Forming stable dispersions of nanoparticles

Live in Amherst – 29th January 2009

Alan F Rawle Ph.D

Malvern Instruments, Westborough, MA, U.S.A.

Alan Rawle = "Learn a Law"

CoChair E56.02 SubCommittee on Characterization: Physical, Chemical, and Toxicological Properties

ASTM E56 Committee on Nanotechnology

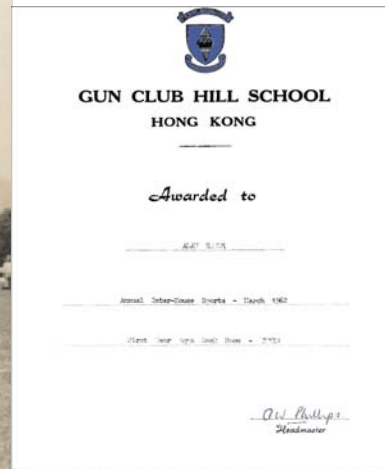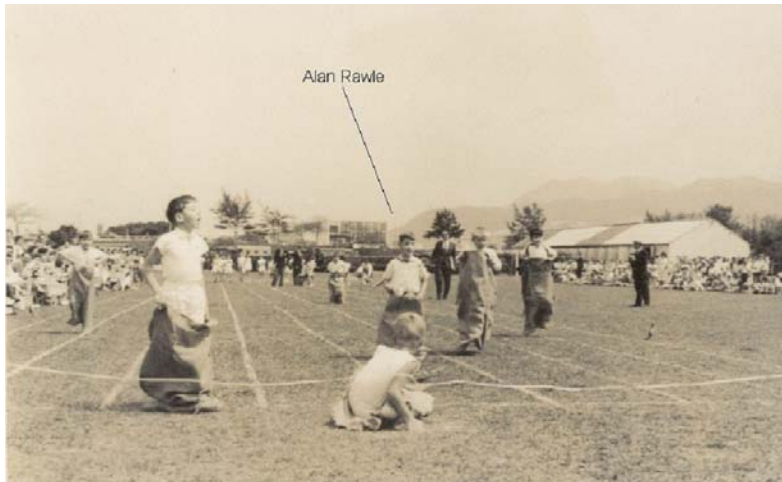ISO TC24/SC4 Particle Characterization
Convener: WG10 Small Angle X-Ray Scattering (SAXS)

Alan Rawle Qualifications
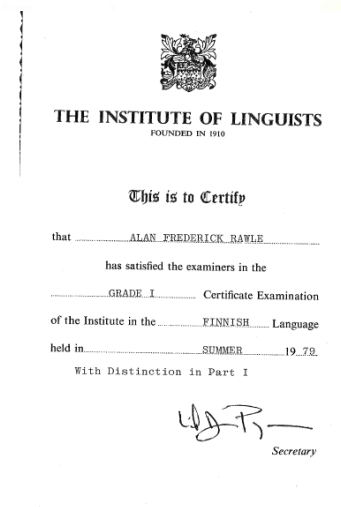

- 3rd Place Potato Sack Race (March 1962)

- Amateur Swimming Association Bronze Award (June 1967) – swim 33 yards
- Institute of Linguists Grade 1 in Finnish Language (1979)
- Hyvää Päivää !

Crow's Law

- **"Do not believe what you want to believe until you know what you need to know"**

- **Attributed to John Crow, who taught at King's College, London**
- **Quoted in: Obituary: Professor R. V. Jones**
- **The Independent (London), Dec 19, 1997 by M. R. D. Foot**
- **http://findarticles.com/p/articles/mi_qn4158/is_19971219/ai_n14140235**

Drexler

▶ **"The micron scale is volumetrically 10^9 times larger than the nanometer scale. Confusing microtechnology with molecular technology is like confusing an elephant with a ladybug"**

▶ **K. Eric Drexler**

   (Q: Who knows what the 'K' stands for?)

▶ **Quoted in: Ed Regis, (1995), Nano: the emerging science of nanotechnology, Little, Brown and Company, 1st Edition, pp 207-208 ISBN 0-316-7358-1**
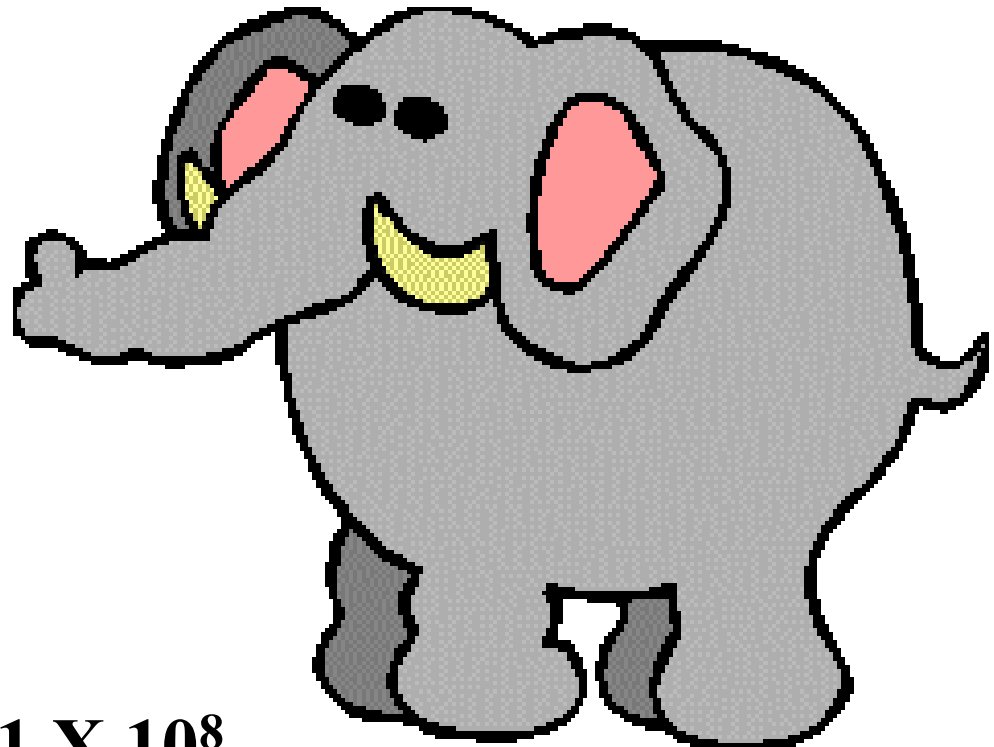
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Ladybug - 35mg
Elephant – cow – not bull – 3500kg

$$3500/(35 \times 10^{-6}) = 1 \times 10^{8}$$

Some examples of nanoparticle (< 100nm) dispersions

▶ **Titanium dioxide of 20 – 50nm used for UV absorbing properties in transparent varnishes**

▶ **Colloidal gold used to carry drugs through a biological barrier**

▶ **Quantum dots where the size of particle dictates the observed color**

TiO$_2$ – optical properties

▶ **Either:**

    - The most opaque/hiding power pigment (due to scattering virtually all the light)

▶ **Or…**

    - A transparent pigment

▶ **Simply dependent on particle size!**

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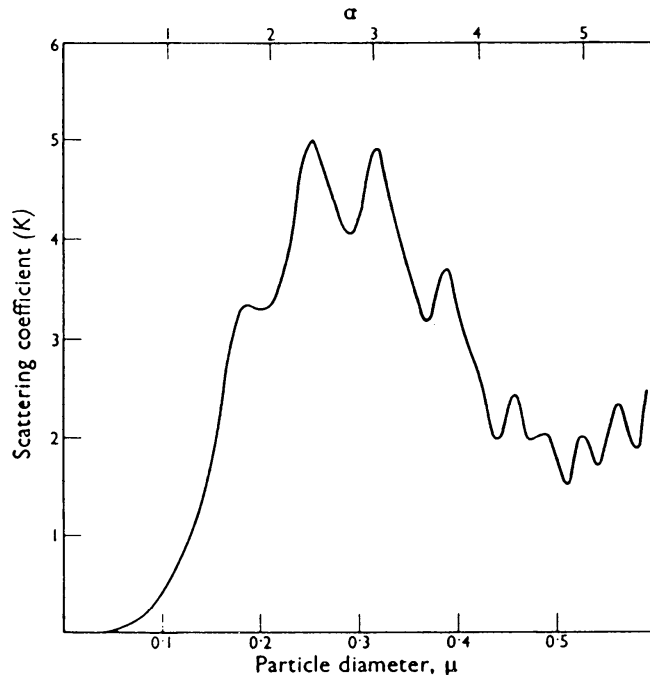
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Fig. C. Variation of scattering coefficient, K, with particle diameter of rutile titanium dioxide, for light of wavelength, λ_0, of 500 mμ, and refractive index ratio, m, of 1·795

S T Loney "Scattering of light by white pigment particles"
Paint Research Station Technical Paper No 213, 1960

Weber simplification of Mie:

$$2r \sim \lambda_m / 1.5(n_1 - n_2)$$

where r is the radius of the particle, λ the wavelength of impinging light and n_1 the RI of the particle and n_2 the RI of the medium the particle resides in

$$2r \cong \frac{\lambda_M}{1.5(n_P - n_B)} \qquad [2]$$

$2r$ = Teilchendurchmesser
n_B = Brechungsindex des Mediums } im
n_P = Brechungsindex des Pigmentes } Vakuum
λ_M = Wellenlänge am Extinktionsmaximum.

Weber H H. Lichtstreuung und Teilchengrößenverteilung kugelförmiger Teilchen II Experimenteller Teil Kolloid-Zeitschrift und Zeitschrift für Polymere, Band 188, Heft 1, 40 – 44 (1962)

But, first… Why?

- Not, "Why am I here?" but rather "Why am I taking the measurement?"

- "For QA"
- "My boss says so"

  not good enough……………..

Why?

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▶ **Bulk Properties (often mass or inertia specific)**

  - Flowability

  - "Filter-ability"/filter blockage

  - Viscosity/rheological properties/flow

  - Agglomeration/lumpiness

  - Dusting tendency

▶ **All 'low energy states**

▶ **"As is"**

Why?

▶ **Primary particle properties (surface area specific)**
- Activity/reactivity rate (e.g. of catalyst)
- Dissolution rate (of pharmaceutical)
- Gas absorption (BET N_2 physisorption)
- Hydration rate (of cement)
- Moisture absorption
- Combustion rate (of fuel)   (α $1/d^2$)
- Toxicity?

