</td>
<td>19 0.14 0.044</td>
</tr>
<tr>
<td>G10</td>
<td>7.0</td>
<td>7.1</td>
<td>134 31</td>
<td>3.4 0.79</td>
<td>62 0.054 0.012</td>
</tr>
</tbody>
</table>

$^a$ radius, $^b$ $\alpha_d = 0$, $^c$ $\alpha_d = 1.0$, $^d$ net charge number, $^e$ net charge density, $^f$ analytical charge density.

Z$_n$: monovalent > bivalent, increases with rising generation no.
I shall certainly admit a system as empirical or scientific only if it is capable of being tested by experience. ….Not the verifiability but the falsifiability of a system is to be taken as a criterion of demarcation. It must be possible for an empirical scientific system to be refuted by experience.

(Sir Karl Popper, The Logic of Scientific Discovery, 1965)
$2D_{\text{exp}} \downarrow$

polymer concentration $c_p \uparrow$:
dielectric constant $\varepsilon \downarrow$:
temperature $T \uparrow$:
charge number $Z_n \uparrow$:
salt concentration $C_s \uparrow$:
When is the DLVO theory correct?

\[ \beta p = \sum c_s + \beta p^el \]

van’t Hoff interaction

High

Low

\[ C_s \]

\[ \rho^{el} \]

(low charge density)
Critical comments against the attraction

“Simply unacceptable because it is against the DLVO concept.”

Is the concept perfect?

A scientific system must be refuted by experience; A system is scientific only if it is capable of being tested by experience.

(Karl Popper)

Unreasonable Exuberance
(2) “The attraction is explainable by the DLVO theory, if a new factor (parameter) is taken into consideration.”
The counterion-mediated attraction can easily be observed, at high charge density particles

at low particle concentrations

at low salt concentrations

even for mono-valent counterions

(at variance with some computer simulations)
Overbeek’s criticism (J. Chem. Phys. 87, 4406 (1987))

$V$ in eq (8) was substituted by $N_0\nu_0$.
($\nu_0$: molar volume of solvent)

\[
(\partial F^e(T, V, N_j)/\partial N_0)_{V,T} = 0 \text{ (D-H theory)}
\]

\[
N_0\partial \kappa^2 / \partial N_0 = -\kappa^2
\]

solute \quad \left(\partial F^e(T, V, N_j)/\partial N_j\right)_{V,T}

\[
\sum_j N_j \partial \kappa^2 / \partial N_j = \kappa^2
\]

The contributions of solvent and solute in eq (8) cancel out, resulting

\[
F^e = G^e = -V \kappa^3 / 8\pi\beta , \text{ and } p^e = 0.
\]
If Overbeek’s criticism were correct, the D-H theory is wrong.

\[ \beta p = \sum c_s + \beta p^{el} \]

\[ p: \text{osmotic pressure} \]

\[ \beta p = \sum c_s + \beta p^{el} \]

\[ \beta p^{el} = -\frac{K^3}{24\pi} \]

D-H

= 0

DLVO