The role of interparticle forces in the fluidization of micro and nanoparticles

A. Castellanos

POWDER FLOW 2009
London, December 16

Acknowledgements

Key idea of the talk

Starting point: in the fluidized state fine cohesive powders form aggregates due to their strong interparticle attractive forces.

Aggregates stop growing when their Cohesive Bond number (ratio of attractive forces to weight) is of order one.

Aggregates may be considered as effective non-cohesive particles, and using the well known empirical relations for non-cohesive powders we extend the Geldart diagram to fine cohesive powders.

Plan of the talk

• Introduction to the fluidized state: Geldart map
• Important forces: boundaries B-A, C-A
• Our materials: toners (microparticles) and silica (nanoparticles)
• Fluidization in fine powders: Solid-like and fluid-like regimes
• The role of van der Waals forces: aggregation and transitions between fluidization regimes
• Prediction of a new regime and experimental confirmation.
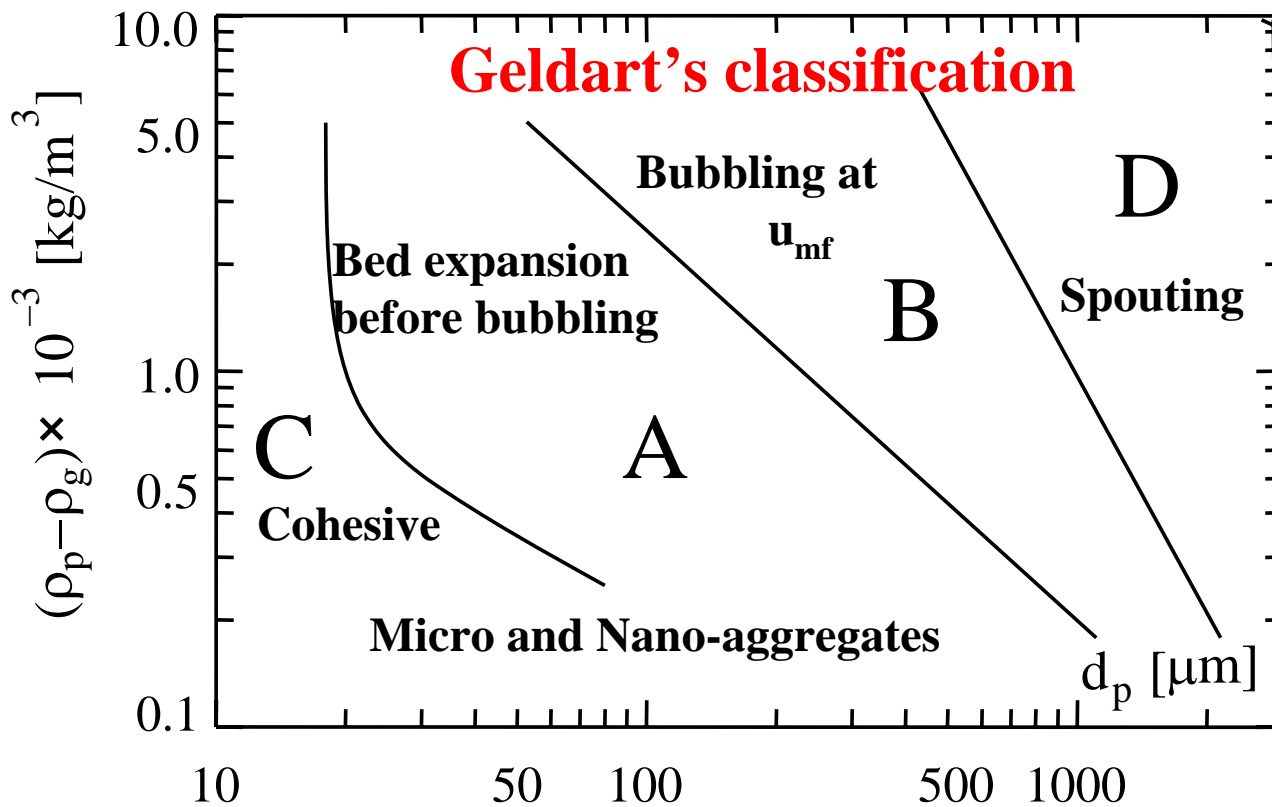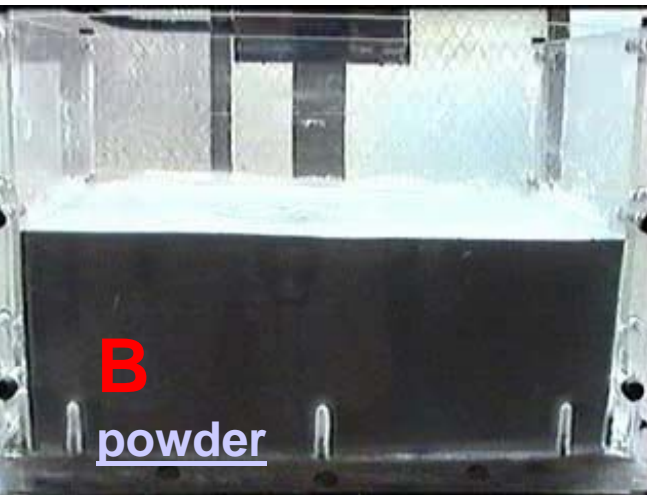• Final result: diagram of fluidization regimes for fine cohesive powders
•Conclusion

The fluidized state

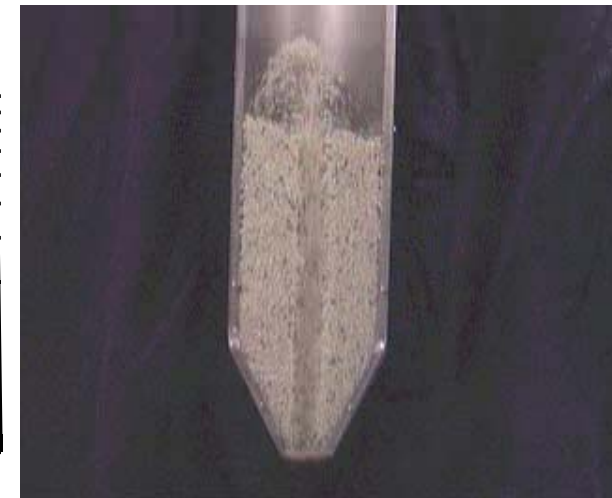The gas-fluidized state is a concentrated suspension of solid particles in the upward gas flow.
1.- The distance between particles is of the order of the size of the particles
2.- The free surface is horizontal (it looks like a liquid but it is not a liquid).

The Fluidized state

B powder

C powder

A powder

Geldart's classification

Bed expansion before bubbling

Bubbling at u_{mf}

C — Cohesive

A

B

D — Spouting

Micro and Nano-aggregates

$(\rho_p - \rho_g) \times 10^{-3}$ [kg/m^3] — vertical axis: 0.1, 0.5, 1.0, 5.0, 10.0

d_p [μm] — horizontal axis: 10, 50, 100, 500, 1000

**Group A powder:
Xerographic toner**

D powder

Forces acting upon grains

- Gravity force (weight) mg (or the force due to a pressure of confinement).

- Attraction force between particles (force of van der Waals for dry neutral powders, capillar forces, electrostatic forces, magnetic forces, forces due to solid bridges (sintering) and other chemical bonds)

- Hydrodynamic resistance force (force acting upon particles due to friction with the ambient fluid) and pressure and inertial forces (not considered here).

The relations between these three forces give the two important non-dimensional parameters of granular materials:

Bond Cohesive number: attractive force / weight

Number C: attractive force / viscous drag

Interparticle and external forces change the type of fluidization

- Decreasing interparticles forces: C ➡ A ➡ B

- Increasing interparticles forces: B ➡ A ➡ C

Varying the external force may also induce transitions between the fluidization types. This have been shown for vibrations, sound, and electric and magnetic forces.

Drag (viscous friction) force

For small Reynolds number Re (ratio of inertial to viscous forces) and spherical particles

$6\pi\eta R v$

η the viscosity of the fluid
R the radius of the particle
v the velocity of the particle relative to the fluid

Dimensionless numbers in fluidization types A, B

- **In the fluidized state:**

<p style="text-align:center; color:red;">**Drag (viscous friction) / weight ~ 1**</p>

- Re <<1 near onset of fluidization for type B
- Re<<1 for micron and nanoparticles (type A if fluidizable)

The boundary A-B

Molerus in 1982 postuled, and experiments confirmed, that number C (attractive force/drag) of order 1 define the boundary A-B. Therefore Bond number (attractive force/weight) is of order 1. Here, we will show the physical mechanism responsible for this transition in fine powders.

The boundary C-A

• We need to break the primary aggregates into the primary particles or smaller aggregates so that the powder becomes fluidizable

• For the fluidization to be stable the subsequent growth by collisions in larger aggregates must be limited in size

• The first step is process dependent (history) and therefore there is not   a clear-cut criterion to define this boundary.
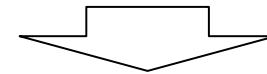
Stresses in fluidization

Gas flow
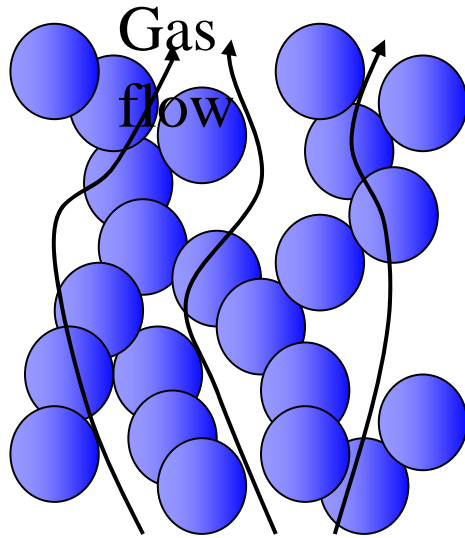
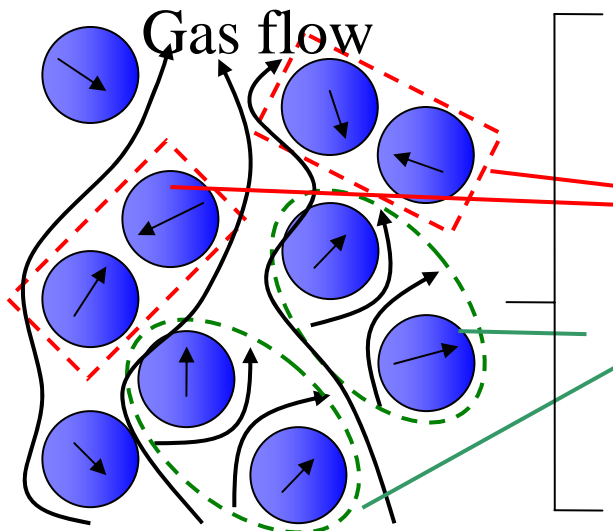Different mechanism of stress transmission in the discrete phase:

Solid-like behaviour

Interparticle contacts

Stress transmitted by interparticle contacts
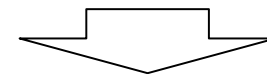
$\sigma_c > 0$

Gas flow

Fluid-like behaviour

Collisions

Hydrodynamic interactions

Stress transmitted by collisions and hydrodinamic interactions
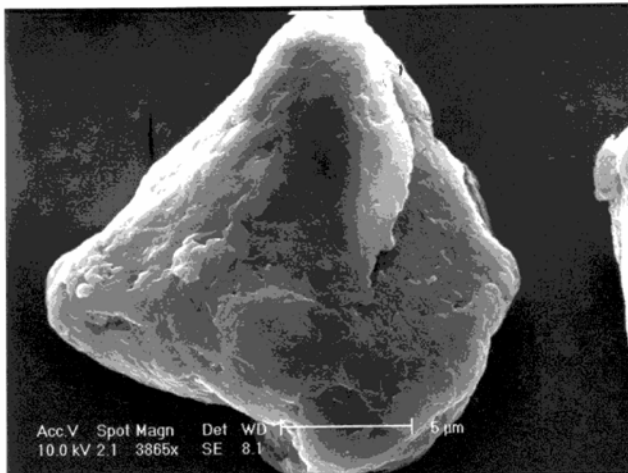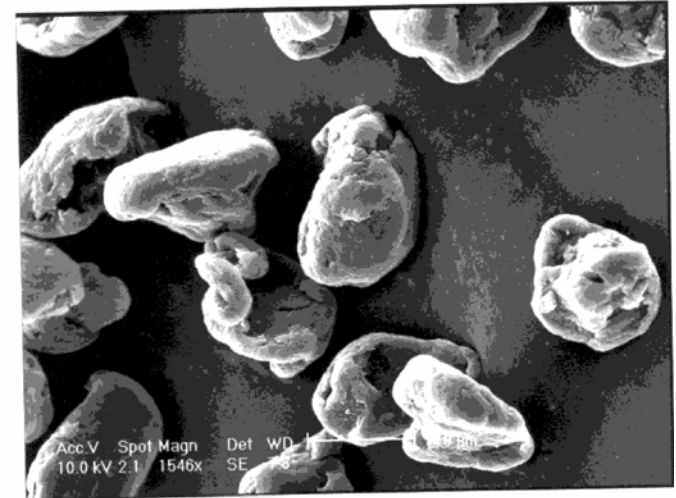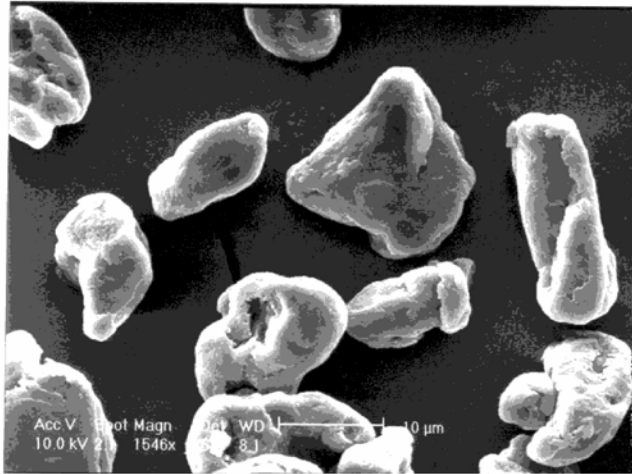
$\sigma_c = 0$

Controversy: has type A a solid-like or fluid-like behaviour?

In previous studies the fluidized region before bubbling was very small (powders above 70 microns in size). This made very difficult to resolve directly this controversy.

We have solved this controversy using micro size fine powders

Our materials: micron size particles

Toners made by attrition
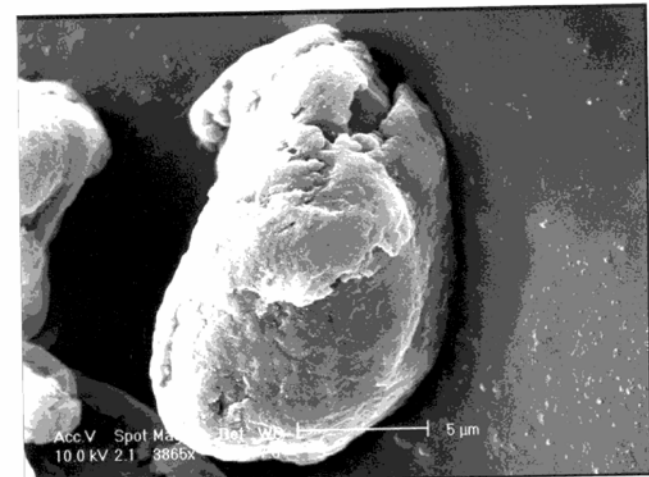
Our materials: nano size particles

- Aerosil R974

  ➤ Primary SiO_2 nanoparticles. 12 nm diameter.

  ➤ Surface treated to render it hydrophobic

Sub-agglomerates due to fusing of contacts in the fabrication process at high temperatures, of size < 1 μm

Sub-agglomerates agglomerate into **simple-agglomerates**, due to van der Waals forces, of size of order 10-100 μm.

20 nm

Acc.V Spot Magn   Det WD ├─────────────┤   20 μm
30.0 kV 4.2 3480x   SE   9.8   Silica R974 agglomerates
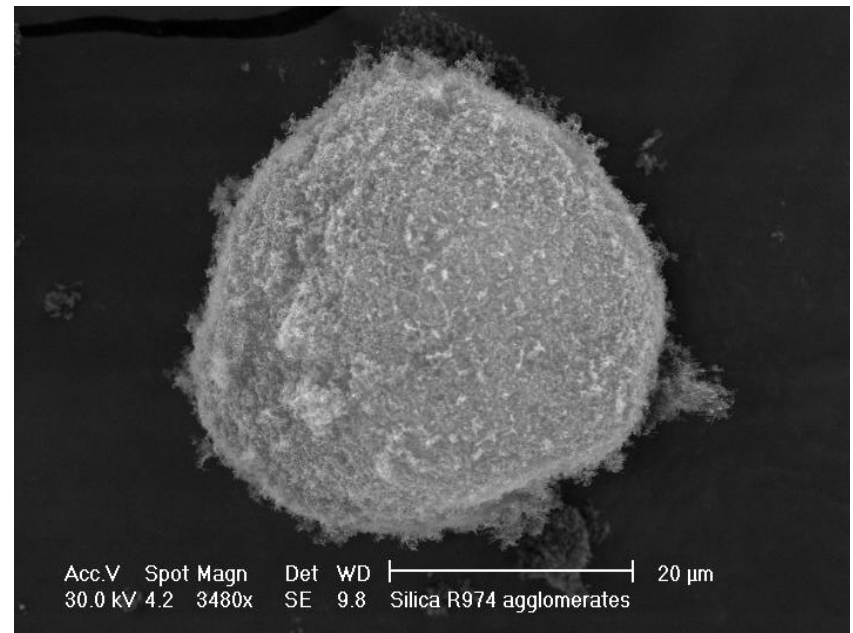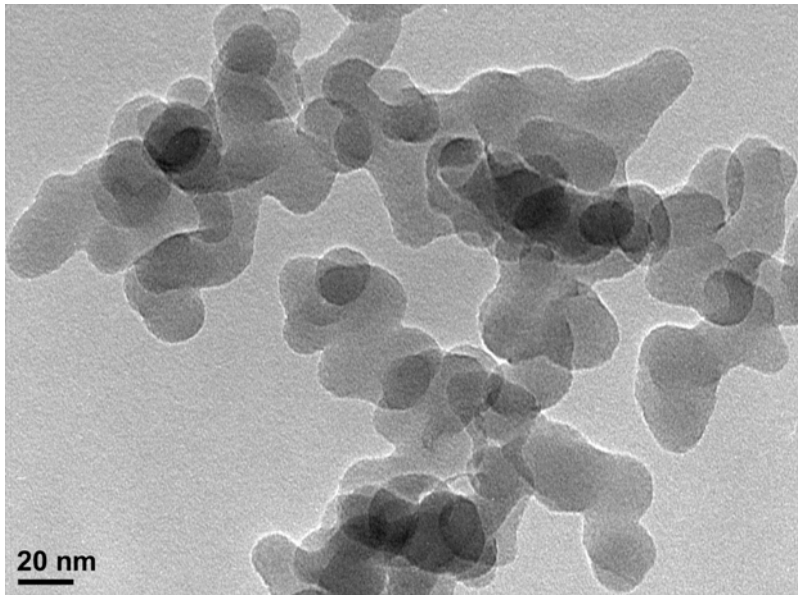
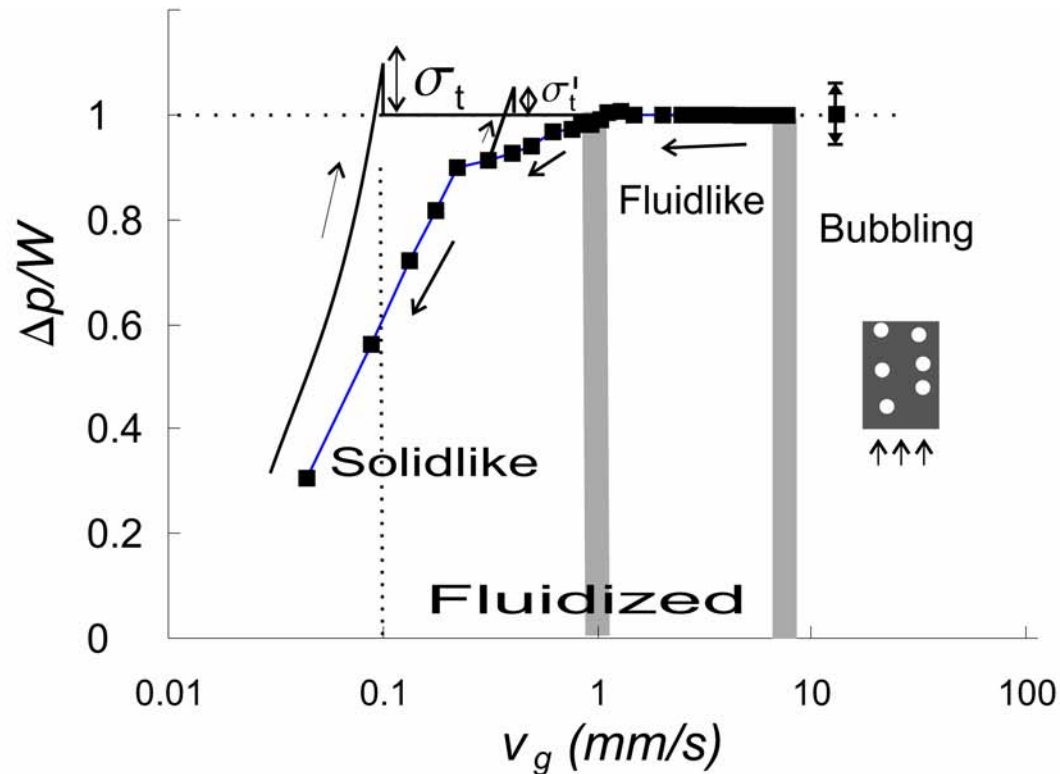# Method of fluidization

