Introduction

The fluidisation phenomenon is best explained by the balance of short and long range forces evaluated in a given powder assembly. The long range body forces include gravity, solid friction, buoyancy, interstitial fluid drag to include both the viscous (skin) friction and the form drag. The short-range forces, also known as particle surface-active forces, can be due to physical (e.g. van der Waals, capillary, electrostatics) or chemical (e.g. hydrogen bonding) or electrochemical effects such as electrophoretics. The relative magnitudes of the short-range and long-range forces are in turn determined by the physical properties of the solid particles such as particle size, particle shape and solid density and the properties of the carrier fluid such as fluid density, fluid viscosity and surface tension. It is well-known that with small particles in the sub-millimeter size range, the interstitial fluid effects dominate when the immersed weight becomes of the same order as the fluid drag forces which scale inversely proportionally to particle size.

Geldart’s well-known graphical classification \(^1, 2\) of the fluidization behaviour is a very effective way of mapping the balance of forces onto measurable particle and fluid properties that determine the relative magnitudes of the immersed weight and the fluid drag forces in a fluidised particle assembly; see Fig. 1 below.

As seen in Fig. 1, the fluidization behaviour is dominated by gravity effects for solid particles in the millimetre range or above (B and D type), and governed by the interstitial fluid permeability effects for...
sub-millimeter particles down to about 50 microns (A type). Below 50 microns, the particle surface forces begin to dominate giving rise to significant bulk cohesion that causes significant reduction in the permeability of the particle assembly by the interstitial fluid. Little or no information is presented for particles below 10 microns in size that are believed to give rise to assemblies that behave as “stable cakes” due to much increased particle surface forces per unit bulk volume such as due to Van der Walls, capillary and electrostatic attractions. Fine cohesive powders (Group C) fluidize poorly, exhibiting channelling, lifting as a plug, and forming “wormholes” when aerated.

According to the above classification, sub-micron and nanoparticles are at the extreme end of Group C particles suggesting at first sight that fluidisation would prove impossible due to the much higher surface active forces. However, the very high magnitudes of the short-range surface interactions in a sub-micron powder assembly has been found to yield in certain cases dynamically stable agglomerate structures made up of the constitutive nano-particles that can then grow to sizes in the micron and millimetre size ranges and thus whose fluidization behaviour could very well fall within groups A and B as well as C. Recent literature of the past five years or so cites many examples of “successful” fluidization of nano-particles by the production of dynamically stable large agglomerates; see for example 3, 4, 5, 6, 7, 8 to name but a few.

In a number of experimental investigations of the past few years, fluidization of ultra fine particles has been extensively studied as a possible route to particle dispersion, particle growth and particle collection processes. Some of these studies consider agglomerate bubbling fluidization (ABF). The dynamic aggregation of particles increases with decreasing particle size, which is attributed to greater inter-particle forces between particles, which attract them into aggregated groups. The existence of these micro-structured aggregates is believed to prevent the formation of cemented or stable cohesive bonds between the constituent particle surfaces and as such presenting a potential deviation from the theoretical behaviour range),

- \(10^9\) reduction in particle surface area per unit bulk volume (compared to particles in the sub-millimetre
- Increased surface-to-volume atomic ratio; (e.g. exponential increase in the portion of constituent atoms at or near surfaces creating more sites for bonding, reactions with surrounding media),
- High surface charge concentration,
- High electric field strength, and
- High electrophoretic mobility.

Ceramic, plastic and metallic nano particles and the various nano-composites comprising synthetic combinations of different inorganic and organic constituents are being used increasingly in manufacturing and process industries to provide i) increased surface area for heat and mass transfer and surface catalytic reactions and ii) advanced material functionality in films, compacts and coatings due to effects that include the modification of the carrier fluid rheology, enhancement of bulk mechanical, thermal and electrical properties, provision of chemically-active adhesive bonding to solid surfaces, highly porous micro-structures that are used for targeted delivery of fluid excipients.

Fig. 1 Geldart's Classification of the fluidisation behaviour of powders.
of “cohesive” materials observed in group C particles in Fig. 1 above. Experimental results show the existence of cells in a well organised structure; see Fig. 2 for examples of agglomerate structures cited in recent literature.