▶ **Needs energy to get to this state from the bulk**
▶ **The need to create this state in a top-down (e.g. comminution) process will involve energy input**

Heywood

▶ "However, it must be realised that particle size analysis is not an objective in itself but is a means to an end, the end being the correlation of powder properties with some process of manufacture, usage or preparation"

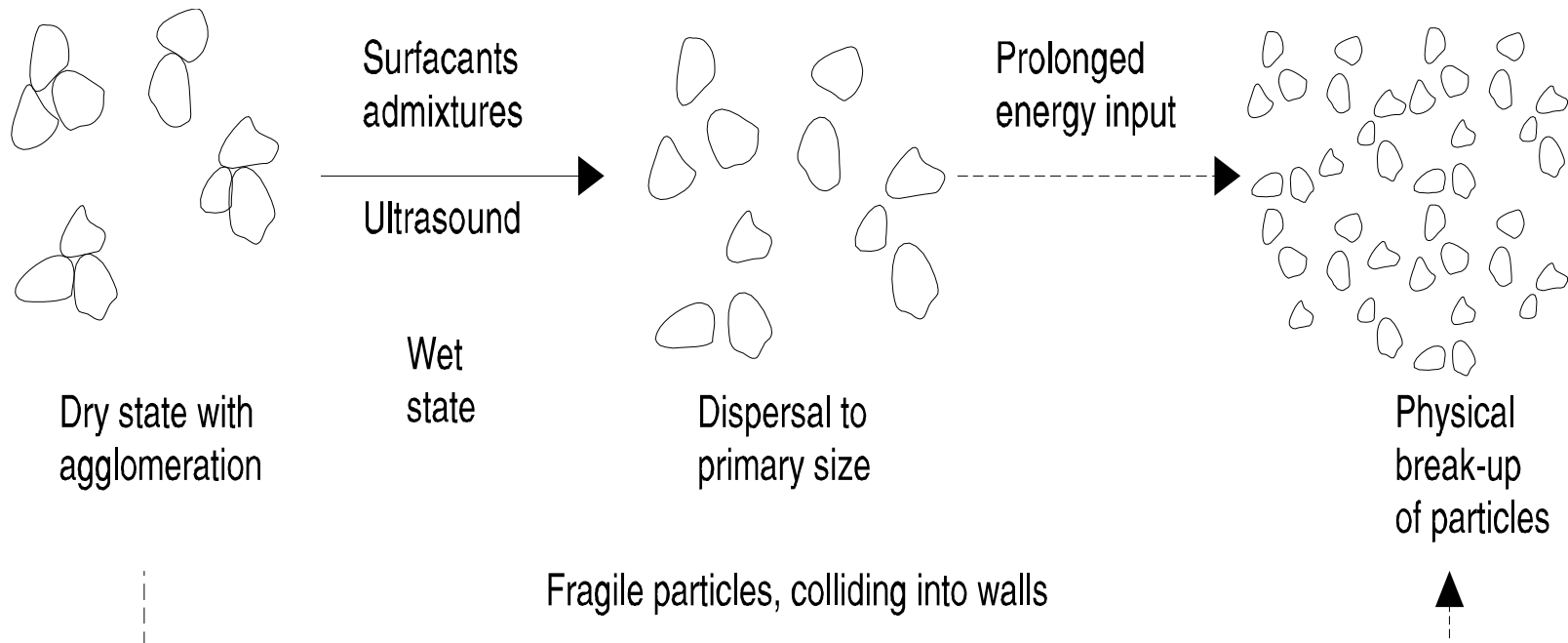▶ H Heywood Proc. 1st Particle Size Anal. Conf.   September 1966 p 355 - 359 (Heffer)

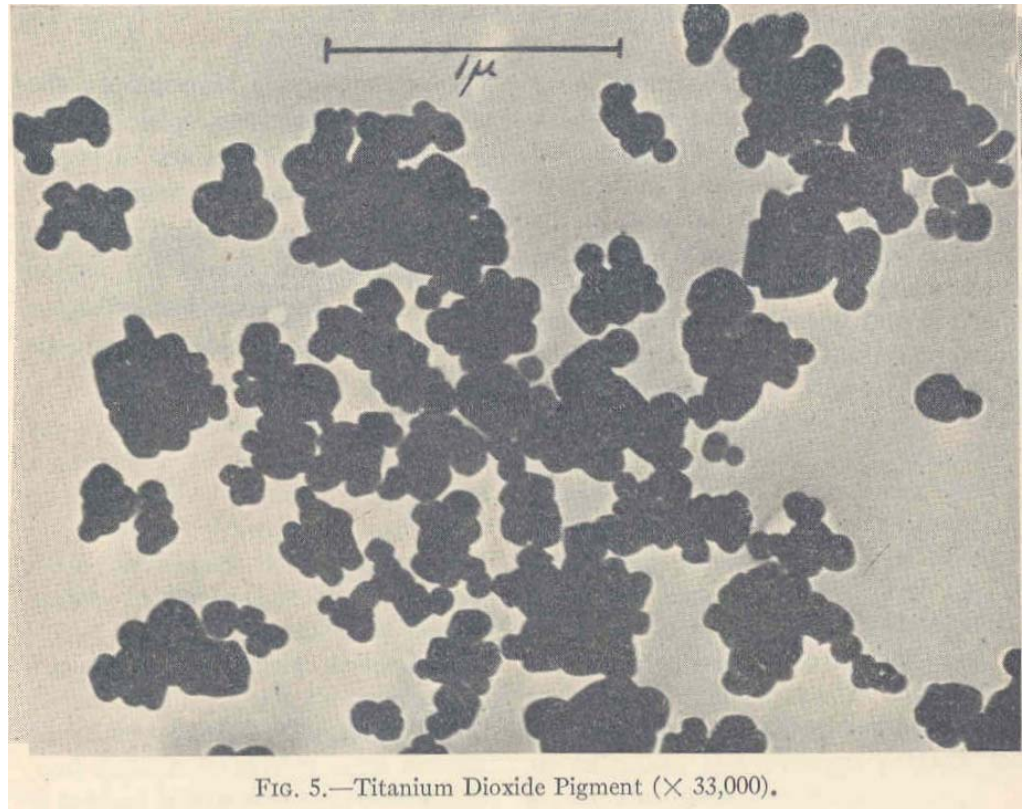▶ Given in the final plenary lecture of this conference

Top-down

- **Top-down (size reduction) processes tend to be energy intensive because of the creation of new surface (separation involves energy)**

- **1% of the world's electrical energy is used in crushing and grinding cement**

  (Particulate Technology Clyde Orr Macmillan 1966, p 45)

De-agglomeration

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TiO$_2$ – bulk and primary sizes
'Dispersion'? How?

FIG. 5.—Titanium Dioxide Pigment ($\times$ 33,000).

J Hillier 'The Electron Microscope in the determination of particle size characteristics' in 'Symposium on New methods for Particle Size Determination in the Subsieve Range'

Washington Spring Meeting American Society for Testing Materials, March 4, 1941, ASTM (1941) pp 90 – 94 Figure 5 (p 93)

Milling/Comminution/ Size Reduction

▶ **General rule:**

$$dE/dX = - cX^n$$

where E = Specific Energy Consumption, X = Particle size, c, n are constants

▶ **Rittinger (1867); n = 2 Applicable to fine grinding (1000 to 10μm or so)**
Energy consumed is proportional to the new surface area produced (SA α 1/d^2 & Weight α d^3 so for a given weight SA α 1/d)

$$E = c[1/X_p - 1/X_f]$$

▶ **Kick (1885): n =1 Applicable to crushing (to 6 or 10mm or so)**
Energy required is proportional to reduction in volume or weight (Energy required is proportional to logR/log2 if R = X_f/X_p

$$E = c.ln[X_f/X_p]$$

▶ **Bond (1951/2): n = 1.5**

$$E = 2c[1/\sqrt{X_p} - 1/\sqrt{X_f}]$$

Useful work is inversely proportional to the square root of the diameter of the new particle (or proportional to the new crack length); SA of unit volume α 1/d as before. Crack length in unit volume α one side of that area and thus inversely α to square root of the diameter

▶ **Hukki 4th Law (1960/1975): n changes with particle size**

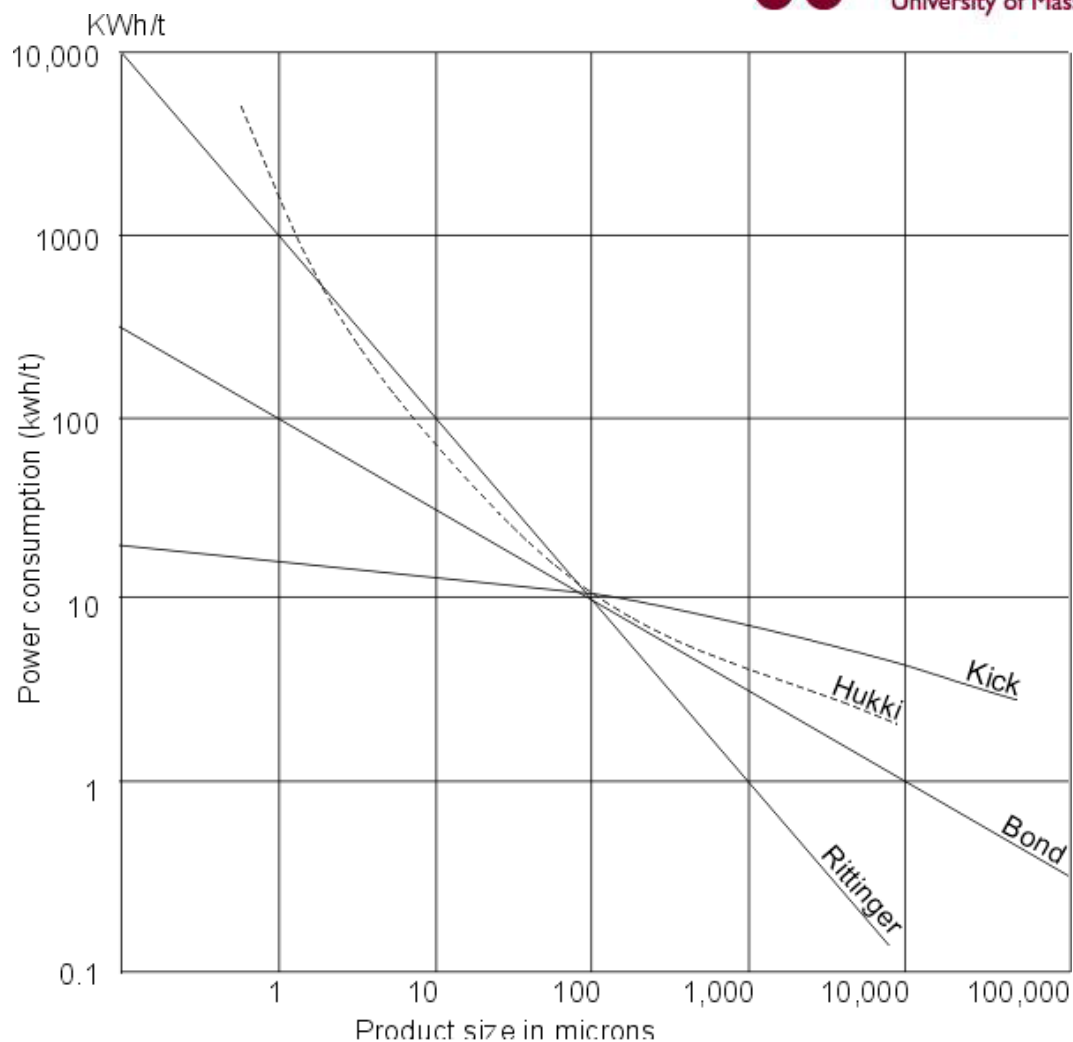▶ **See graph on next slide (based on 10kWh/tonne for 100μm)**