Initial state: Fluidize the powder past the bubbling point, turn off the gas and let it settle under gravity.
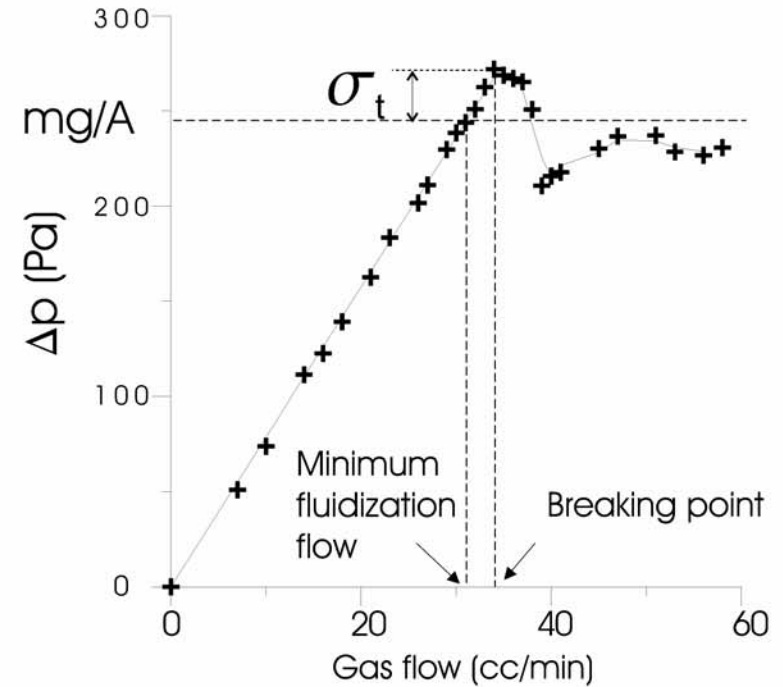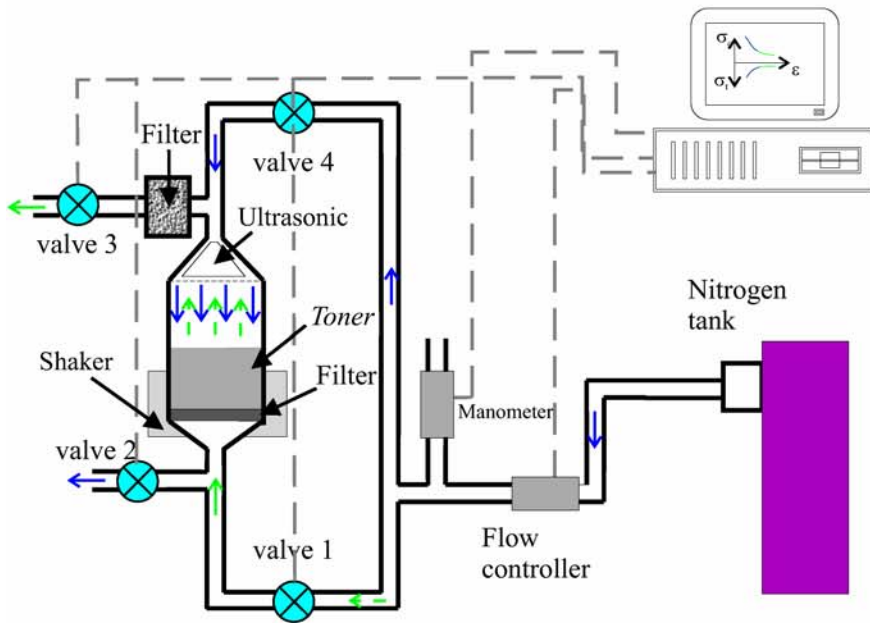
Uniaxial tensile stress: $\sigma_t = f(\sigma_c, \epsilon)$, with $\sigma_c = \frac{mg}{A} + \Delta p$ the consolidation, and $\epsilon = 1 - \frac{m}{\rho_p A h}$ the porosity. By consolidating against an upward flow ($\Delta p < 0$) we can reach $\sigma_c = 0$

# Both solid-like and fluid-like regimes exist for fine powders

Gas pressure drop, made nondimensional with the powder weight per unit area ($W = mg/A$), versus gas velocity.

Diffusion in the fluidized bed (type A)

Removable slide
↓

Toner CLC700

Gas flow

↑
Porous filter

⇑ ⇑

• The bed is set to bubble and then then flow is reduced to the desired value

• The slide is removed and the toners start mixing

• White paper strips are immersed in the yellow side of the cell at regular intervals
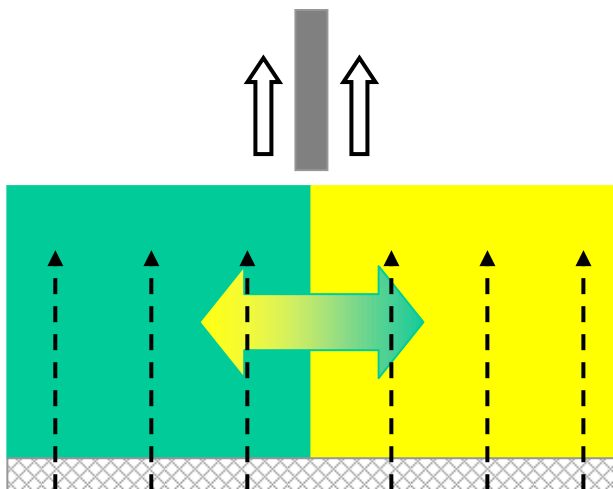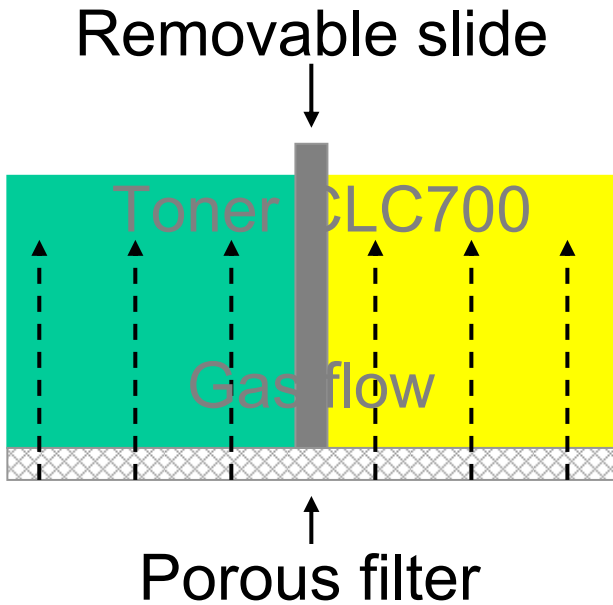
Example: gas velocity U_0 = 1.8 mm/s

Δt = 14 s

Δt = 96 s

Δt = 51 s

Δt = 188 s

Fine powders: solid fraction-gas velocity
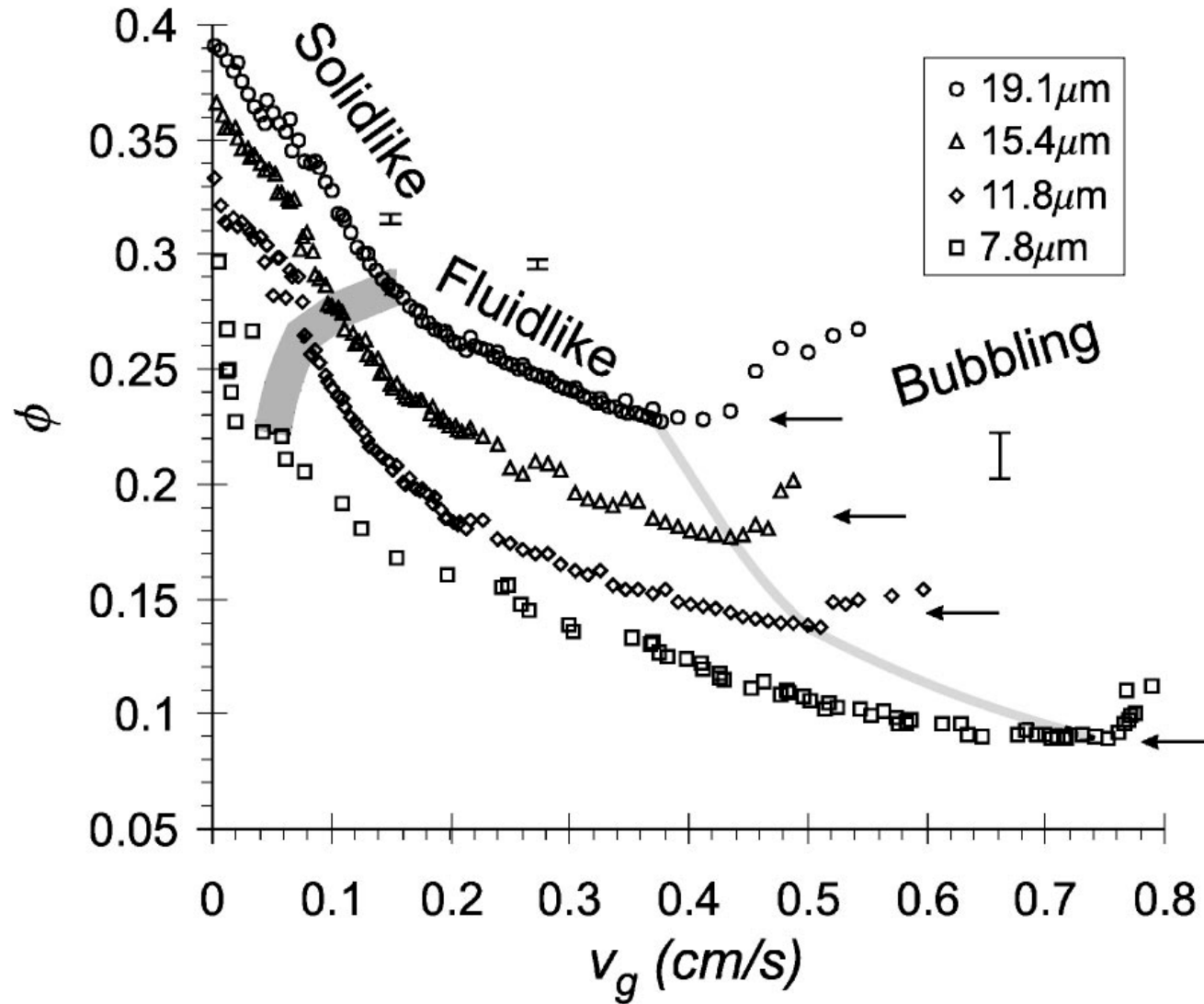
The fluid-like region shrinks to zero as the particle size increases and type A changes to type B (particles above 75 microns)