In the case of nano-particles, it is the agglomerates rather than individual particles that homogeneously fluidise, and this is achieved in a number of stages as described by Yao et al. Wang et al. state that the properties of the primary particles determine the properties of the agglomerates, which control the behaviour of the two-phase flow in a fluidized bed. SiO₂ nanoparticles with a size range of 7 to 16nm are quite different from normal Geldart-C particles and can be smoothly fluidized in a gas-solids particulate fluidization regime with a high bed expansion ratio and bubbleless behaviour via micro-structured self-agglomeration. As distinguished from the ABF of Geldart-C particles, this homogeneous fluidization phenomenon of SiO₂ nanoparticles is called agglomerate particulate fluidization (APF). A number of studies also state that unique fluidization behaviour of nano particles is due to multi-stage agglomerate (MSA) structure.

To increase understanding of APF behaviour, the relationship between the intrinsic characteristics of the primary particles and the agglomerate properties and macroscopic flow behaviour would have to be studied. It is for this reason density, size, porous structure and size of agglomerates need to be measured. The current theoretical and modelling studies all require direct measurement of voidage, local solids concentration, particle size measurements, agglomerate size and distribution, agglomerate structure and porosity. In all the studies on ultrafine/nanoparticle fluidization reported in the literature, physical properties of the particles were either estimated by making some simple theoretical assumptions or using other tentative imaging techniques or used intrusive measures such as local probes which would interfere with the flow around them. There is therefore, a serious need to determine these parameters dynamically and non-intrusively.

2. X-Ray Microtomography

The application of x-ray imaging techniques for fluidised beds has existed for around fifty years. One of the earliest recorded occurrences of this was by Grohse using x-ray absorption to calculate density profiles. According to Simons and Chaouki et al., much of the work carried out on fluidised beds using x-ray systems has been conducted by Rowe, Yates and co-workers at University College London. The original work conducted by Rowe and Partridge involved the observation of bubble behaviour using x-ray imaging, as this method involves using a single source and detector a small range of gas velocities had to be used to maintain an accurate 2D image. In further experimentation Yates et al. investigated the voidage distribution around a rising bubble within a fluidised bed. The technique follows earlier work by Rowe and Partridge that shows that there is not a straight division between the bubble and the surrounding emulsion phase. van Dijk et al. employed the use of x-ray imaging on a three-dimensional apparatus to allow bubbles to rise unhindered investigating the effects of the presence of an internal baffle. Kantzas et al. demonstrates the practical benefit of a CAT system by utilising the technology to observe channelling in a polyethylene fluid bed. Lehner and Wirth have utilised an X-ray computed tomography system in order to obtain solids distribution data on a downer reactor under a variety of conditions. They have stated that the spatial resolution of this system is 0.7 x 0.7mm with a 10% error in a standard sample compared to the actual concentration. Kai et al. have used a fast CT unit to capture both a high spatial and time resolution. The use of x-ray imaging techniques on industrial sized fluidized beds is also a well-researched field. Recent developments in x-ray sources and detectors now allow fluidized beds to be studied at length scales down to 400nm and with temporal resolutions of 1 ms. X-ray imaging also has the advantage of studying the bulk of the fluidized bed, rather than the surface, in a nondestructive and dynamic manner.

The X-ray microtomography technique developed at Surrey University in collaboration with the Department of Physics is providing valuable in-situ, non-destructive structural information on the morphological changes that take place nano fluidisa-
tion of powder samples. We can look into changes of agglomerates dynamically and examine the final microstructural features. Unlike other available imaging techniques which are usually surface techniques, X-ray microtomography imaging allows us to see through the sample and allow us to reconstruct 3-D internal structure of the sample. This powerful techniques allows us to identify processing routes that would provide better preserved nanostructural features. Combining high spatial resolution X-ray microtomography with fast radiographic imaging (i.e. 40 milliseconds), dynamic changes in the agglomerate structure and density can clearly be seen with different fluidisation conditions. The structure of three-dimensional assemblies of nanoparticles can be examined using high resolution x-ray microtomography apparatus, details of this technique have previously been described. The apparatus was used with the following operating parameters for these experiments: x-ray tube voltage 60kVp and current 0.1mA from a molybdenum transmission target with a 100mm zirconium filter. The magnification used resulted in the reconstruction of a (1024)³ cube of data with a linear dimension of 4.5mm.