Credit?
F.L. Smidth, International
Cement Production Seminar?

$$E_s = W(k_1)(k_1/k_2).n.\log R_0(k_2)/R_f(k_2)$$

where E_s = Specific energy consumption (open circuit)

R_0, R_f are residues on a k_2 micron sieve

$W(k_1)$ is the Comminution Index (Bond's Work Index) to particle size k_1 (often 80% to 100μm)

n is the slope (tanx) for the RRSB plot

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…..or more simply using Rosin-Rammler

▸ **Number of ways of expressing:**

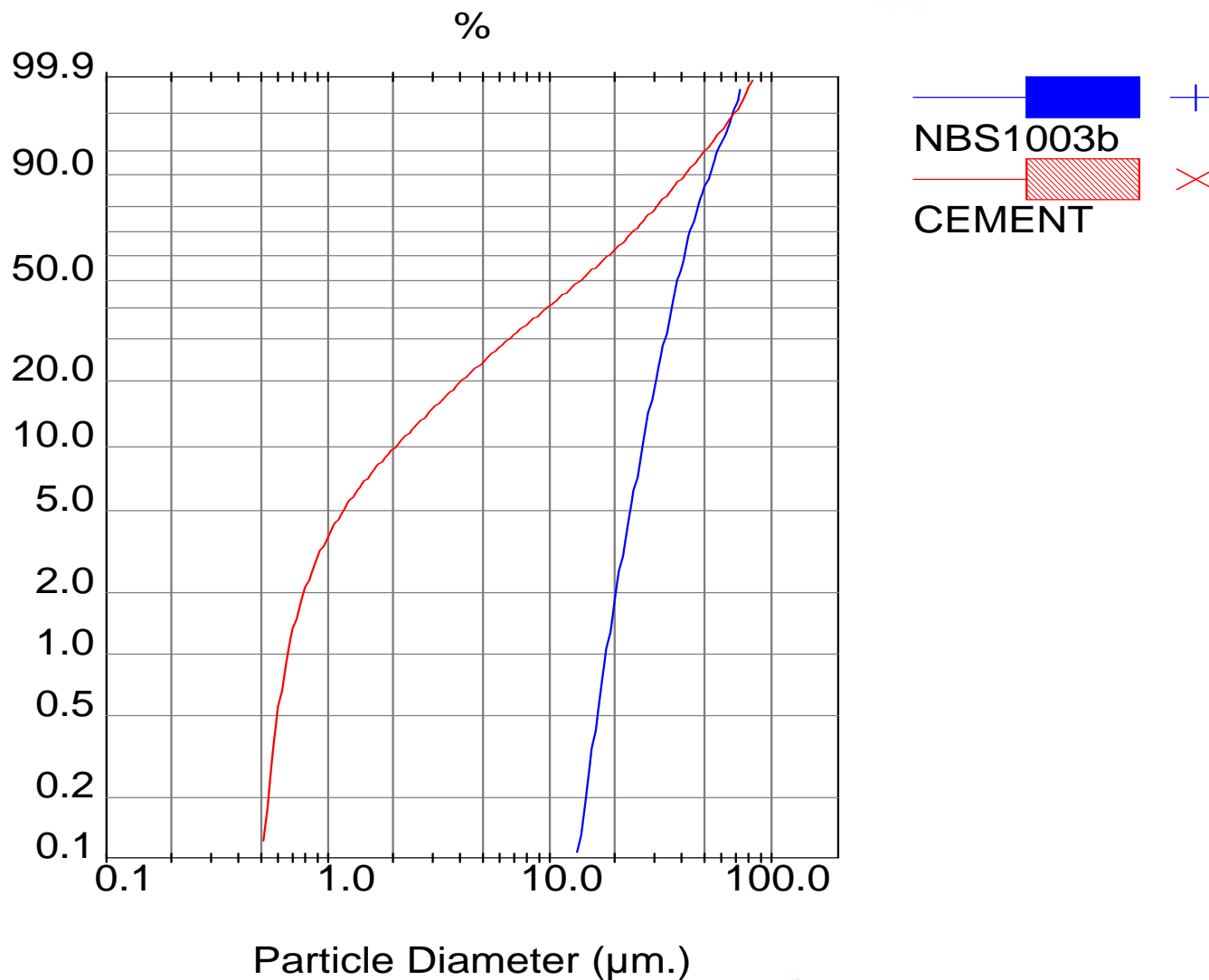$$R = 100 \exp - (x/x^*)^n$$

where R is weight % over size x

x* is 100/e = 36.8% of the oversize frequency plot

log.log100/R = n.logx + c

▸ **Plot log.log 100/R versus logx and this will be linear if Rosin-Rammler is obeyed**

▸ **x* - Position Parameter, n = slope**

▸ **Normally find deviations under 1μm (agglomeration in equilibrium with breakage)**

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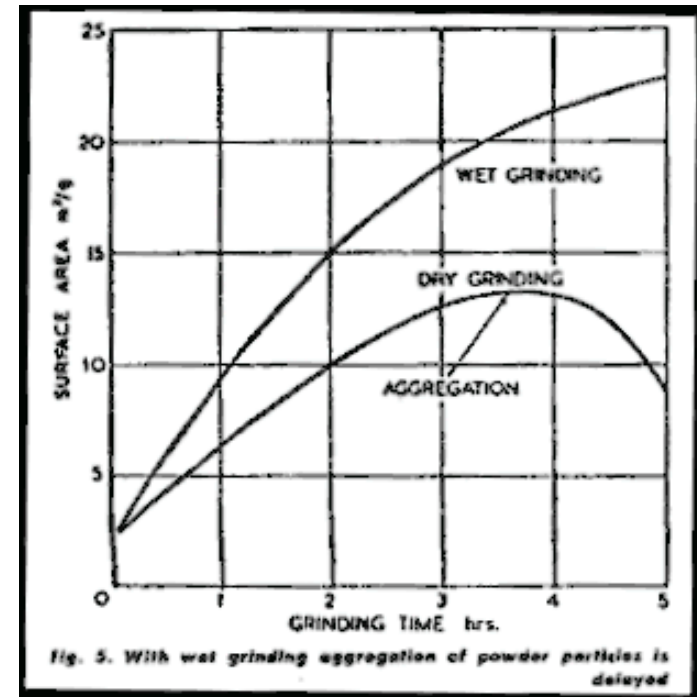
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Wet reduces (tendency to) aggregation

Michael Peters, Plant Manager, Pfizer Pty. Ltd, West Ryde, NSW, Australia
"Size reduction in pharmaceuticals" Australian Chemical Processing and Engineering July 1969 pp 22 - 27

fig. 5. With wet grinding aggregation of powder particles is delayed

Also: F.C. Bond, Wet versus dry grinding,

Mining Congress J., 43, 38-40, (1957)

What does this mean?

▶ **Closed circuit grinding expends much more energy efficient than open**

▶ **Efficiencies and cost savings are made in the separator circuit**

▶ **Example: open circuit 55kWh/t, closed 43kWh/t for grinding cement to 4000 Blaine**

3 themes

- **Particle-particle interactions**
- **Fick's Law**
- **Zeta potential**

The 4 S's

▶ **Size**

▶ **Shape**

▶ **Surface**

▶ **Solubility**

Why can a gecko walk on the ceiling?

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▶ **Glue not involved! Entire weight of lizard can be supported by this mechanism**

▶ **Millions of nanohairs on the ends of bumps on the gecko's feet (setae). Bend and conform to surface maximising the Van der Waals attraction forces**

Evidence for van der Waals adhesion in gecko setae

Kellar Autumn[†‡], Metin Sitti[§], Yiching A. Liang[¶], Anne M. Peattie[†‡], Wendy R. Hansen[†], Simon Sponberg[†], Thomas W. Kenny[¶], Ronald Fearing[§], Jacob N. Israelachvili[**], and Robert J. Full[†‡]

[†]Department of Biology, Lewis & Clark College, Portland, OR 97219; Departments of [§]Electrical Engineering and Computer Science, and [‡]Integrative Biology, University of California, Berkeley, CA 94720; [¶]Department of Mechanical Engineering, Stanford University, Stanford, CA 94305; and [**]Department of Chemical Engineering, University of California, Santa Barbara, CA 93105

Fig. 2. Tokay gecko (*Gekko gecko*) adhering to molecularly smooth hydrophobic GaAs semiconductor. The strong adhesion between the hydrophobic surface of the gecko's toes and the hydrophobic GaAs surfaces demonstrates that the mechanism of adhesion in geckos is van der Waals force.

www.pnas.org/cgi/doi/10.1073/pnas.192252799

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C:\Amherst\GeckoClimb.mov

Van de Waals forces

- **Operate over small distances and are extremely powerful – for that short distance (4 – 10Å typically)**

- **In dry systems ensure irreversible aggregation dependent on size**

- **At room temperature and 100nm there is enough (thermal/Brownian motion) energy to initiate solid-solid diffusion and generate bridging between particles**

Attractive (van der Waals) and inertial forces

▶ **The adhesion between quartz spheres via Hamaker is shown to be F = 212$d_1 d_2$/($d_1 + d_2$) dynes (in cgs units) where d_1 and d_2 are the diameters of the spheres respectively**

▶ **Force of gravity, w = mg = 981 X 1/6.$\pi\rho d^3$ and the van de Waals attractive force, F = 212d**

▶ **The particle will stick if F is greater than w, i.e. if 212d is > 981 X π/6.ρd^3 or ~ 0.4 cm for r = 2.6g/cm^3**

▶ **Now if we try to dislodge the particle from itself or a surface then we have, if a is the acceleration needed parallel to the surface:**

$$ma = \pi/6 * \rho d^3 a$$

Attractive (van der Waals) and inertial forces

▶ Adapted from D W Jordan The adhesion of dust particles pages S194 – S198 The Physics of Particle Size Analysis Institute of Physics Supplement No. 3, 6 – 9 April 1954

▶ **Hence the particle can be removed from the surface if:**

$$212d = \pi/6 * \rho d^3 a \text{ or } a = 156/d^2 \text{ putting } \rho = 2.6 g/cm^3$$

▶ **Thus if d = 100μm (0.01cm) then the acceleration needed is approximately 1600g and at 10nm ~ 1.6 X 10^{11}g**