Can we predict where are the boundaries solid-like to fluid-like and fluid-like to bubbling?

- Yes, but for that we need to understand the behavior of particles in the fluidized state.

- The crucial factor is:

  cohesive particles may aggregate, and the aggregates behave as cohesionless particles (**key idea**)

For our materials the dominant interparticle forces are van der Waals forces, and we need first to determine the size of these aggregates.

Attractive forces: dry uncharged grains

Van der Waals forces between particles
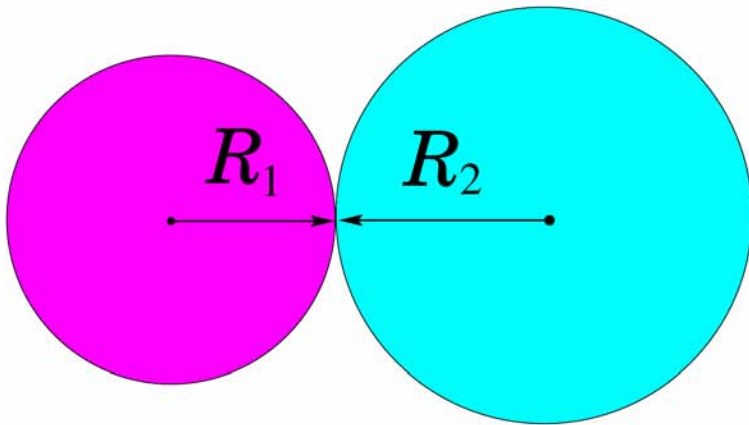
$$F_a = \frac{AR}{10z_0^2} \qquad\qquad F_a = \frac{AR_a}{10z_0^2}$$
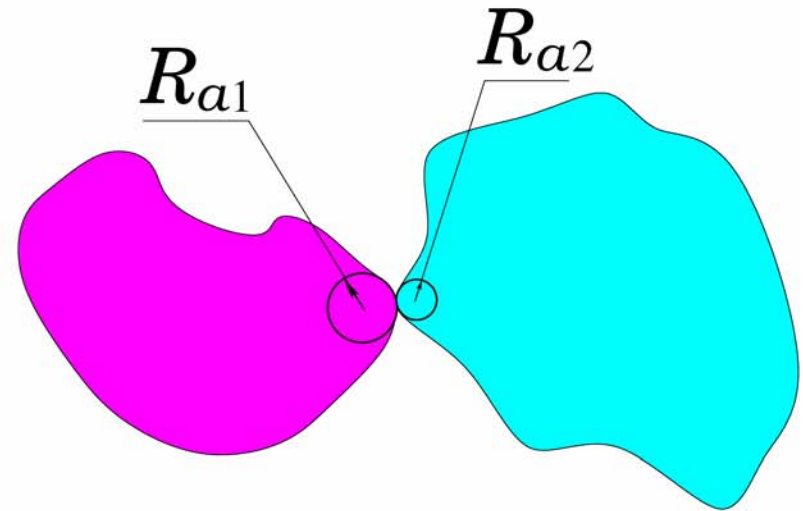
$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \qquad\qquad \frac{1}{R_a} = \frac{1}{R_{a1}} + \frac{1}{R_{a2}}$$

$A \simeq 10^{-19}$ J Hamaker constant, $z_0 \simeq 4$ Å

Fine-coarse particle classification

For polymer particles $A \simeq 0.5 \times 10^{-19}$ J, $\rho \simeq 10^3$ kg/m³. For 10μm diameter particles made by attrition the average asperity size is of order of 0.2μm.
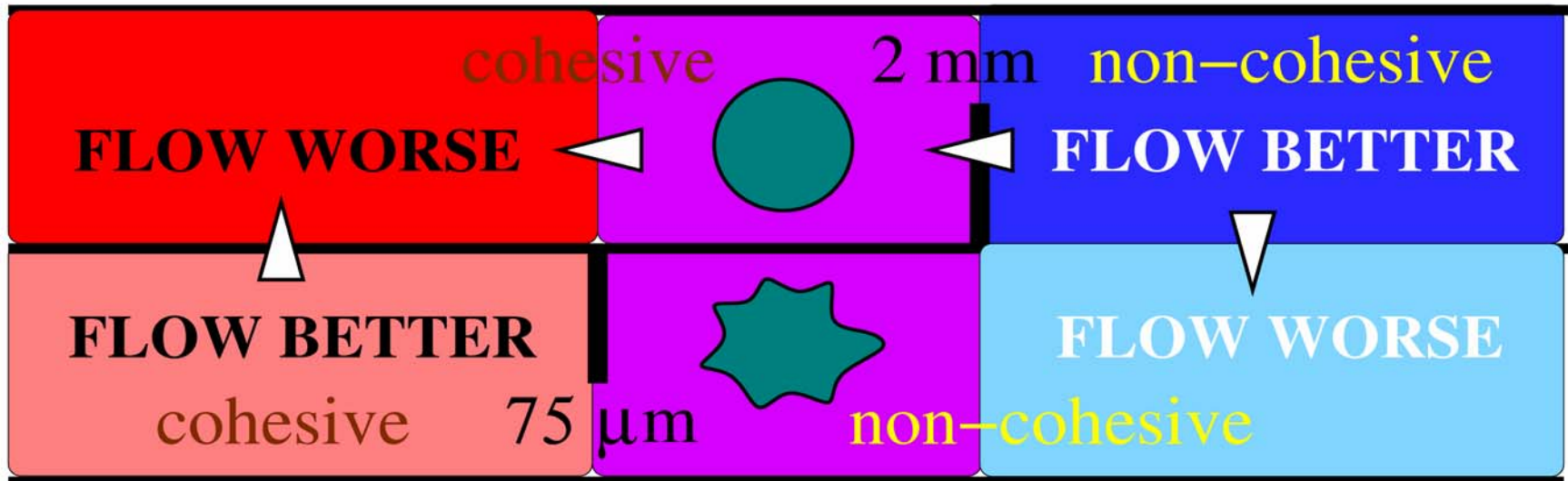
Smooth spheres

Irregular particles

of equivalent volume diameter d_p

$$Bo_g = \frac{3A}{20\pi\rho g d_p^2 z_0^2}$$

$$Bo_g = \frac{3Ad_{asp}}{20\pi\rho g d_p^3 z_0^2}$$

cohesive	2 mm	non−cohesive
FLOW WORSE ◁	◯ ◁	**FLOW BETTER**
FLOW BETTER △	✦	**FLOW WORSE** ▽
cohesive 75 μm		non−cohesive

Aggregation of fine particles in fluidized beds

200 μm 40 μm particle size

a) 100 μm 19.1 μm particle size

b) 100 μm 7.8 μm particle size
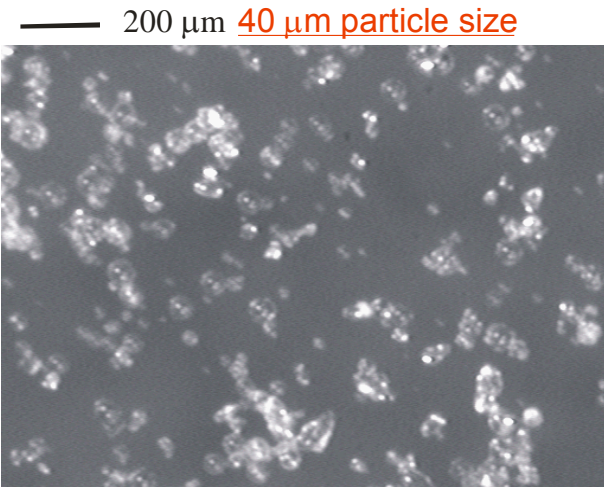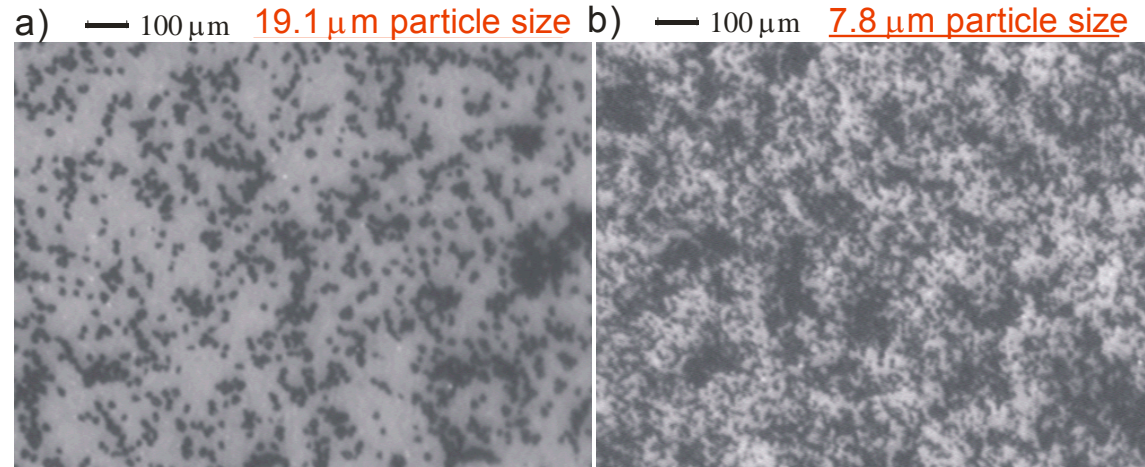
Bo ~ 10

Bo ~ 100

Bo ~ 1000

Distribution of adhered particles in a paper strip immersed in the bed

$$Bo = \frac{Interparticle\ attractive\ force}{particle\ weight} = \frac{F_0}{w_p}$$

How to predict the solid-like/fluid-like boundary? Our plan

The boundary between solid-like and fluid-like regimes is given by the jamming transition (when the aggregates start to be in permanent contact).