Metallic oxide particles such as zinc and copper oxides were used in 2-D and 3-D fluidisation experiments at different gas velocities and the resulting internal bed microstructures were compared before and after fluidisation. The mean diameter of the ZnO nanoparticles (Tetronics, UK) were measured as 50nm using a Scanning Electron Microscope. The X-ray microtomography equipment provides the 3-D agglomerate size distribution as shown in Fig. 3. This is used for calibration of the bed contents prior to fluidisation. The agglomeration of these nanoparticles was studied using X-ray microtomography. High resolution X-ray microtomography enables us to evaluate rate of change of agglomerate size under different fluidization conditions.

The zinc oxide nanoparticles were placed in a small fluidized 2D bed of dimensions 4mm by 40mm and 300mm in height and in a 3D bed with a 10mm diameter. Homogeneous air distribution was ensured by using an area of free space below a sintered metal plate filter at the bottom of the bed. Nitrogen from a pressurized cylinder was used as the source gas to minimize the possibilities of capillary forces from air moisture. The gas flow velocity was controlled using a Brooks Instrument model 5850S mass flow controller. Different gas flow velocities were used.

The strong cohesive nature due to electrostatic and van der Waals interparticle forces of the nanoparticles leads to the production of even up to millimeter-sized agglomerates; the mean size and distribution of these agglomerates were determined using the 3D microtomography data. The agglomerate volume distribution is shown in Fig. 3 b.

The distribution was fitted to a log-normal distribution with a mean value of $0.695 \times 10^9 \mu m^3$ and a variance of $3.56 \times 10^{21} (\mu m^3)^2$ for the agglomeration volume. It can be seen that nanoparticles are capable of creating observable agglomerate structures even

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![Fig. 3](image-url)  

(a) Microtomographic scan of 3-D static bed.  
(b) Agglomerate size distribution within the 3-D static bed.
A histogram of the natural logarithm of the agglomerate volume versus frequency resulted in a distribution closely resembling a log-normal distribution. A description of the statistical features associated with log-normal distributions of coalescing particles is described by Granqvist and Buhrman. The mean of the agglomerate volume distribution $\mu$ and the variance, $\sigma^2$, can be extracted from a mean of the normal distribution fit, $M$ and the variance $V$ to log(e(agglomerate volume)) using the Equation 1.

$$
\mu = e^{\left(\frac{2M+V}{2}\right)} \quad \text{and} \quad \sigma = \mu e^{\frac{V}{2}} - 1
$$

A log-normal distribution fit to log. (agglomerate volume) yields $M = 15.95$ and $V = (2.97)^2$, which implies a mean value of $0.7 \times 10^9 \mu m^3$ (corresponding to an agglomerate mean size of about 700 $\mu m$). It is clear from the log-normal distribution that there is a diverse range of agglomerate sizes with some extending into the millimeter size range.

**Fig. 4** shows the detail of multi-modality of small agglomerate sizes determined below 75 $\mu m$ down to less than 5 microns. Here the peaks correspond to the indigenous (primary) structures of nanoparticles which are subsequently are seen to be dispersed into the dilute suspension phase above the fluid-bed at increasing fluidisation velocities. It is believed that the cloud formations observed in the x-ray images seen in **Figs. 5 and 6** below support networks of individual clusters of less than 5 micron in size. This aspect needs further detailed study using a finer scrutiny of length scale examination than the one presented in **Figs. 3 and 4** above.

As a further future, the three dimensional tomographic data presented above also allows the density of the agglomerates to be determined directly from the tomographic measurements; see reference 5) for details. Here, by calibrating the reconstructed data against data of reference materials, the mean bulk density of the ZnO agglomerates was found to be 2900 kgm$^{-3}$ compared to the 5600 kgm$^{-3}$ of the specific solid density of the individual nanoparticles. This result implies an internal porosity of agglomerates of about 0.5 which compares well with the incipient fluidisation state of the packed bed. However, once the agglomerates are introduced to the suspension phase above the bed, then other literature reports internal porosities as low as 0.1; see for example, reference 9).

The images presented in **Figs. 5 and 6** below are taken from an X-ray projection video with a spatial resolution of 30 microns and a temporal resolution of 40 milliseconds.

**Fig. 5** below shows snapshots of X-ray images during fluidisation of 50 nm mean size CuO nano particles at different superficial gas velocities using a planar (2-D) fluidised bed.