	μm	m	cm	a	g required
1m	1.00E+06	1.00E+00	1.00E+02	1.56E-02	1.59E-05
	1.00E+04	1.00E-02	1.00E+00	1.56E+02	1.59E-01
	1.00E+02	1.00E-04	1.00E-02	1.56E+06	1.59E+03
1μm	1.00E+00	1.00E-06	1.00E-04	1.56E+10	1.59E+07
	1.00E-01	1.00E-07	1.00E-05	1.56E+12	1.59E+09
	1.00E-02	1.00E-08	1.00E-06	1.56E+14	1.59E+11
1nm	1.00E-03	1.00E-09	1.00E-07	1.56E+16	1.59E+13

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Attractive (van der Waals) and inertial forces

▶ **This is based on VDW alone and disregards larger attractive forces possible with capillary action (which can't happen on the lunar surface, for example)**

▶ **A sharp blow may be able to dislodge some particles. For example, if a plate is moving at 10m/s and stopped in 0.1mm (= 100μm) then the acceleration is around 10^{8}cm/s^2 and this would be enough to dislodge particles around 10μm.**

▶ **Davis (Aerosol Science, Ed. C N Davies, Academic Press, London and New York, Page 60, 1966) gives lower values lower by about a factor of 100 in his plot in Aerosol Science but these accelerative values are still substantial**
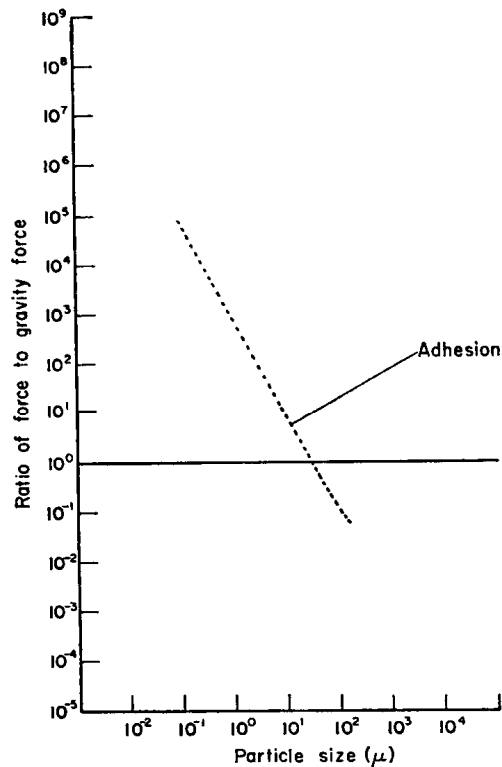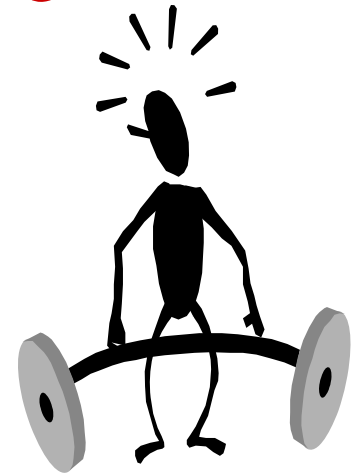
Strength of adhesion

FIG. 1. Electrical and other forces that can be exerted on aerosol particles.
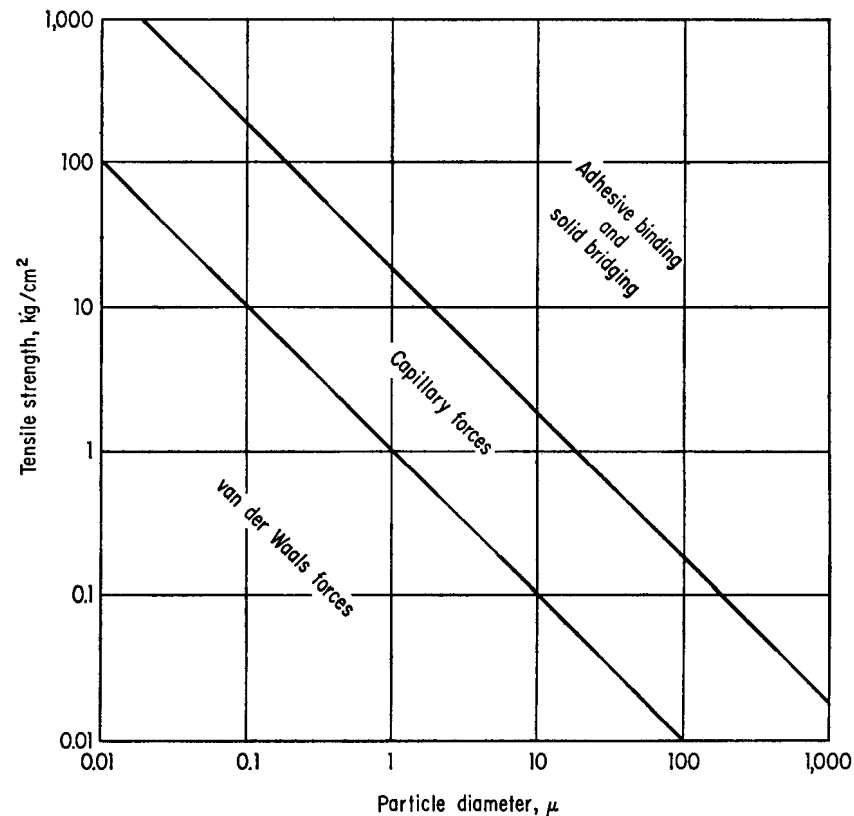
Adhesion Forces

$1\mu m = 1000g$

$0.1\mu m = 100,000g$!

(Aerosol Science, Ed. C N Davies, Academic Press, London and New York, Page 60, 1966)

Rumpf - agglomerate strengths

Figure 9.3. Particle-size and agglomerate-strength regions in which various binding mechanisms predominate. [After H. Rumpf, "The Strength of Granules and Agglomerates," in W. A. Knepper (ed.), *Agglomeration* (New York: Wiley, 1962), p. 399.]

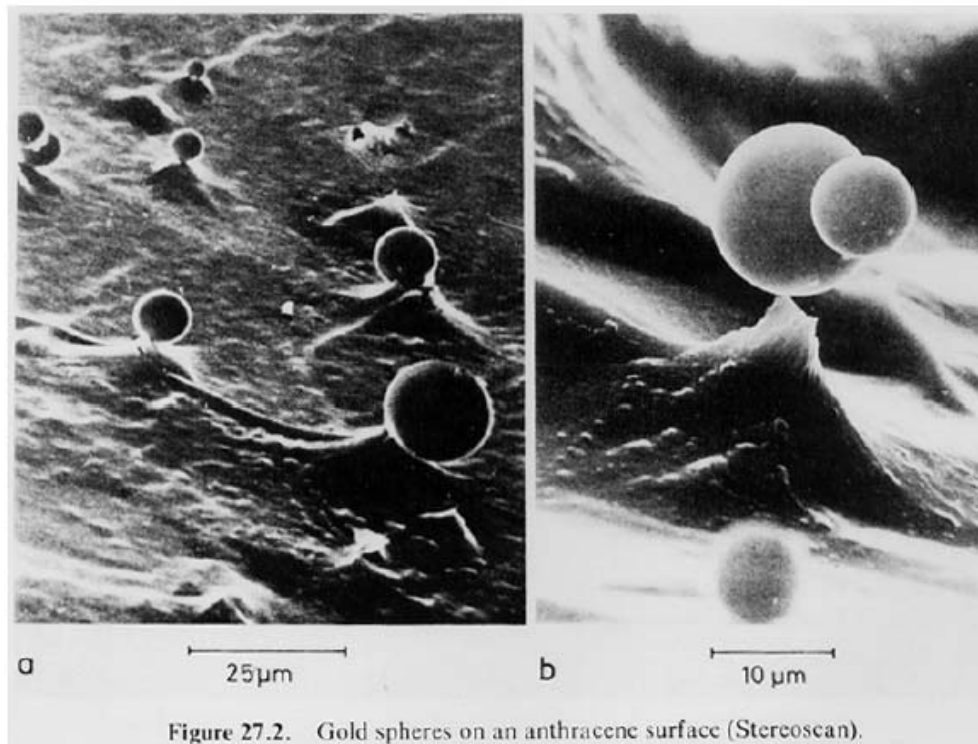**Original slide from**

Professor Jim Adair, Penn State

Figure 27.2. Gold spheres on an anthracene surface (Stereoscan).

from H. Rumpf and H. Schubert, "Adhesion Forces in Agglomeration Processes," Chapter 27 in *Ceramic Processing Before Firing*, G.Y. Onoda, Jr. and L.L. Hench (editors), John Wiley and Sons, New York, 1978, pp. 357-376.

Fick's Law

Fick's Second Law

Fick's second law predicts how diffusion causes the concentration field to change with time:

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$$

Where

- ϕ is the concentration in dimensions of [(amount of substance) length^{-3}], [mol m^{-3}]
- t is time [s]
- D is the diffusion coefficient in dimensions of [length^2 time^{-1}], [m^2 s^{-1}]
- x is the position [length], [m]

It can be derived from Fick's First law and the mass balance:

$$\frac{\partial \phi}{\partial t} = -\frac{\partial}{\partial x} J = \frac{\partial}{\partial x}\left(D \frac{\partial}{\partial x} \phi \right)$$

Assuming the diffusion coefficient D to be a constant we can exchange the orders of the differentiating and multiplying by the constant:

$$\frac{\partial}{\partial x}\left(D \frac{\partial}{\partial x} \phi \right) = D \frac{\partial}{\partial x}\frac{\partial}{\partial x} \phi = D \frac{\partial^2 \phi}{\partial x^2}$$

and, thus, receive the form of the Fick's equations as was stated above.