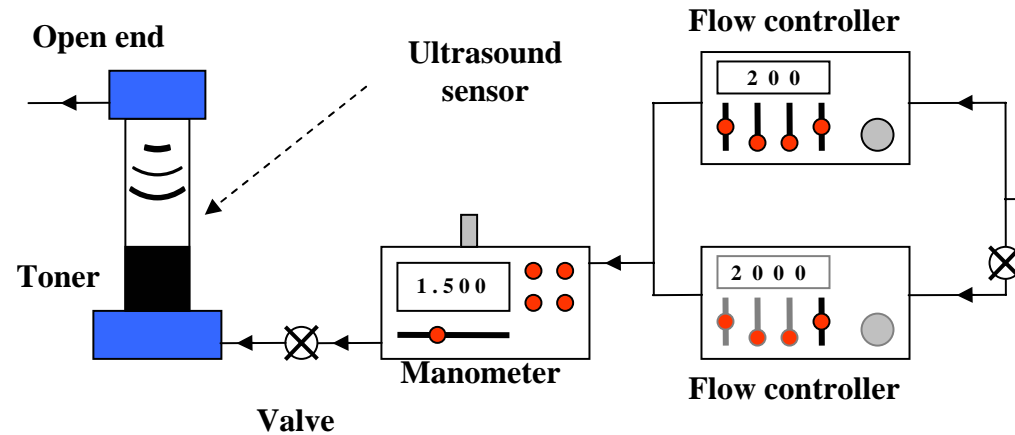We assume that the aggregates sediment like effective cohesionless spherical particles (key idea). Then, in the boundary solid-like/fluid-like their *effective volume fraction sho*uld be 0.56 (the random loose packing volume fraction of spheres).

If we are able to estimate the particle solid fraction (total mass/volume) as a function of the *effective volume fraction of aggregates* in the fluid-like region, then we can estimate the particle solid fraction at the solid-like/fluid-like boundary.

The last step is comparison of the model with experiments.

Settling experiments to characterize aggregates

Open end

Ultrasound sensor

Flow controller

2 0 0

Toner

1 . 5 0 0

Manometer

2 0 0 0

Flow controller

Valve

The valve shuts the gas flow and the bed collapses.

The ultrasound sensor measures the height of the bed to determine the settling velocity (Acquisition rate 10 - 40 Hz)

$V_s = dh/dt$

h (cm) vs time (s)
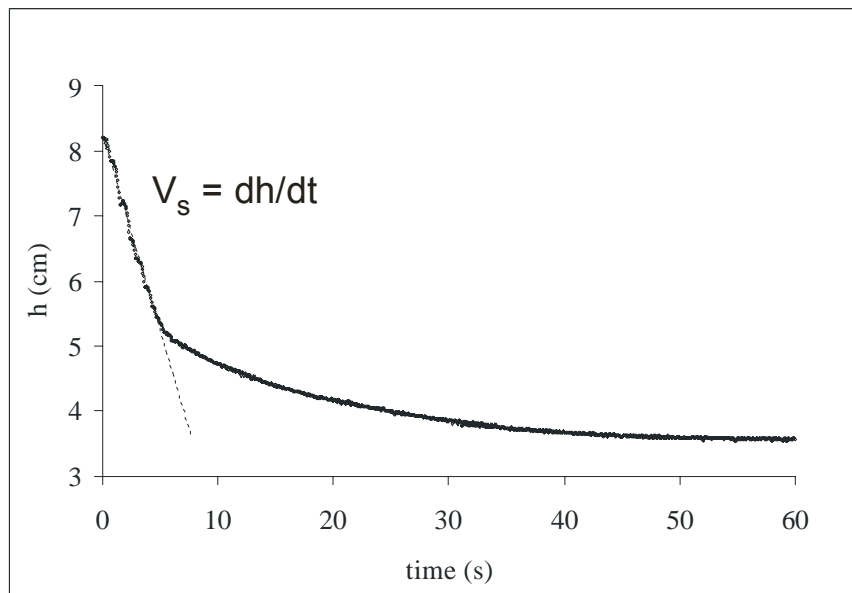
Toner (Seville)

Modified Richardson-Zaki law for aggregates

$$\frac{v}{v_{p0}} = \left(1 - \phi\right)^n$$

v_{p0}: terminal velocity of an isolated particle

$$v_{p0} = \frac{1}{18}\frac{\rho_p g d_p^2}{\mu}$$

- For aggregated particles, the R-Z law must be modified:

N: number of particles in aggregate

ϕ^*: volume fraction occupied by aggregates

d^*: size of aggregate

$$\kappa = \frac{d^*}{d_p}$$

$$\phi^* = \phi\frac{\kappa^3}{N}$$

Velocity of an aggregate

$$v^* = \frac{N}{\kappa}v_{p0}$$
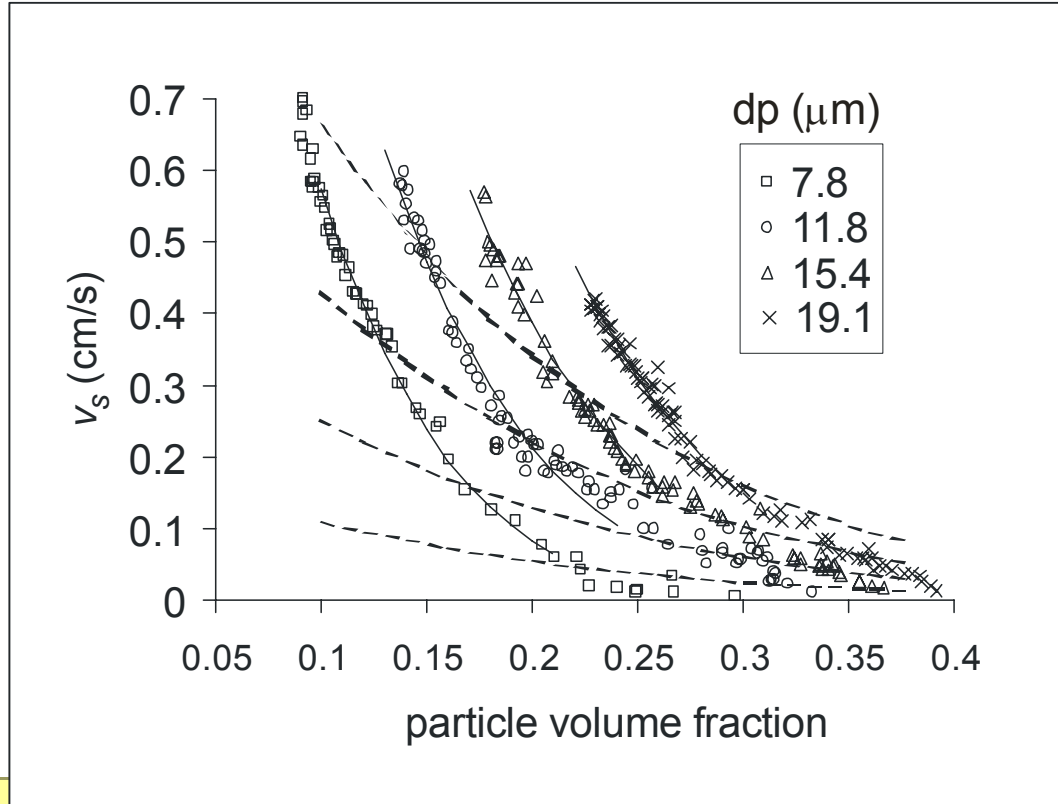
- Assuming hydrodynamic and geometric radius are equal:

$$\frac{v_s}{v^*} = \left(1 - \phi^*\right)^n$$

$$\Longrightarrow \quad \frac{v_{ag}}{v_{p0}} = \frac{N}{\kappa}\left(1 - \phi\frac{k^3}{N}\right)^n$$

where n = 5.6 if $Re_t(v^*) < 0.1$

Effect of particle size on aggregation

d_p(μm)	N	k	D
7.8	63	5.218	2.523
11.8	23.7	3.549	2.512
15.4	12.4	2.724	2.499
19.1	9.6	2.448	2.508

SAC=32% (constant F$_0$)

$$d^* = \kappa d_p \approx 40 - 45\,\mu m$$

Theoretical estimation of the maximum size of stable aggregates

Drag acts mainly at the surface of the aggregate whereas gravity is a body force acting uniformly through the aggregate. This results in shear forces distributed across the aggregate limiting its size.