As seen in **Fig. 6**, at lower gas flow velocities (<0.052ms$^{-1}$) the nanoparticle agglomerates act
Fig. 5 X-ray images of CuO nanoparticle fluidization. a) static bed. b-c) incipient fluidisation, d-e) bed expansion post incipient fluidisation f) onset of aggregative fluidisation g-h) aggregative fluidisation with homogeneous expansion. i) return to static bed condition.

Fig. 6 X-ray images taken during planar (2-D) fluidisation at gas flow velocities: a) 0.026 ms⁻¹ b) 0.052 ms⁻¹ c) 0.078 ms⁻¹ d) 0.104 ms⁻¹ e) 0.208 ms⁻¹ f) 0.313 ms⁻¹.
as Geldart class A (aeratable) / B (bubbling) type systems, the fluidized bed exhibits a region of fixed larger agglomerates, through which channeling of the gas is occurring, below a region of fluidization of smaller and medium sized agglomerates, in which bubbling and turbulent flow is occurring, as observed by Wang et al \(13\). Agglomerates which are representative of the mean volume can be seen a few millimeters above the larger agglomerates at the base of the fluidized bed in Fig. 6(a). It can be seen in Fig. 6(c) that as the gas velocity is raised above 0.078 ms\(^{-1}\) that the collision energy of the particles is enough to break them apart to sizes below the imaging resolution.

The dynamic process of larger agglomerates being broken down and then re-agglomerating due to cohesive forces is shown in a series of images extracted from the original data sets collected with a temporal resolution of 40 ms in Fig. 7. Future work will, instead of making simple assumptions about the bulk properties of the agglomerate system, track down colliding agglomerates measure their spatial and temporal properties used to understand how different sized agglomerates behave. The agglomerate, labeled (a), in Fig. 7 can be seen to break down, due to collisions in the fluidized bed. In the same region a similar sized agglomerate, labeled (b), reforms, all within approximately 440 ms.

3. Determination of break-up energy of agglomerates from tomographic data

If the agglomerates are assumed to have the mean volume, \(\mu\), and density, \(\rho\), obtained from the tomographic data (\(\mu=0.695 \times 10^{-9} \text{m}^3\) and \(\rho=2900 \text{kgm}^{-3}\)) seen in Fig. 3(b) above, and are travelling at the gas velocity, \(v_g\), before colliding with effectively stationary agglomerates of the same size, that the break-up energy, \(E_b\), can simply be calculated from the kinetic energy of the moving agglomerate. This gives a break-up energy of \(2 \times 10^{-8} \text{J}\) for the average size of \(\text{ZnO}\) nanoparticle agglomerates in the system examined if an internal porosity of 0.5 is assumed. The corresponding magnitude of the break up energy needed for agglomerates with an internal porosity of 0.1 will be about \(4 \times 10^{-9} \text{J}\). A more detailed model for calculating the break-up energy is provided by Morooka et al \(16\) which suggests for powder agglomerates with a volume of \(0.695 \times 10^{-9} \text{m}^3\), the energy required to break the agglomerate is of the order of \(10^{-8}\text {J}\). The range of values calculated for agglomerates of different internal porosity appear to agree well with this figure reported in previous literature.

![Fig. 7](image-url) Consecutive X-ray images of the planar fluidized bed above the distributor at a gas flow velocity of 0.313 ms\(^{-1}\); the time between images is 40 ms. N.B. The images should be viewed in sequence from top left to bottom right.
The fluidized beds seen in Figs. 5 and 6 exhibit regions of stationary larger agglomerates, through which channelling of the gas is occurring, below a region of fluidization of smaller and medium sized agglomerates, in which bubbling and turbulent flow is occurring, as observed by Wang et al. 17). Furthermore, comparison of the images shown in Figs. 6 and 7 reveal that at sufficiently high gas flow velocities, the collision energy between the agglomerates exceeds that of the cohesive forces as predicted by Morooka et al 16) and the larger agglomerates are broken down into a distribution of individual nanoparticles and smaller agglomerates. This dynamic process of larger agglomerates being broken down and then re-agglomerating due to cohesive forces is clearly visible in the series of images extracted from the original data sets collected with a temporal resolution of 40ms as seen in Fig. 7. Our experiments with axially-symmetric (3-D) beds have also revealed similar processes which are currently under investigation.