For the case of diffusion in two or more dimensions the Second Fick's Law is:

$$\frac{\partial \phi}{\partial t} = D \nabla^2 \phi.$$

which is analogous to the heat equation.

http://en.wikipedia.org/wiki/Fick's_law_of_diffusion

Fick's Law of diffusion
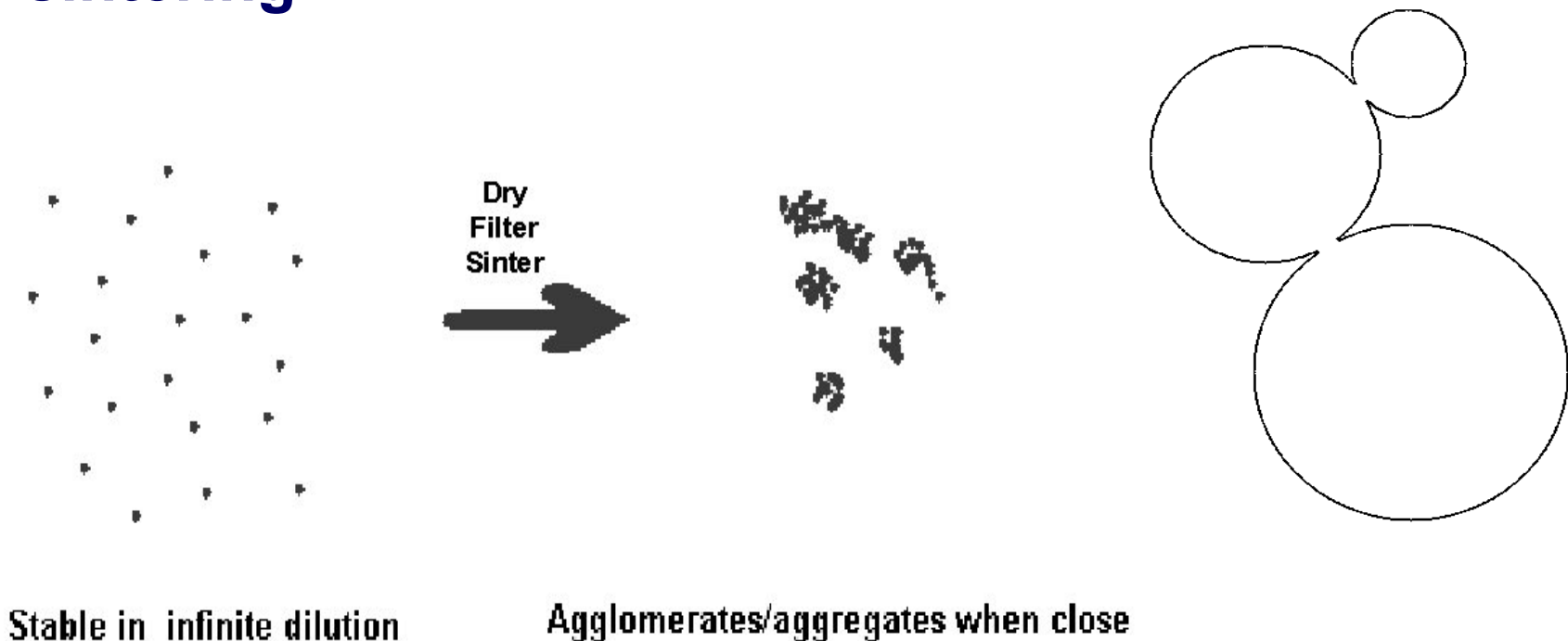
- **Solid-Solid diffusivities are of the order of:**

$$10^{-10} - 10^{-11} \text{ cm}^2/\text{sec}$$

- **At 10nm this implies that solids will diffuse into each other in about 100 - 1000 seconds….**

- **Adair reports a Pd black where the SSA went from 100m²/g to 2m²/g in 15 minutes**

Inertial and van der Waals forces…..

▸ **This is key as the attractive forces actually increase with increasing size!**

▸ **But the relation of the van der Waals forces to the inertia forces is what matters**

▸ **> 5 μm particles can be (relatively) easily separated**

▸ **Nano materials in the dry state cannot…**

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Bulk/Primary: solid bridging; room temperature sintering

Dry
Filter
Sinter

Stable in infinite dilution

Agglomerates/aggregates when close

MOLECULAR DYNAMICS COMPUTATION OF
GAS-PHASE NANOPARTICLE SINTERING:
A COMPARISON WITH PHENOMENOLOGICAL MODELS

Michael R. Zachariah* and Michael J. Carrier

Chemical Science and Technology Laboratory, National Institute of Standards and Technology,
Gaithersburg, MD 20899, U.S.A.
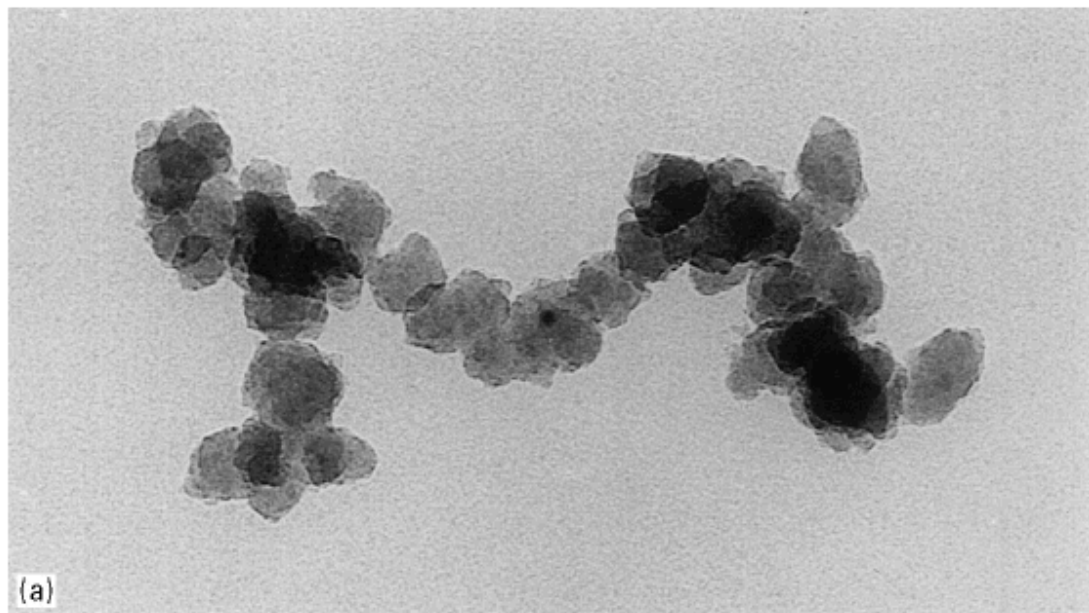
GAS PHASE PARTICLE GROWTH
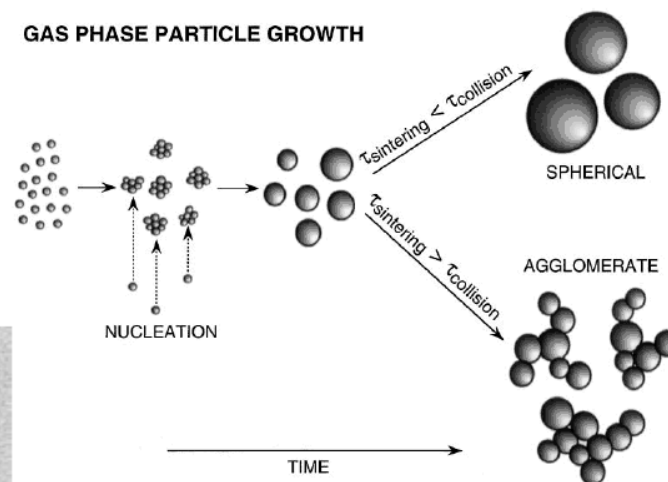
Fig. 1. Temporal evolution of vapor-phase particle growth.

(a)
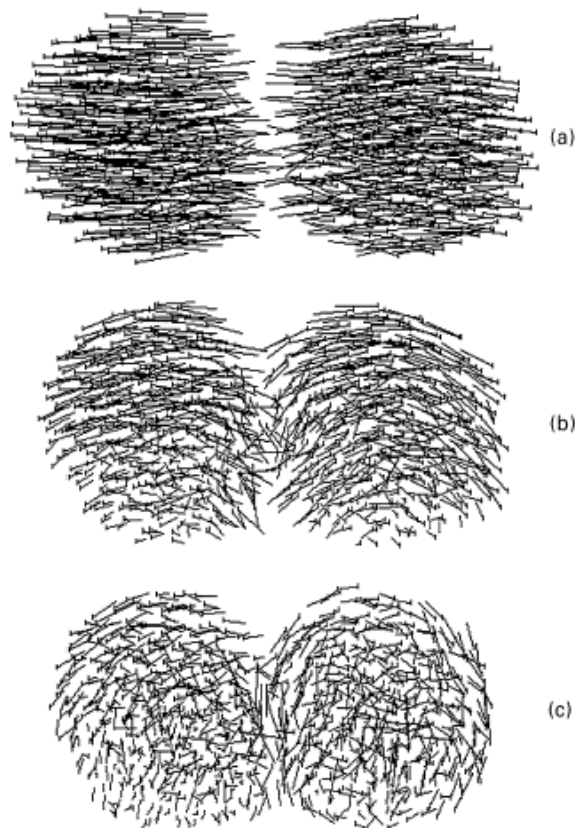
Fig. 5. Time series of particle morphology imaged with respect to atomic velocity vectors for two 480-atom particles at 900 K.
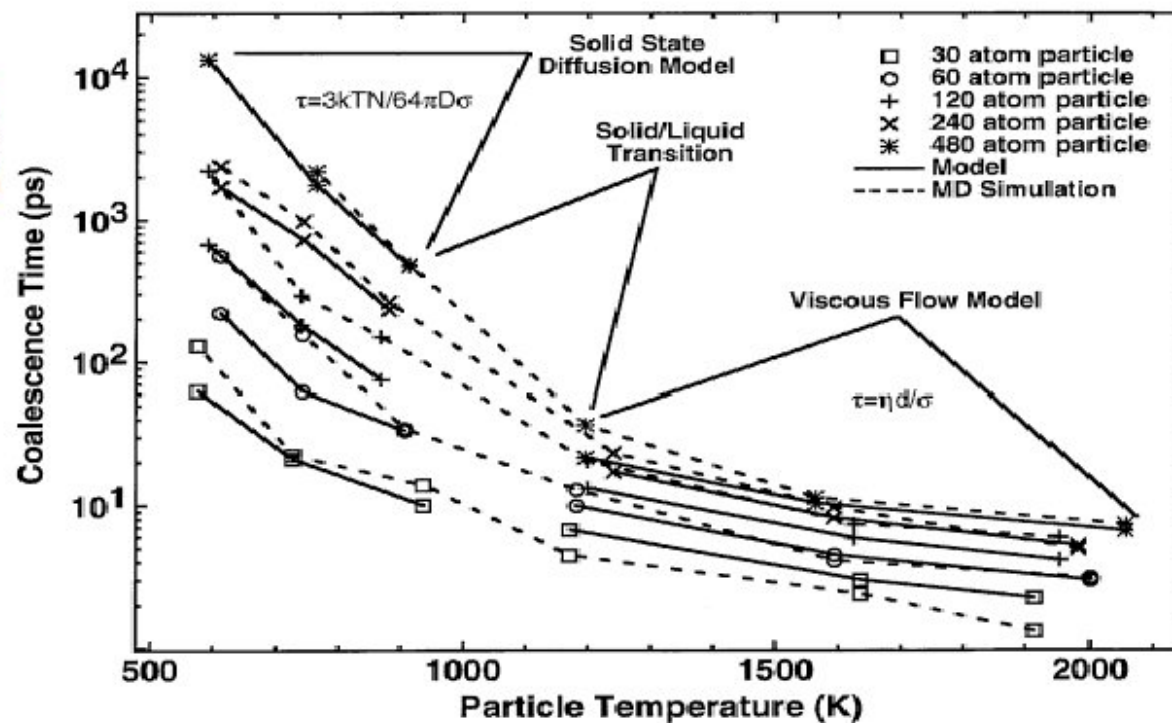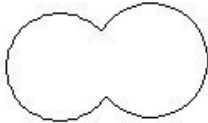
Fig. 8. Coalescence times as a function of particle size and temperature. Dotted lines connect the MD computations. The solid curves represent the viscous and solid state diffusion models. Note: The model results for the liquid phase were increased by a factor of ten so they would line up with the MD simulations.