Theoretical model

Shear forces distributed across the aggregate limit its size:

$$K_{ag}(\gamma R_{ag}) \sim N m_p g,$$

γ the typical strain on the aggregate, $K_{ag} = k_0/\kappa^\beta$ the aggregate spring constant (k_0 is the interparticle spring constant, and $\beta \simeq 3$ is the elasticity exponent for DLA aggregates)
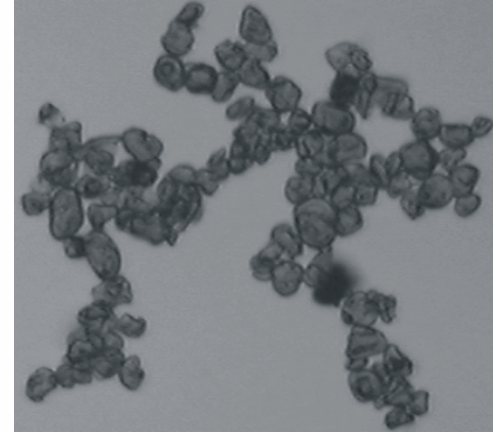
Thus the local shear force is

$$F_s \sim k_0 \gamma d_p/2 = k_0(\kappa^D)(m_p g d_p/2)/[(k_0/\kappa^3)(\kappa d_p/2)] \sim (m_p g)\kappa^{D+2}$$

For $F_s^{max} \sim F_a$, $Bo_g \sim \kappa^{D+2}$, thus

$$N = \kappa^D \sim Bo_g^{D/(D+2)} \sim Bo_g^{0.6}$$

For constant F_a,

$$R_{ag} = \kappa d_p/2 \propto d_p^{\frac{D-1}{D+2}} = d_p^{\frac{1}{3}}$$

The size of the aggregates is almost independent on $d_{p\sim}$
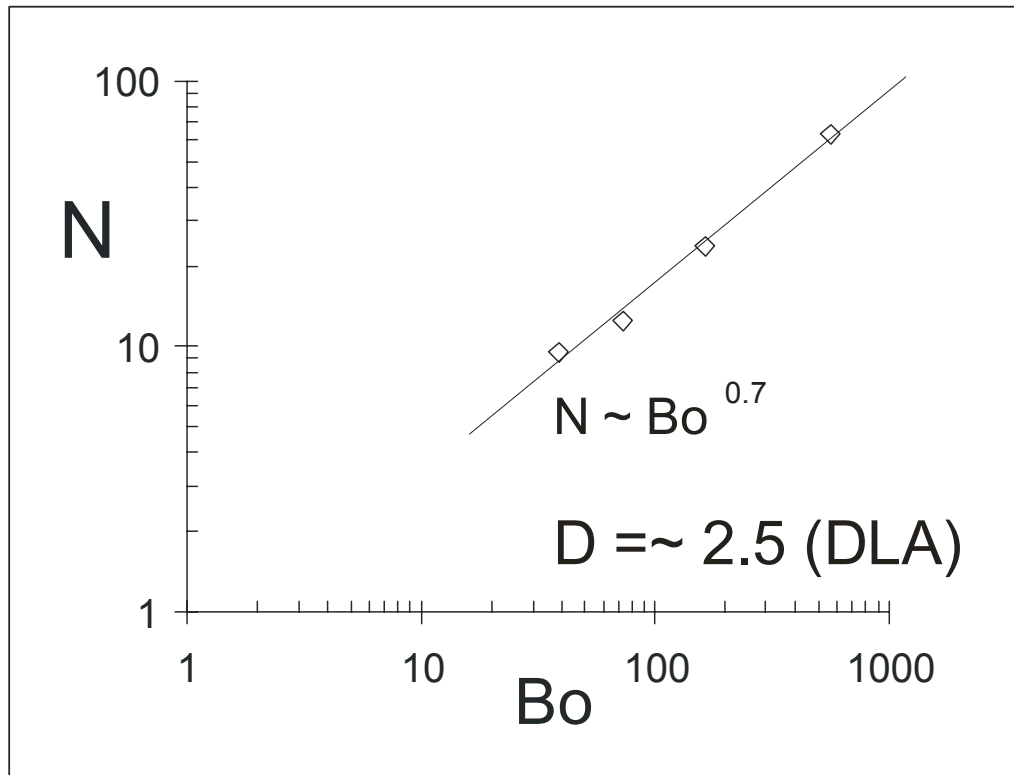
$$Bo_g \equiv \frac{\text{Interparticle attractive force}}{\text{particle weight}}$$

$$Bo_g \approx k^{D+2}$$

$$k \equiv \frac{\text{size of aggregate}}{\text{particle size}}$$

$D \equiv$ fractal dimension of aggregate $\quad N = \kappa^D$

Size and number of particles in the aggregate

N
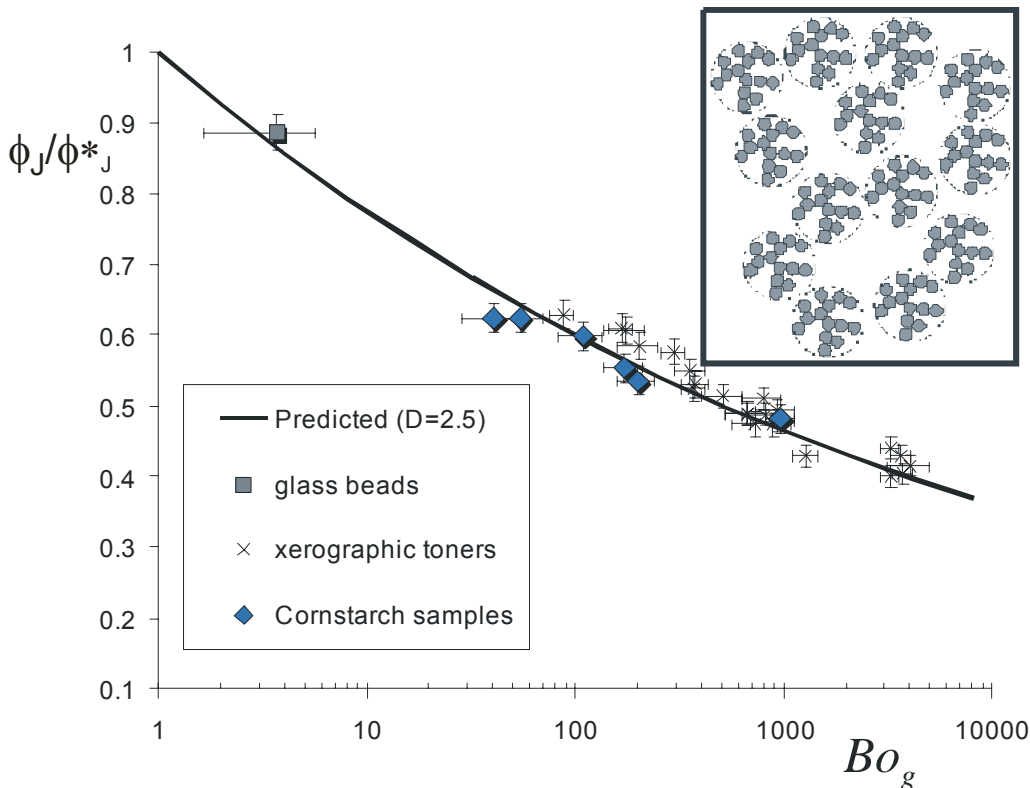
$N \sim Bo^{0.7}$

$D =\sim 2.5$ (DLA)

Bo

Theoretical prediction:

$$N = k^D \approx Bo_g^{\frac{D}{D+2}} \cong Bo_g^{0.6}$$

Solid-like Fluid-like boundary

At the fluid-to-solid transition aggregates jam in a expanded solidlike structure with a particle volume fraction ϕ_J.

$$\phi_J = \phi_J^* \frac{\kappa^3}{N} \approx \phi_J^* Bo_g^{\frac{D-3}{D+2}} \Longleftarrow Bo_g \approx \kappa^{D+2}$$

Legend:
- —— Predicted (D=2.5)
- ▪ glass beads
- × xerographic toners
- ◆ Cornstarch samples

Axes: ϕ_J/ϕ^*_J (vertical), Bo_g (horizontal)

ϕ_J is measured at the jamming transition

k and N are obtained from settling experiments

ϕ^*_J must be close to the RLP limit of noncohesive spheres (0.56) (aggregates behave as low cohesive effective particles).

Transition A-B

If $\phi_b = \phi_J$ the bed will transit directly from solid to bubbling (Geldart B)

How to predict the fluid-like/bubbling boundary? Our plan

We estimate this boundary via Wallis criterion for aggregates as effective non-cohesive particles (key idea).

Bubbling boundary

Macroscopic bubbling is a nonlinear process that has been related to the formation of solids concentration shocks when the propagation velocity of a voidage disturbance (u_ϕ) surpasses the elastic wave velocity (u_e) of the fluidized bed (Wallis 1969)

$$u_\phi = -\phi \frac{dv_g}{d\phi}; \quad \left\{ R-Z: \ v_g = v_{p0}(1-\phi)^n \right\};$$

$$u_e = \left[\frac{1}{\rho_p} \left(\frac{\partial p}{\partial \phi} \right) \right]^{1/2}; \quad \left\{ p \ \square \ \rho_p g d_p \phi^2 \right\}$$

$$u_\phi \approx u_e \quad \text{at bubbling onset}$$

Modified Wallis criterion for aggregates

$$Bo_g \equiv \frac{Interparticle\ attractive\ force\ \ F_0}{particle\ weight}$$

$$k \equiv \frac{size\ of\ aggregate\ \ d^*}{particle\ size\ \ d_p}$$

$$Bo_g \approx \kappa^{D+2}$$

$D \equiv$ fractal dimension of aggregate $\quad N = \kappa^D$

$$\phi^* = \phi\frac{\kappa^3}{N} \equiv \text{volume fraction of aggregates}$$

$$v^* = v_{p0}\frac{N}{\kappa} \equiv \text{settling velocity of individual agregate}$$

$\rho^* \equiv$ aggregate density
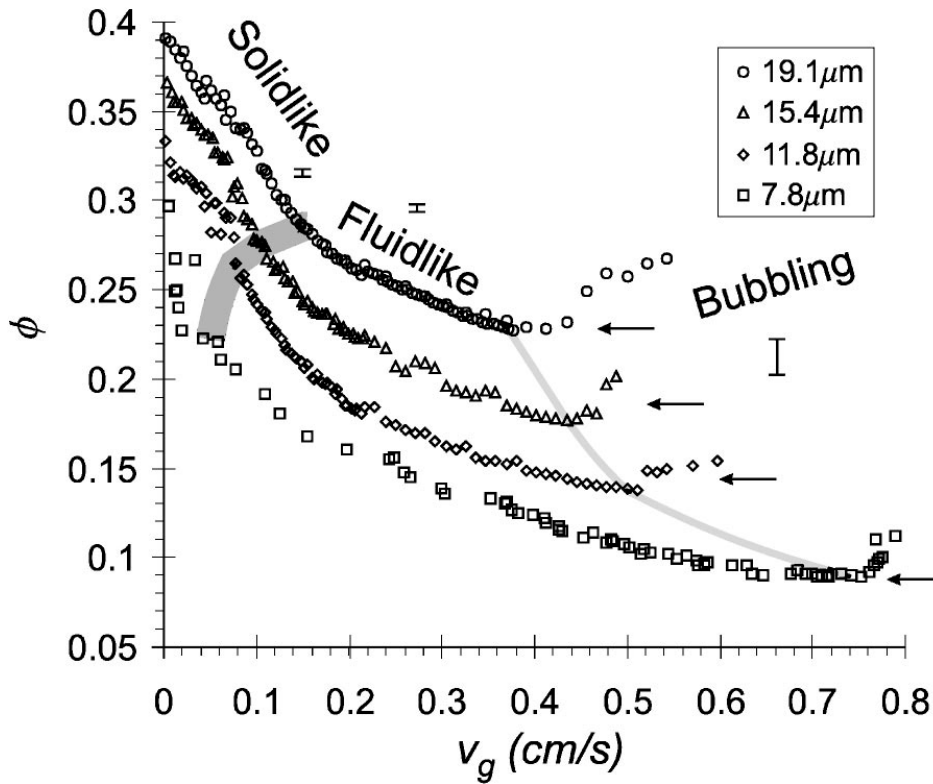
$$u_\phi^* = -\phi^*\frac{dv_g}{d\phi^*}; \quad \left\{R-Z: \ v_g = v^*(1-\phi^*)^n\right\};$$