Morooka et al. 16) studied fluidity of several kinds of submicron particles and reported that all tested ultrafine particles form agglomerates during fluidization. The energy balance model was proposed for estimating agglomerate size. Iwadate and Horio 12) developed the force balance model to predict agglomerate size in a bubbling system. Two models have been proposed to predict the size of agglomerates in fluidized beds of Geldart C group powders by Iwadate and Horio 12). Chaouki et al. 20) assumed that the drag force due to gas flow, which is approximately equal to gravity force acting on an agglomerate, is equal to the van der Waals force of attraction between primary particles. Morooka et al. 16) assumed that agglomerate breaks if the collision energy exceeds the energy that is required to break it into two parts. However, no bubble dynamics has been considered in these two different models. Iwadate and Horio 20) put forward a model that considers the bubble dynamics by including the particle pressure around the bubble. They then consider the cohesion force between the two agglomerates and use an expression for cohesive rupture force and make use of the bubble dynamics and work out the agglomerate breakage and agglomerate size estimation. However, for this or any other physical model validation, in-situ dynamic measurements of agglomerate size evaluation is needed. However, in the absence of direct measurements, most researchers use the minimum fluidization velocity and incipiently-fluidised bed bulk density as the value for the mean agglomerate density in their calculations. Sugihara 19) measured the bed pressure drop to determine the minimum fluidization velocity and utilizing the Carman’s equation, he obtained the agglomerate sizes. However, it was assumed that agglomerate density \( \rho_a \) was equal to primary particle density \( \rho_p \) instead of \( \rho_a = \rho_p (1 - \varepsilon) \). Since neither \( \rho_a \) nor \( \varepsilon \) were measured, the predicted size values were much lower that the observed ones. Chaouki et al. 20) assumes that the drag force due to gas flow, which is approximately equal to gravity force acting on the agglomerate, is equal to the van der Waals force of attraction between the primary particles. Morooka et al. 16) assumed that the agglomerate will break down if the collision energy exceeds the energy that is required to break it into two parts. In fact, these two models are not very different from each other.

There is a serious need to determine the agglomerate size and density at resolutions not attained in previous X-ray applications to determine dynamically and non-intrusively the agglomerate size, agglomerate density, agglomerate porosity, inter-agglomerate voidage and local solids fraction and its dependency, bubble evolution as the hydrodynamic effect of bubbles on the behaviour of particles also needs to be considered by using high resolution x-ray microtomography. In all the studies on ultrafine/nanoparticle fluidization studies reported in the literature, these parameters were either estimated by making some simple theoretical assumptions or using other tentative imaging techniques. This technique would also make it possible to measure the amount of agglomeration of primary particles due to the tendency of nanoparticles to agglomerate before the fluidization. In some of the reported studies for example this was achieved by sieving the powders before the fluidization process. It is therefore crucially important to determine these parameters through dynamic measurements in situ.

The fluidised beds were also used to measure the tappings placed at the walls interstitial pore pressure drop as a function of the fluidising velocity using pressure tapings placed at the walls; see Fig. 8 for a typical set of results. From these graphs, it has been possible to obtain a mean value of the “pseudo-agglomerate” size using the conventional Carman-Kozeny equation as applies to the incipient fluidisation conditions.

\[
d = \sqrt[3]{\frac{E(1-\varepsilon)\mu U}{(\Delta p/\mu) \varepsilon}}
\]

(2)
The fluidization parameters are \( E=180, \Delta p/\mu = \ldots \)
By putting these values back into Carman-Kozeny equation, the mean agglomerate size is found to be between 700mm and 1mm. This mean agglomerate size is in good agreement with the results obtained from the application of 3-D high resolution X-ray microtomography shown earlier in Fig. 3.

The predicted values of the mean effective agglomerate sizes compare well with the size distribution of agglomerates observed during x-ray imaging of the static and incipiently fluidised beds; refer to Fig. 3 above. Further work is underway to characterise the dynamics of growth and decay of agglomerates above the distributor as a function of the fluidisation velocity, particle loading and fluidising gas density and viscosity; see Fig. 5 above. Measurements of the bed expansion following the onset of the aggregative fluidisation has resulted in values of the mean dynamic voidage of the bed according to

\[ \frac{H_d}{H_m} = \left( \frac{1 - \epsilon_{mf}}{1 - \epsilon_2} \right) \] (3)