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Bridging *will* always occur - in the dry state!

▶ **But where is it important?**

10nm bridge in 20nm particles
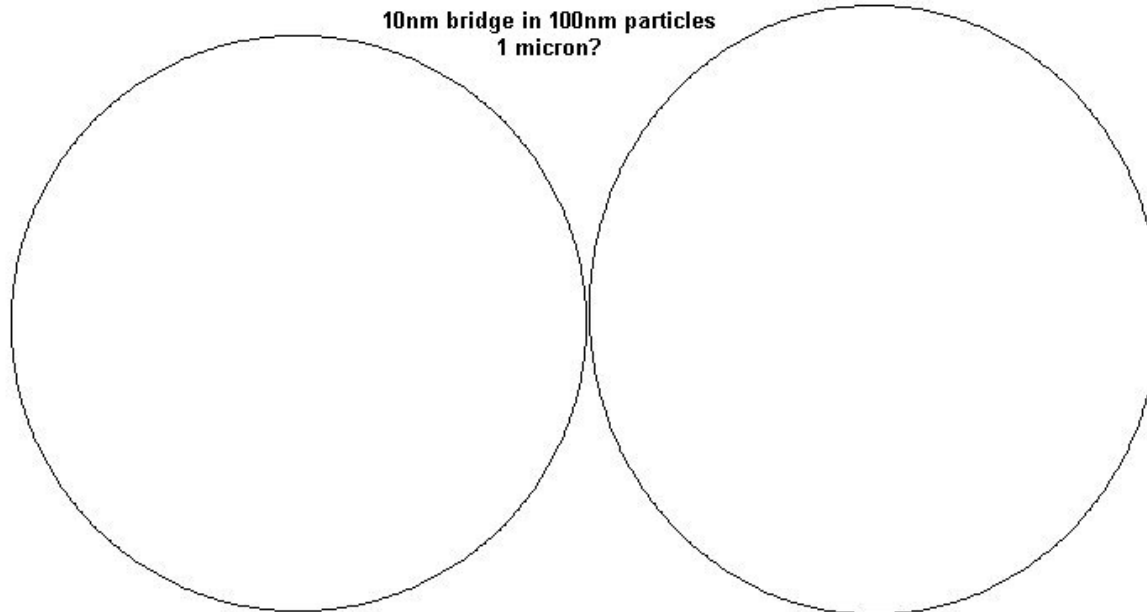
10nm bridge in 100nm particles
1 micron?

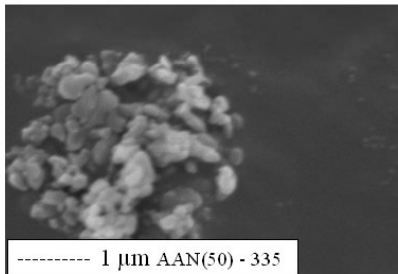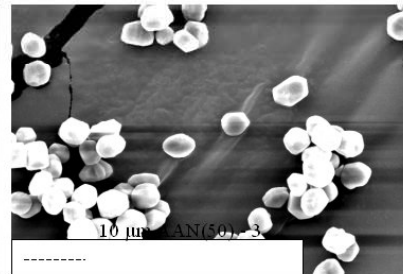QUALITATIVE MEASURE OF DISPERSION EFFICIENCY

Average Agglomeration Number (AAN(50))

$$AAN(50) = \frac{V_{N,V}}{V_S}$$

$V_{N,V}$ - mean volume by light scattering

V_S - average volume by BET

Alcoa A16-SG   Sumitomo AA5   MZF00103 milled 15 min

1 μm AAN(50) - 335   10 μm AAN(50) - 3   2 μm AAN(50) - 21
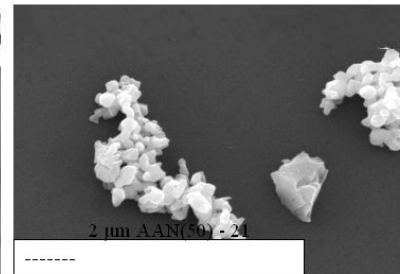
Ref: J. H. Adair, A. J. Roese and G. L. McCoy, "Particle-Size Analysis of Ceramic Powders,"Processing for Improved Productivity, Advances in Ceramics, Vol. 11, K. M. Nair (editor) The American Ceramic Society, Columbus, Ohio 1984.
H. Krarup, M. Mandanas and J. Adair, "Physical Characterization of Fine Powders" Fine Powder Processing 99 University Park, PA 1999.

Powder

"If the particles are agglomerated and sub-micron it may be impossible to adequately disperse the particles……"

"The energy barrier to redispersion is greater if the particles have been dried. Therefore the primary particles must remain dispersed in water…."

J H Adair, E. Suvaci, J Sindel, "Surface and Colloid Chemistry" Encyclopedia of materials: Science and Technology pp 8996 - 9006 Elsevier Science Ltd. 2001 ISBN 0-08-0431526

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Adhesion forces - dry milling
Theoretical limit of a ball mill

$$d = 10.7E\gamma_\pi/\sigma^2_y$$

where E = Young's Modulus (~ 20 GPa)

γ_π = Specific surface energy per unit

area (work) ~ 0.05Jm^{-2}

σ_y = Yield strength/stress ~ 100MPa

gives d ~ 1μm

"These restrictions led technologists to develop ultrafine powders
and fibres for making the new nanophase ceramics by routes
other than mechanical processing"

See: Ceramic Processing   Eds. R A Terpstra, P P A C Pex, A H De Vries p 17   Chapman and
Hall 1995 ISBN 0 412 59830 2

Nanopowder…..

▶ "I think dry nanotechnology is probably a dead-end"

Rudy Rucker

http://www.transhumanism.org/index.php/th/print/303/
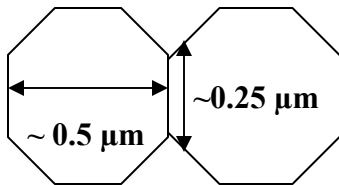
Dissolution

- **May be able to dissolve the solid bridge (it's a weak region)**

- **Appropriate (careful!) pH change**

- **I've accomplished this with Cu powders and HNO_3 (10 seconds as opposed to 60 minutes @ 600W ultrasound)**

- **Lose some (or all!) material**

- **May not be feasible on large scale**

- **Hence best to keep material in nano form (e.g. in slurry)**

Stress Corrosion Cracking

System: 0.5 µm particles, with a neck diameter of ~0.25 µm

Can crack propagate through neck at the rates observed?

~0.25 µm

~ 0.5 µm

For SiO$_2$ in 1 M KOH
crack velocity: 10^{-2} - 10^{-9} m/sec
for K_I = 0.6 - 0.2 MPa m$^{1/2}$

Estimated time (range) for crack to propagate through neck

fast   0.25 µm/10^3 µm/sec -->> 2.5 x 10^{-5} sec

slow   0.25 µm / 10^{-3} µm/sec -->> 250 sec

from SSA vs. time data

in 3600 sec, SSA increased -->> 2 m^2 to 10m^2 /g

in 1-D - $\sqrt{10m^2}$ - $\sqrt{2 m^2}$ = 1.75 m/3600 sec

                   = 4.8 x 10^{-4} m/sec

S. Wiederhorn and E. Fuller, Jr., JACERS 72[2] 248-51, 1989

Examples of Bottom-up processes
Liquid phase

- **Physical**
    - **Crystallization**
    - **Dissolution (small molecules)**
    - **Mixing ('microemulsions') – usually with shear**
    - **Heating to cause decomposition (e.g. labile nickel compound in high temperature solvent)**
- **Chemical (reaction)**
    - **Sol-gel – $Ti(OEt)_4 \rightarrow TiO_2$**
    - **Polymerization (including emulsion)**
    - **Mixing ('microemulsions') – surfactants in solution**
    - **Reduction/metal colloids**
        - **$HAuCl_4 \rightarrow Au^0$**
        - **$Ag(NH_3)_2NO_3 \rightarrow Ag^0$**

- **Note1: none of the above must involve drying, filtration or other processes where the dry particles will contact each other**
- **Note2: Nature does a lot of these self-assembly jobs….**

Malvern

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Examples of Bottom-up processes
Gas phase

▶ **Physical**

- ▪ **Atomization**
- ▪ **Condensation**

▶ **Chemical (reaction)**

- ▪ **Decomposition (e.g. $Ni(CO)_4 \rightarrow Ni^0$)**

▶ **Note: none of the above must involve drying, filtration or other processes where the dry particles will contact each other**

Producing a stable dispersion

▶ **Wetting – if in the dry state then recovery of the primary particle size is basically impossible if the primary particles are much below 1μm or so. Where we use or need a surfactant.**

▶ **Separation – the KEY step. We get an equilibrium set up between fracture and recombination. Takes energy**

▶ **Stabilization – generally over several orders of magnitude is stabilizer concentration**

- ▪ **Charge ('electrostatic') – optimum [C] of additive/admixture**
- ▪ **Steric – geometric; polymer of 15000 MW (e.g. PEI)**
- ▪ **Combination**

▶ **Only dispersing agent is energy! Surfactants and admixtures (e.g. phosphate) are stabilizing agents once particles have been made to separate – they are NOT dispersing agents**
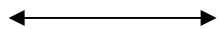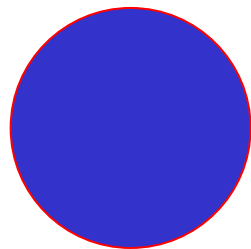
Dispersion of Nanometer Size Particles – after Adair

▶ **Critical issue is _deagglomeration_ not necessarily maintaining stability**

▶ **Sintering at low temperatures must be prevented with nm-size particles**

▶ **Aggregation tends to be irreversible**

▶ **Conventional large molecular weight polymers are _inefficient_ dispersants**

▶ **Surfactants are generally _not_ effective dispersants**

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Dispersants for Nanometer Size Particles
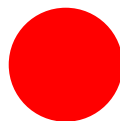
Nanometer Size Particle

$D_s = 10$ nm
$S \sim 105$ nm^2

Typical
Polymeric Dispersant

$$R_g = \frac{l\sqrt{M/M_o}}{\sqrt{6}}$$

$D_g \sim 5$ nm
$S_{ads} \sim 20$ nm^2
$D_g + 2D_s \sim 20$ nm
for l~0.5nm,
M ~ 15000
$M_o \sim 100$