$$u_e^* = \left[\frac{1}{\rho^*}\left(\frac{\partial p^*}{\partial \phi^*}\right)\right]^{1/2}; \quad \left\{p^* \ \Box \ \rho^* g d^* \phi^{*2}\right\}$$
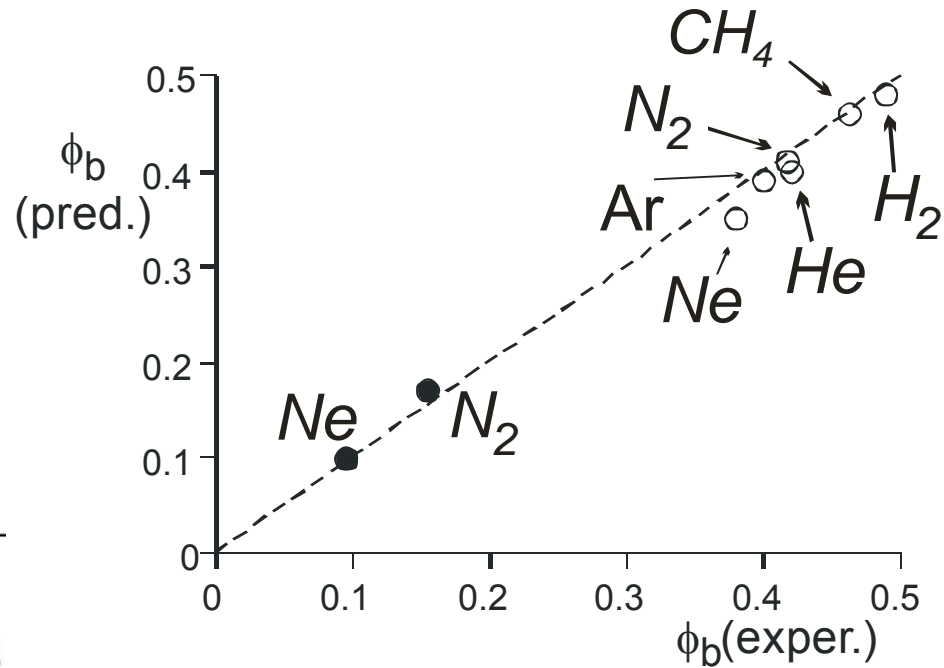
$u_\phi^* \approx u_e^* \quad$ at bubbling onset

Comparison with experimental results

Fluidization with Nitrogen of toners

| d_p	N	k	ϕ_b exp.	ϕ_b pred.
7.8μm	63	5.22	0.089	0.087
11.8 μm	23.7	3.55	0.140	0.146
15.4 μm	12.4	2.72	0.177	0.188
19.1 μm	9.6	2.45	0.228	0.229

Fluidization with other gases

○ FCC 63μm, Rietema 1991
● Canon CLC700 toner 8.5μm

Criterion for existence of homogeneous fluidization before bubbling

The maximum stable size D_b of bubbles (Harrison et al. 1961)

Fig. 1.—Bubbles breaking surface at the top of a bed of sand particles fluidised by air
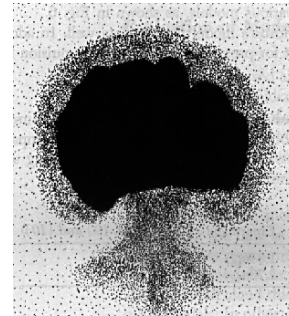
Single, isolated bubble in gas-fluidized bed showing a cloud (Davidson, 1977)

To have an estimation of D_b/d_p, Harrison et al. hypothesized that bubbles are no longer stable if their rising velocity U_b exceeds the settling velocity of the individual particles.

$$
\begin{aligned}
v_{p0} &\approx \frac{1}{18}(\rho_p - \rho_f)\frac{g\,d_p^{\,2}}{\mu} \\
U_b &\approx 0.7\sqrt{g\,D_b}
\end{aligned}
\right\rangle
\quad
\frac{D_b}{d_p} \approx \frac{1}{18^2 0.7^2}\frac{(\rho_p - \rho_f)^2 g\,d_p^{\,3}}{\mu^2}
$$

Implications of the Harrison and Wallis criteria

$$u_e^* = (g \, d^* \, \phi^*)^{1/2};$$

$$u_\phi^* = \phi^* \, v^* \, n \, (1-\phi^*)^{n-1}$$

$$0.7\sqrt{g \, D_b} = v^*$$

$$\frac{u_e^* - u_\phi^*}{u_e^*} = 1 - 0.7n\left(\frac{D_b}{d^*}\right)^{1/2} \underbrace{\left(\phi^*\right)^{1/2} (1-\phi^*)^{n-1}}$$

$$\boxed{\text{max } 0.195}$$
$$\boxed{at \; \phi^* = 0.098}$$

$$\boxed{\begin{array}{l} \min(u_e^* - u_\phi^*) > 0 \\ for \; \dfrac{D_b}{d^*} < 1.72 \end{array}}$$
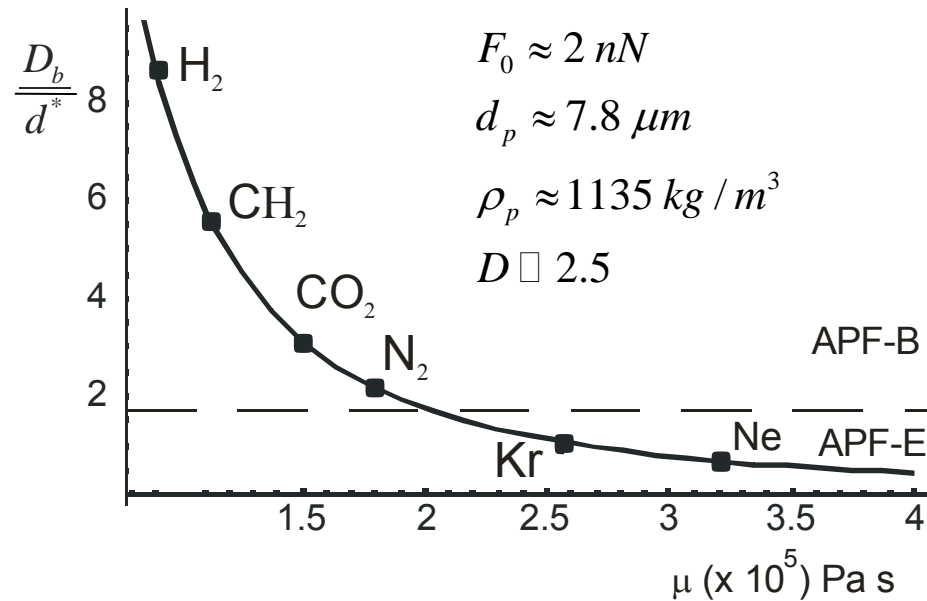
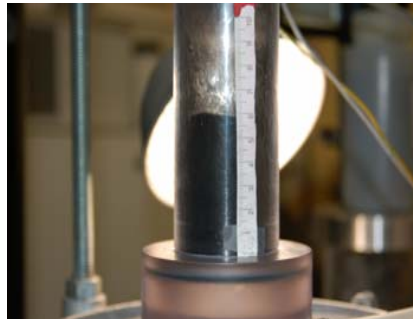*Thus* $u_e^* > u_\phi^* \; \forall \phi^* > 0$ *for* $\dfrac{D_b}{d^*} < 1.72$

$$\boxed{\frac{D_b}{d^*} \approx \frac{1}{18^2 \, 0.7^2} \frac{\rho_p^2 \, g \, d_p^3}{\mu^2} Bo_g^{(2D-3)/(D+2)} = 1.72}$$

determines the SFE-SFB boundary

$F_0 \approx 2 \, nN$

$d_p \approx 7.8 \, \mu m$
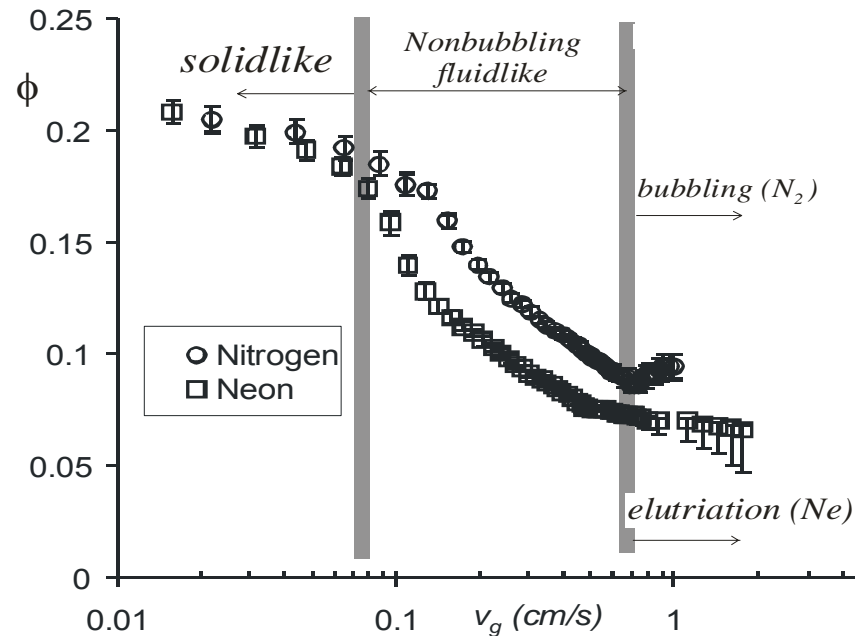
$\rho_p \approx 1135 \, kg/m^3$