which results in values of 0.7 - 0.8 as predicted by the Richardson and Zaki correlation at the limit of particle terminal velocities;

\[ U_d = U_1 \epsilon^* \] (4)

in which \( U_d \) and \( \epsilon_d \) are the superficial gas velocity and the bed voidage, respectively, and \( U_1 \) and \( \epsilon \) are the two adjustable parameters of the equation. The exponential index \( n \) assumes a nearly constant value of 4.65 for Group A powders. The Richardson-Zaki equation is particularly useful for high-bed voidage ranges. The Richardson-Zaki equation and all other existing bubble-free bed hydrodynamic models assume that the bed is homogeneous and its void structure is represented by a single characteristic voidage. However, this view represents only an approximation to the real cavity structure that is heterogeneous, consisting of strings of clustered particles and interstitial cavities of gas. A comprehensive characterisation of the cavity structure would require two or more characteristic voidages as seen below.

Castellanos et al.\textsuperscript{21} have investigated the settling of fine powders to find that existing equations to describe these phenomena need to be extended in order to account for aggregates that form due to strong inter-particle attraction. Aggregates form up to an order of 100\( \mu \)m which is significant given the size of a single particle. They state that despite the simplicity of Richardson-Zaki equation, at high solidosity values, it has no theoretical justification. They propose a modified Richardson-Zaki equation for complex agglomerates along with a straightforward criterion using a force balance. Using, particle volume fraction \( \varphi \),

\[ \frac{U_d}{U_1^*} = (1 - \varphi^*)^n \] (5)

where \( U_1^* \) = \( U_1/N/k \) is the settling velocity of an individual agglomerate and \( \varphi^* = \varphi k^3/N \). They modelled the fluidized bed as an ideal system of simple agglomerates each one consisting of \( N \) primary particles and with a radius of gyration \( R_G \) equal to the hydrodynamic radius \( R_v \) (let us define \( k = 2R_v/d_p \)).

\[ \frac{U_d}{U_1} = \frac{N}{k} \left( 1 - \frac{k^3}{N} \varphi^* \right)^n \] (6)

However, complex agglomerate structures should be considered in the evaluation of this equation. As stated above, smaller agglomerates themselves form bigger agglomerates in different shapes i.e. Multistage Agglomeration (MSA). Nam et al.\textsuperscript{33} makes use of this
modified model to adapt to multiscale, multistage agglomerate structures. In an attempt to include these multistage agglomeration, a new version of Eqn. (5) is put forward as by Valverde and Castellanos and (private communication):

\[
\frac{v_s}{v_{po}} = \frac{N}{k} \frac{N^*}{k^*} \left(1 - \frac{k^3}{N^* k^*} \phi \right)^n
\]

(7)

4. Modelling of dynamic clustering effects

A closer examination of the clustering and aggregation of nano-particles above the fluidised bed by x-ray micro-radiography is found to reveal a very high degree of mobility of individual particle separations; refer to Fig. 5g-h above. This is believed to be due to the manifestation of the “cohesive energy” produced by electric field strength at large contact separations. Jung and Gidaspow provide discussions of such effects in fluidisation of ultra-fine particles with reference to the existence of highly thermalised, dynamic clusters held together by long-range Van der Waals and electrophoretic forces. This result is in stark contrast to the established observations of the Geldart C Type behaviour. Particles in the micron size range are often found to exhibit cohesive/adhesive force bonding of (almost) touching contacts marked by very low degree of mobility of particle contact separations. The presence of strong short-range Van der Waals or capillary type forces often result in dense agglomerate structures which can be further compacted to “stable cakes” at quite small compressive forces as in powders in the micron size-range; see for example reference 2).

In the studies presented here, the formation and preservation of dynamic agglomerates and clusters of nano-particles in the 100 micron -1 mm size range allows homogeneous bed expansion coupled with increased aggregation of the particle assembly as the fluidising gas velocity is increased; refer to Fig. 5 above. Hence, with nano-particle clusters in high fluidising velocities much in excess of the minimum fluidisation velocity, the fluidisation behaviour is described by continuous expansion similar to Group A behaviour in stark contrast to the group C behaviour observed typically with particles in the micron size-range; see modified Geldart diagram below incorporating dynamic clustering effects observed in the expansive suspension phase in nano-agglomerate fluidisation.