Typical
Surfactant Molecule

$D_{surf} \sim 0.8$nm
$S_{ads} \sim 0.5$ nm^2
$D_s + 2L(8CH_2) \sim 14$nm
Length ~0.25nm/CH$_2$

**Critical Criteria:
Small, charged adsorbate**

Zeta potential

- Deals with the system and is related to the interaction of the surface of the particle to the external environment – it's the charge measured in what is known as the 'slipping plane'

- Easier to measure the movement of a particle under an electrical field and relate this to the zeta potential:

- Smoluchowsky (also spelled Smoluchowski) approximation (f(κα) = 1.5 for water/ionic systems) of Henry's function:

$$U_\varepsilon = 2\,\varepsilon\,\zeta\,f(\kappa\alpha)/3\eta$$

  where U_ε is the electrophoretic mobility, ζ is the zeta potential, f(κα) is Henry's function and η is the viscosity that the particle experiences in its movement through the fluid

- The function f (κα) is made up of 2 parts – κ is the Debye length and κ^{-1} is used to define the thickness of the electrical double layer. The symbol α refers to the radius of the particle and thus $\kappa\alpha$ measures the ratio of the particle radius to that of the electrical double layer thickness. This double layer thickness can be best defined in an ionic medium as the location of ions and counter ions is easily assumed. The interpretation of converted mobility to zeta potential measurements in non-aqueous or non-conductive systems is still not exactly defined either in theory but even more so in practice
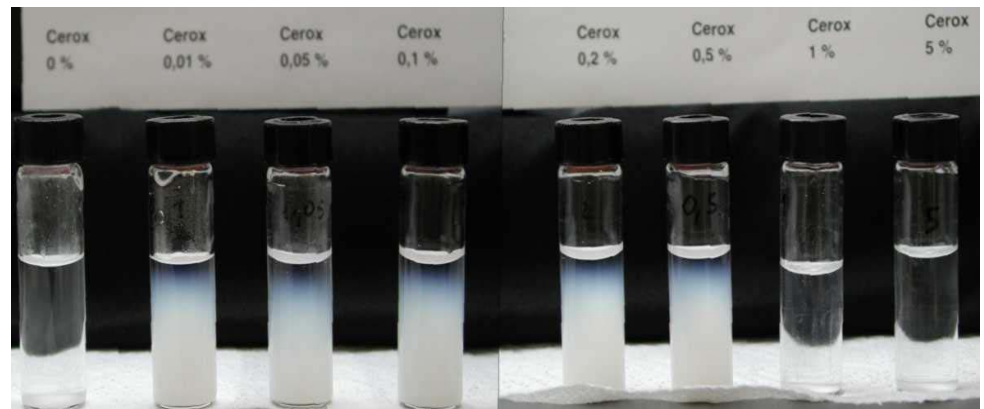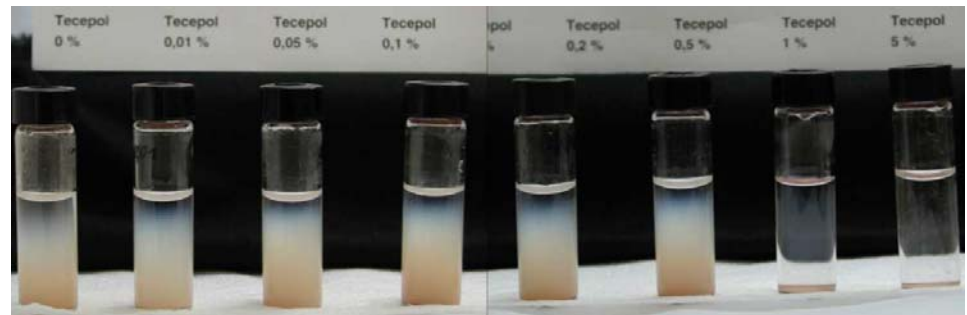
TiO$_2$

X$_{50}$ = 0.25 μm approx. Calgon additive
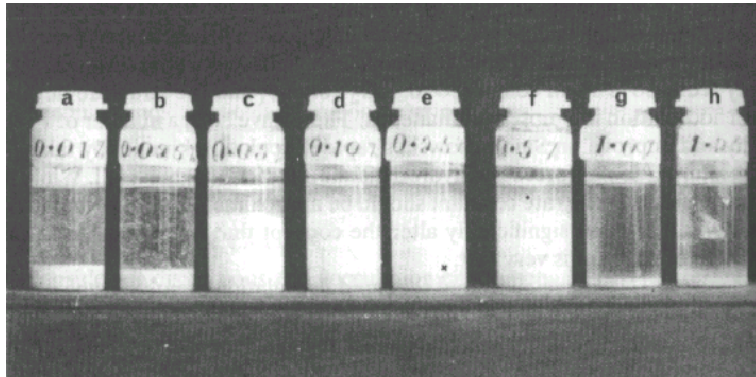
CeO$_2$

Paint and surface coatings – theory and practice.
Ed. R Lambourne, Ellis Horwood Ltd. (1993)
ISBN 0-13-030974-5Pbk

Indications that there is a stability issue Removal of ultrasound in DI water - BDAS

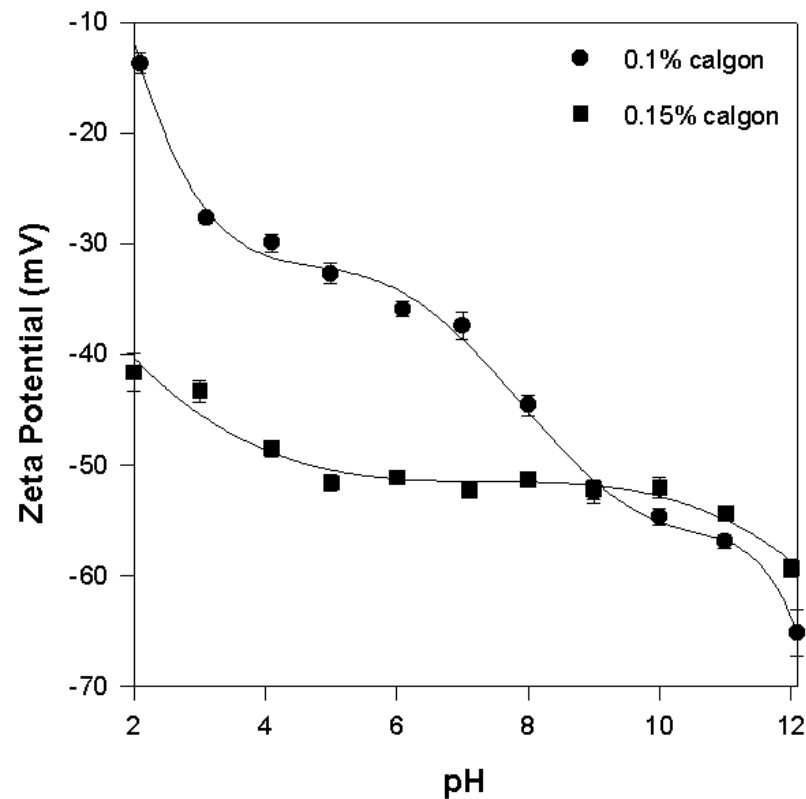Titania before, during, after ultrasound
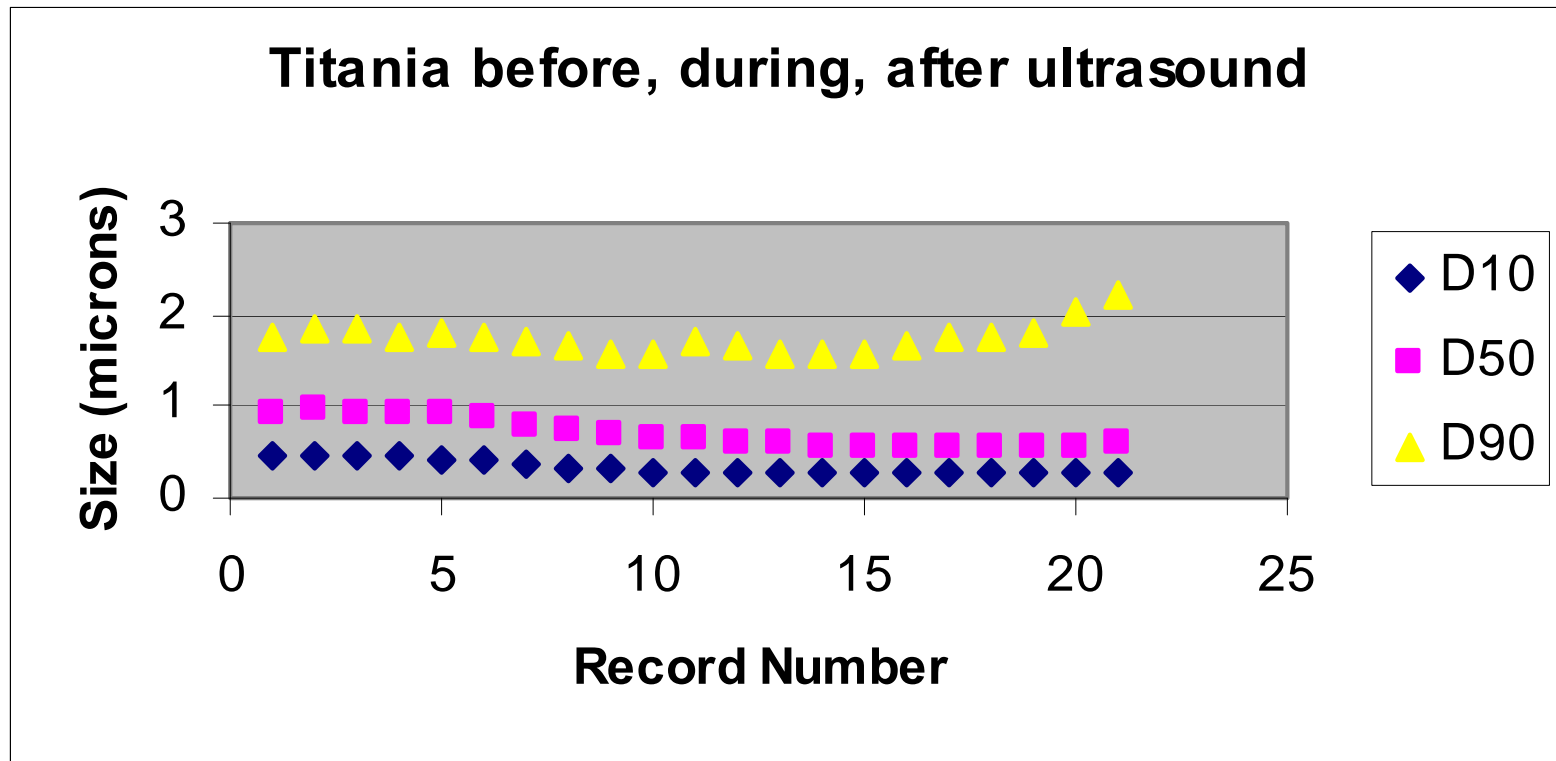
Stability studies with Zeta3000HS plus titrator