$D \simeq 2.5$

Comparison with experimental results

Fluidization of **7.8μm** toner with Nitrogen and Neon

Nitrogen

Neon

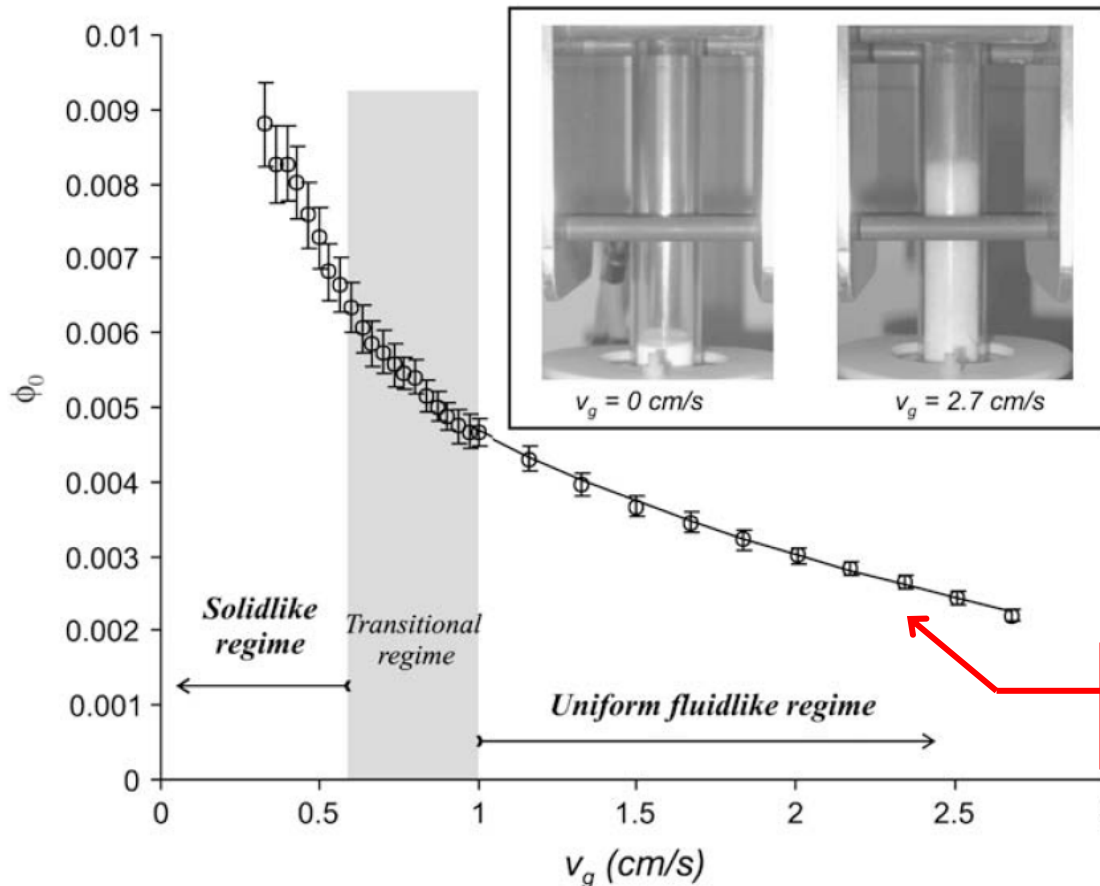**Direct transition to elutriation is observed when Neon is used (as predicted)**

Final agglomerates in unsieved nano-silica powders

This powder is non-fluidizable

Using the agglomerate diameter d_a and fractal dimension D in the RZ equation to fit the expansion of the bed in the **uniform fluidlike regime**, we obtain:
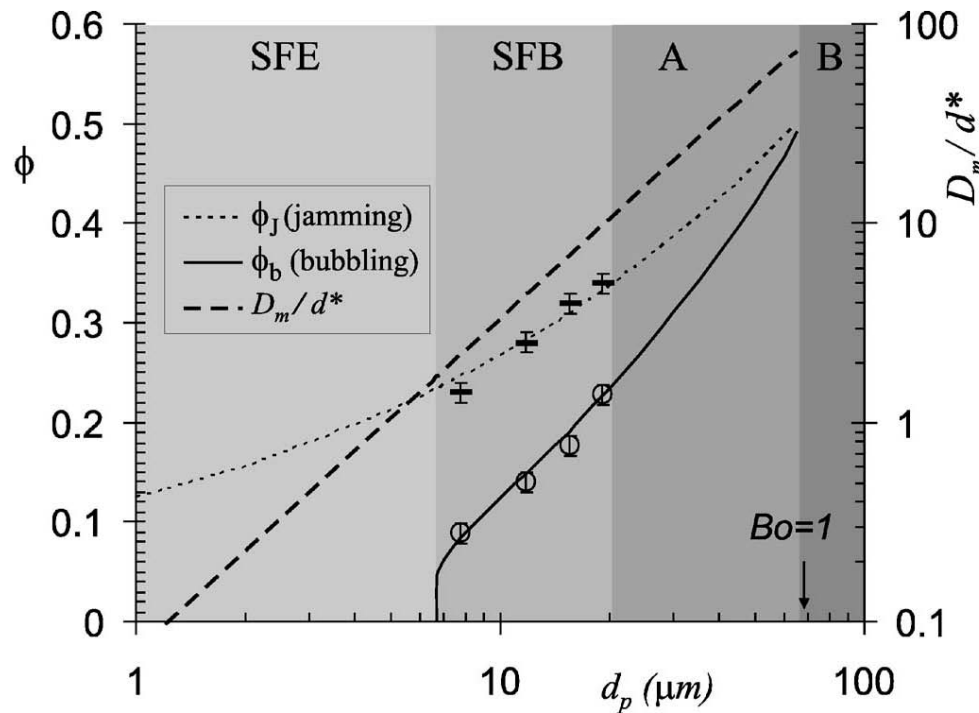
d_a: 226 μm

D: 2.588

These are the values we have used in the calculations.

$v_g = 0$ cm/s $v_g = 2.7$ cm/s

ϕ_0

Solidlike regime   Transitional regime

Uniform fluidlike regime

v_g (cm/s)

$$v_g = k^{D-1} v_p \left(1 - k^{3-D}\phi\right)^n$$

Types of fluidization of cohesive particles
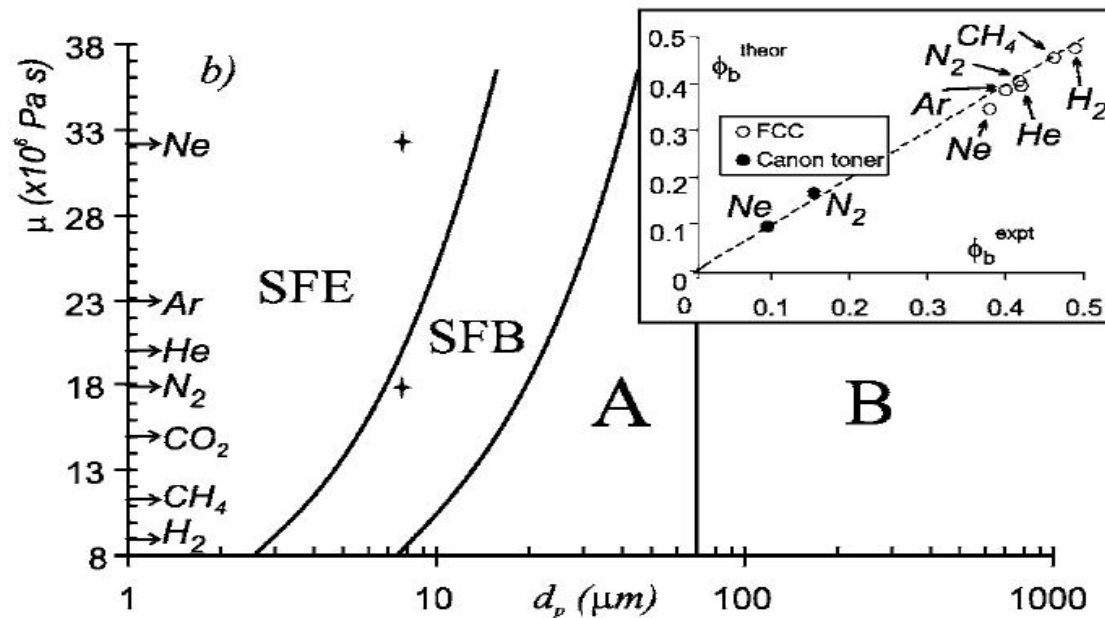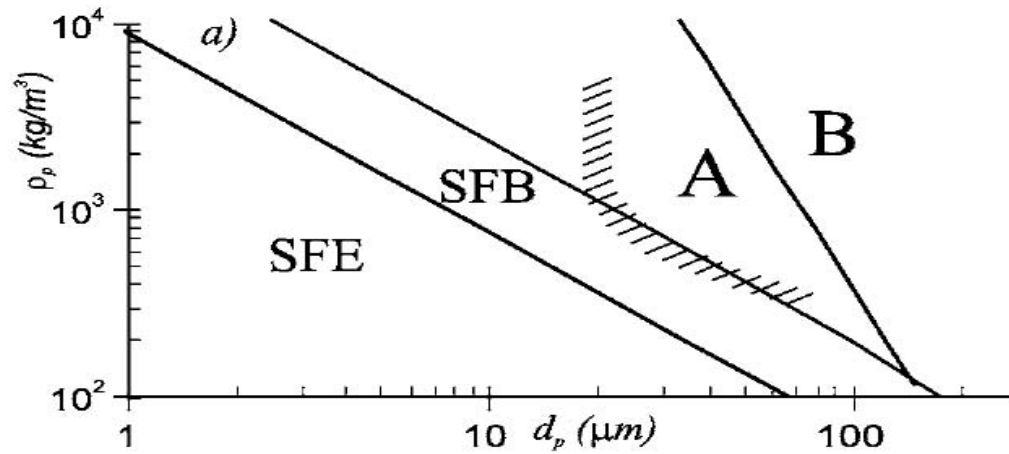

The A-B boundary, identified by $\phi_J=\phi_b$ coincides with $Bo_g=1$ (limit for aggregation).

Thus the existence of an expanded nonbubbling regime is directly related to aggregation of the cohesive particles

$\rho_p = 1135kg/m^3$, $\rho_f = 1kg/m^3$, $\mu = 1.79 \times 10^{-5}Pa\ s$, $F_0 = 2nN$, g $=9.81m/s^2$, D = 2.5 (typical values).

Types of Fluidization (in other variables)

Conclusion

Using the well known empirical relations for the behaviour of fluidized beds of noncohesive powders and applying them to aggregates:

1.- We have estimated the boundaries between the different types of fluidization, and

2.- We have predicted a new type of fluidization (solid-like to fluid-like to elutriation).

Thank you very much for your attention