Further on-going studies of the dynamic clustering effects are likely to reveal further evidence of the sustainability of long-range clustering at very small values of the immersed weight \( (\rho_p - \rho_f) \approx 10^{-2} \text{ kg m}^{-3} \) of the clusters as seen in Fig. 10.

With varying particle and carrier fluid properties, it is believed that it would be possible to represent the aggregative fluidisation of these nano-particle assemblies with continuous and homogeneous expansion without bubbling (i.e. Geldart A-type behaviour) by allowing gas percolation through the bed contents at multiple porosity length scales as depicted by the schematic in Fig. 9 above. Therefore, we add this region where dynamic nanoparticle clusters are observed as “E: expandable” in the modified Geldart diagram presented in Fig. 10. It is also important to establish here the effects of 2-D and 3-D bed ge-
concerning the observed transitions from particulate to aggregative states of fluidisation both within the agglomerates as well as with in the cavity space between the “effective” agglomerates in the bed. The other very recent literature cited above in 3-D beds suggests that the transitions from particulate fluidisation to aggregative and/or bubbling regime is markedly different in 2-D and 3-D geometries. All of these phenomena could be fitted into the Geldart classification above by a further systematic study of the dynamics of the agglomerate/cluster growth and decay processes in 2-D and 3-D fluidised beds.

5. Conclusions

Through the use of novel x-ray micro imaging techniques, highly accurate data are produced of the mean size and shape of nano-agglomerates in incipiently fluidised beds and in expanding clusters above the bed region. In the latter regime, the multi-scale nature of the interstitial voidage and gas percolation has been demonstrated to produce nano-agglomerates of substantial size (5-75 microns) as seen in Fig. 4 with immersed cluster/agglomerate densities of a factor of 10 of the density of the gas phase whilst within an incipiently fluidised bed, denser and more stable agglomerate sizes were found to grow to the millimetre scale; as seen in Fig. 3b above. Tomographic data to date presented here is indicative of the way that such data could be used to predict quite accurately the size and internal porosity of the said agglomerate structures. The uncertainties associated with tomographic calibrations will no doubt be reduced substantially with ever increasing spatial and temporal resolutions afforded by further state-of-the-art scanner hardware developments.

A modified Geldart chart is proposed to take in to effect the dynamics of the expanding dynamic clusters observed at high fluidisation velocities which result in E type expandable dynamic cluster behaviour in stark contrast to the much more dense agglomerates observed with particles in the micron size range in conventional Group C type fluidisation behaviour. The literature to date attributes the differences to the predominance of different long and short range forces in sub-micron particle assemblies. It therefore remains very important to establish the effects of the physical and chemical properties of the different particle species on the magnitude and the nature of these force fields. Current investigations are underway to quantify the contributions to the nanoparticle cluster force fields from long range van der Waals, electrostatic and electrophoretic forces.