Measurement with optimum conditions
Before, during and after ultrasound
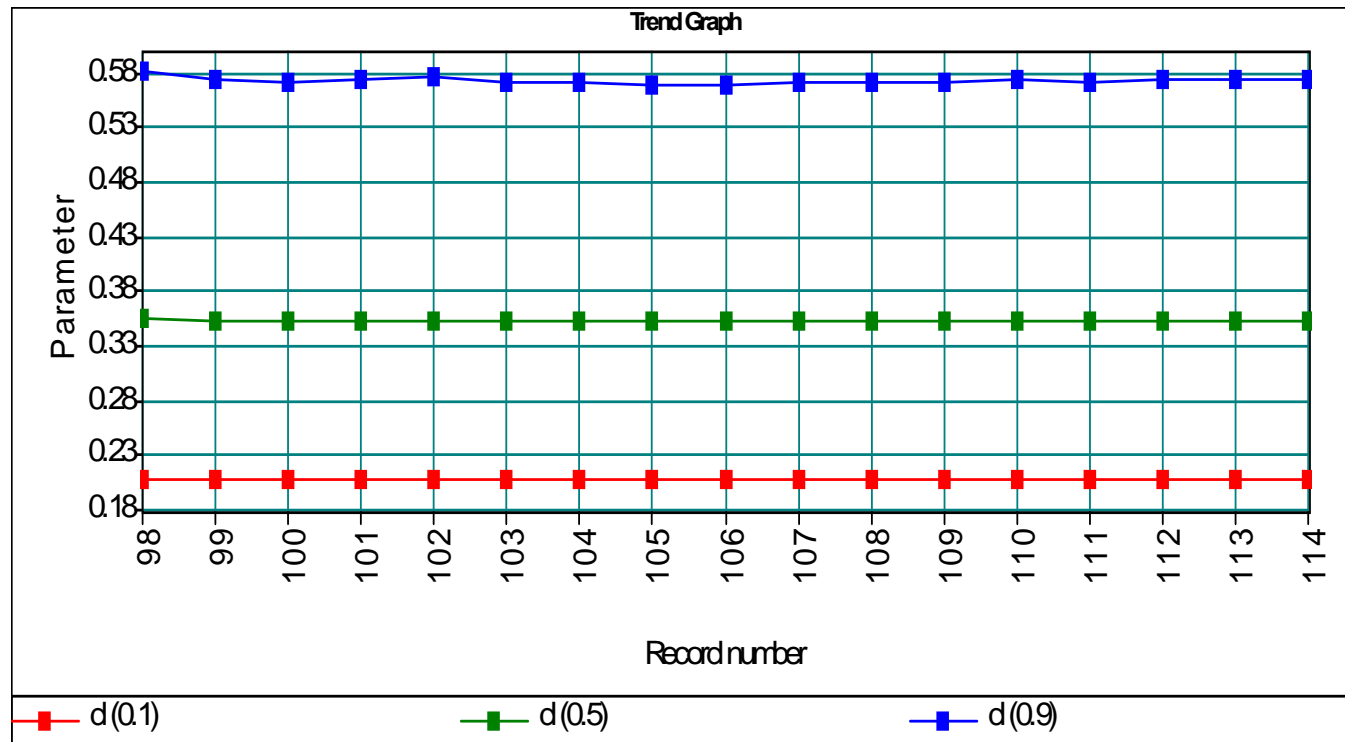
Comparison between properly dispersed and poorly dispersed material
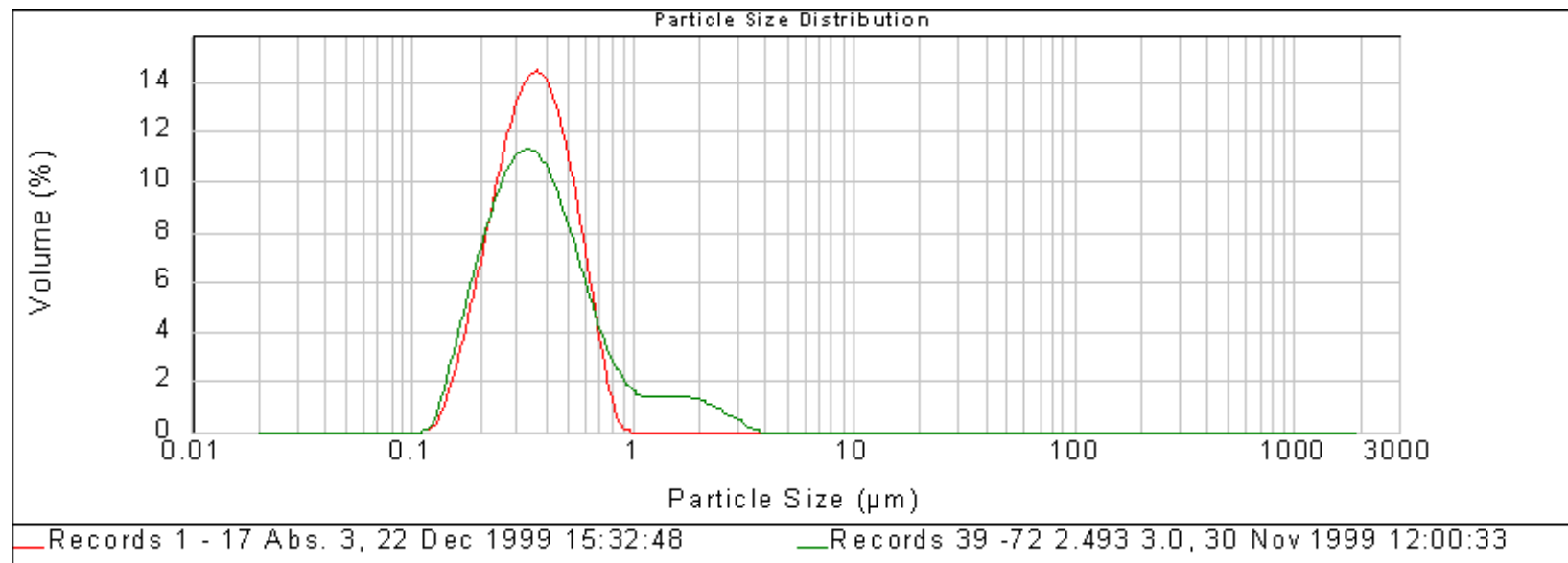
Tests

- **< 100nm (US Govt. definition. See Roco)**
- **Made by bottom-up (e.g. sol-gel, chemical reaction, crystallization, reduction) not top down (comminution) process. Remember the dictionary!** *(Powder: a solid that has been pulverized)*
- **Likely to be supplied in liquid "suspension" which is either clear (e.g. microemulsion) or coloured/transparent (e.g. gold sol: Purple of Cassius)**
- **Will not settle after many weeks or months**
- **If a white slurry unlikely to be truly nano**
- **Not a powder!**

Settling rates – taken from E2490

Standard Practice Guide for Measurement of particle size distribution of nanomaterials in suspension by Photon Correlation Spectroscopy (PCS) ASTM E56.02

Diameter	Diameter	ρ (Material)	ρ (Water)	η (Water)	Time to settle 1cm (1 X 10^{-2} m) in water		
μm	nm	kg/m^3	kg/m^3	298K, Poise	Minutes	Hours	Days
0.01	10	2500	1000	0.0008905	1815494.39	30258	1261
0.1	100	2500	1000	0.0008905	18154.94	302.58	12.61
1	1000	2500	1000	0.0008905	181.55	3.03	0.126
10	10000	2500	1000	0.0008905	1.82	0.03	0.001
100	100000	2500	1000	0.0008905	0.02	0.00	0.000
0.01	10	3500	1000	0.0008905	1089296.64	18154.94	756
0.1	100	3500	1000	0.0008905	10892.97	181.55	7.56
1	1000	3500	1000	0.0008905	108.93	1.82	0.076
10	10000	3500	1000	0.0008905	1.09	0.02	0.001
100	100000	3500	1000	0.0008905	0.01	0.00	0.000
0.01	10	4200	1000	0.0008905	851013.00	14183.55	591
0.1	100	4200	1000	0.0008905	8510.13	141.84	5.91
1	1000	4200	1000	0.0008905	85.10	1.42	0.059
10	10000	4200	1000	0.0008905	0.85	0.01	0.001
100	100000	4200	1000	0.0008905	0.01	0.00	0.000
0.01	10	5500	1000	0.0008905	605164.80	10086.08	420
0.1	100	5500	1000	0.0008905	6051.65	100.86	4.20
1	1000	5500	1000	0.0008905	60.52	1.01	0.042
10	10000	5500	1000	0.0008905	0.61	0.01	0.000
100	100000	5500	1000	0.0008905	0.01	0.00	0.000

Settling rates - comment

▶ **Most differences will make a particle settle more slowly than Stokes' Law predictions!**

  ▪ **Porosity: absorbed fluid lowers the density of the material and increases settling time**

  ▪ **Non-sphericity. Increases drag and increases settling time**

  ▪ **Brownian motion – competes with gravitational settling and increases the settling time**

▶ **So any settling over a week or so then not nano in the strict sense (< 100nm)**

▶ **Consider "submicron"**

▶ **Not strictly "nano" if in powder form**

Drexler

- **K Eric Drexler's Nanosystems book**
  ISBN 0-471-57518-6 (pbk.)
- **Page xviii "Criticism of criticism"**
  - **……assuming that nanomachines swim from point to point, then warning that Brownian motion makes such navigation impossible…These observations constitute not criticisms, but rediscoveries of elementary engineering constraints"**

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Heywood – we expect a quote!
(Lunar dust)
So we could have predicted the Mars problems...

In the evolution of a dust there is a conflict between the processes of comminution and agglomeration; in the case of a terrestial dust of desert type, the process of comminution is generally predominant, but in the lunar dust it would appear that the process of agglomeration exerts a considerable, if not predominating, influence on its evolution.

Proceedings of the Second Lunar Science Conference, Vol. 3, pp. 1989–2001
The M.I.T. Press, 1971.

Particle size and shape distribution for lunar fines sample 12057,72

H. HEYWOOD
Chemical Engineering Department, University of Technology, Loughborough, England

Summary

- Solid bridging in dry systems means that there is a bulk and primary particle size – techniques can measure either or both
- Dispersion or separation of primary (nano)particles within powdered systems is not easy or even possible
- Best to keep the material in colloidal or separated form without drying, filtration or other processes where the particles will come in contact

- **Top-down – energy inefficient**
- **Bottom-up – way to go**

Thank you!

- **Professor Mark Tuominen: for the invitation**
- **Michael Westort: for liaison and organization**

- **And to you all for attending!**