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References

1) Geldart, D., Powder Technology, 7, 287 (1973)
2) Jung JW, Gidaspow D, Journal of Nanoparticle Research, 4 (6), 483 (2002).
3) Hakim LF, Portman JL, Casper MD, Weimer AW, Powder Technol, 160, 149 (2005).
4) Dukhin S., Zhu C., Dave R.N., Yu Q., Adv. in Colloid and Interface Sci. 114 (2005).
5) Jenneson PM, Gundogdu O, Appl. Phys. Lett., 88, 034103 (2006).
6) Valverde JM, Castellanos A, AIChE Journal 52 (2): 838-842 (2006).
7) C. Zhu, G. Lui, Q. Yu, R. Pfeffer, R. N. Dave, and C. H. Nam, Powder Technol., 141, 119 (2004).
8) Valverde J.M. et al., Physics Review, E , 67, 051305 (2003).
9) Yao W., Gu G., Wei Fei, Wu J., 2002, Powder Technology, 124, 152 (2002).
10) Matsuda S., Hatano H., Muramoto M., Tsutsumi A., AIChE Journal, 50 (2004).
11) Kwauk M., Li J., Liu D., Powder Technology, 111, 3 (2000).
12) Granqvist C.G.and Buhrman R.A., Appl. Phys. Lett., 693 (1975).
13) Wang, M. Kwauk, and H. Li, Chem. Eng. Sci. 53, 377 (1998).
14) Jenneson PM., Lugar R.D., Morton E.J., Gundogdu O., Tuzun U, J. Appl. Phys., 96, 2889 (2004).
15) Zhu C et al, Powder Technology, 141, 119 (2004).
16) Morooka S., K. Kusakabe, A. Kobato, and Y. J. Kato, Chem. Eng. Jpn., 28, 41 (1988).
17) Y. Wang, F. Wei, G. Luo, H. Yu, and G. Gu, Chemical Physics Letters, 364,588 (2002).
18) Chauuki J., Larachi F. and Dedukoni- M. P., Ind. Engm. Chem. Res., 36, 4476 (1997).
19) Sugihara M., J. Res. Assoc. Powder Technol., Jpn., 3, 21 (1966).
20) Chauuki J., Chaverier C., Klvana D., Pajonok G., Powder Technol., 43, 117 (1985).
21) Castellanos A, Valverde J. M., Quintanilla M. A. S, Phys. Rev. E, 64 (2001).
22) Iwadate Y., Horio M., Powder Technol. 100, 223 (1998)
23) Park, Y.J., Chemical Engineering Science, 58,193 (2003).
24) Peirano, E., Delloume, V, Leckner B, Chem. Eng. Sci., 56, 4787 (2001).
25) Simons, S. J. R., Chem. Eng J., 56, 83-93 (1995).
26) Grohse, E. W., AIChE J., 1, 358-365 (1955).
27) Rowe, P. N., Partridge, B. A, Trans. Instn. Chem. Engrs., 43, T157-T175 (1965).
28) Yates J. G., Ruiz-Martinez R. S., Cheeseman D. J., Chem. Eng. Sci. 45, 1105-1111 (1990).
29) van Dijk J.J., Hoffmann A.C, Cheesman D., Yates J.G., Powder Techacleology, 98, 273-278 (1998).
30) Kantzas A., Wright I., Kalogerakis N., Chem. Eng. Sci. 52, 2023-2035 (1997).
31) Lehner P. and Wirth K., J., Chem. Eng. 77, 199-206 (1999).
32) Kai T., Misawa M., Takahashi T., Tiseanu I., Ichikawa N. and Takada N. J., Chem. Eng. Jpn., 33, 906-909 (2000).

Author's short biography

Dr. Özcan Gündogdu

Dr Gündogdu received his PhD in Applied Physics from the University of Birmingham where he developed novel Positron Emission Tomography (PET) multiple particle tracking techniques for powder processing and particle interactions. He then worked on developing novel filtration techniques exploring complex multiphase systems, developing theoretical models. He has been working as senior research fellow at the University of Surrey since 2003, in nano-powder processing, polymer-nano hybrid systems, nanocomposites and developing novel imaging and theoretical models which will prove crucial to exploit exciting properties nanopowders and nanotechnology offer. He has a wide range of research interests from tomographic imaging techniques to zone plates and holography, optics, radiation physics, cluster analysis, fractal and percolation models, image processing and especially nanoparticle interactions and processing in multiphase systems. He has been awarded the most prestigious "2003 Gold Medal" given biennially by International Filtration Society for his work on novel filtration systems with Prof. Curt Koenders at Kingston University prior to his arrival at the University of Surrey.

Prof. Ugur Tüzün

Professor Ugur Tüzün, C.Eng, C.Sci, FIChemE, FRSA is a professor of chemical and process engineering in the School of Engineering of Surrey University. He heads a large research group studying the mechanics of particulate and multiphase flow systems. During the last decade, this group has been instrumental in developing a significant number of mathematical models (and software) using novel computational simulation techniques (e.g. CFD, FEM, MD, SPH, LGA) relating the microscopic properties of particles to the assembly behaviour in complex fluid rheologies and complex device configurations. Alongside the model development, Prof. Tüzün and his colleagues have been responsible for pioneering work on the development of novel 3D tomographic techniques to image multi-phase flows and multi-component particle systems in process equipment. Most recent applications include imaging and modelling of nano-particle compaction and fluidisation processes with applications in advanced materials and pharmaceutical industries. Prof. Tüzün also has considerable experience of continuum modelling of bulk solids velocity and stress fields with experimental validations in pilot plant equipment. Prof. Tüzün's research has attracted research funding over £1.7M with output of some 80+ research publications and over 10 PhD's during the past decade. Prof. Tüzün was honoured with the Nisshin Engineering (Japan) Distinguished Professor in Particle Technology Award in 2001.