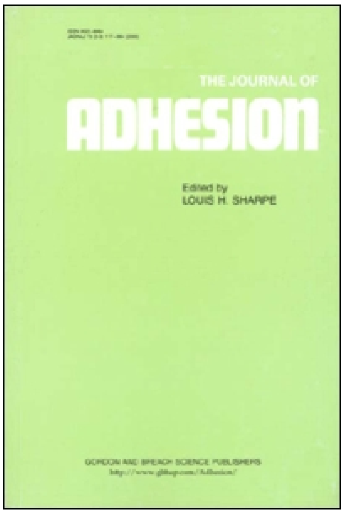

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Adhesion of Fine Particles in Dispersions

K. Kendall[a]; W. Liang[a]; C. Stainton[a]
[a] Chemistry Department, Keele University, Keele, Staffs, UK

To cite this Article Kendall, K. , Liang, W. and Stainton, C.(1998) 'Adhesion of Fine Particles in Dispersions', The Journal of Adhesion, 67: 1, 97 — 109

To link to this Article: DOI: 10.1080/00218469808011101

URL: http://dx.doi.org/10.1080/00218469808011101

J. Adhesion, 1998, Vol. 67, pp. 97–109
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published under license
under the Gordon and Breach Science
Publishers imprint.
Printed in India.

Adhesion of Fine Particles in Dispersions*

K. KENDALL, W. LIANG** and C. STAINTON

Chemistry Department, Keele University, Keele, Staffs. ST5 5BG, UK

(Received 1 October 1996; In final form 21 February 1997)

When a dispersion of fine particles is concentrated, the product can contain clumps which arise from the aggregation of the particles. There are several drivers: sedimentating, drying, filtration, forcing the particles together to produce agglomerated structures which are much larger than the primary particles. The problem of understanding this phenomenon is twofold: on the one hand, it is difficult to measure aggregates in a concentrated slurry; on the other, there is no theory to predict when aggregates should form in an apparently-stable dispersion. This paper describes a new experimental method for measuring aggregates in concentrated suspensions, showing that the aggregation phenomenon can be followed over a wide range of experimental conditions. In particular, the results show that the aggregates exist at small concentrations in ostensibly stable dispersions even before concentrating takes place. Colloids based on polymers, ceramics, biological cells and emulsions all showed this aggregation effect. We have called these aggregated structures "multiplets" to distinguish them from the more normal flocs produced by destabilising the colloid. A theory of aggregation is proposed to fit the experimental results. This theory is based on the idea that multiplets form as a consequence of small adhesion forces between particles immersed in liquid; a molecular dynamics simulation using this concept of adhesion forces is used to demonstrate the formation of multiplet material at low concentrations. The theory seeks to show how the size of multiplets should vary with adhesion and with particle concentration.

Keywords: Adhesion; fine particles; dispersions; aggregation phenomenon; multiplets; molecular dynamics; hard spheres with square well adhesion

1. INTRODUCTION

A simple question relating to the adhesion of particles concerns the amount of adhesion needed to solidify a fluid particle dispersion.

---

*Presented at the Symposium on *Fundamentals of Adhesion and Interfaces* at the Fall Meeting of the American Chemical Society in Orlando, Florida, USA, August 25–28, 1996.

**Corresponding author.

E-mail addresses: (K.K) cha15@cc.keele.ac.uk (W.L) cha04@cc.keele.ac.uk (C.S) chd34@cc.keele.ac.uk.

Consider a dispersion which has been made by mixing fine particles into a liquid. Under certain conditions, the colloid is stable for many years, and microscopic examination reveals that the particles are moving with Brownian motion, colliding with, but not sticking to, neighbouring particles [1, 2]. However, when the colloid is altered in some way, for example by chemical change, by drying, filtration or centrifuging, the particles can stick together to form solid aggregates of particles, evidently held together by adhesion [3–5]. How much adhesion is needed to cause this effect, and what are the mechanisms by which the solid aggregates form from the fluid?

These questions are relevant to several important problems. One is the condensation of gas molecules which solidify as the temperature is reduced, thereby defining the gas/solid phase change [6]. Another problem is that of nucleation, in which molecules must overcome an energy barrier to grow into large solid crystals from a solution [7]. These questions are formally similar to those of aggregation in colloids [8]. Finally, there is the practical issue of making high-quality materials from particulate dispersions. Paints, foods, powder metals and ceramics are often made from colloids [9]. Aggregates can generally be found in the products, causing defects which limit performance [10–12].

The purpose of this paper is to describe new experimental and theoretical studies of the aggregation of dispersed colloids. First, a new method is presented for detecting small numbers of aggregates within a concentrated dispersion [13]. This method reveals for the first time that apparently-stable dispersions contain clumps much larger than the primary particles. Also, a simple molecular-dynamics-based model was performed using a short range adhesion. The simulation shows that adhesion around 2 kT causes particles to stick together, producing aggregates whose size and number increase with the particle concentration.

2. NEW METHOD FOR DETECTING AGGREGATES

The new method [13, 14] made use of a desensitised Coulter Multisizer II instrument. This instrument operates normally by sensing the blockage of an electrical field across an aperture through which the particles are pumped. The Multisizer is usually used on very dilute suspensions of fine particles such as blood cells. However, we have found that by using a relatively large aperture to desensitise the instrument to the primary particles the Multisizer can be used on concentrated dispersions, to detect the small number of large clusters in a very sensitive way.

Electrostatically-stabilised silica spheres (Nippon Shokubai, Japan) with particle diameter $D = 1.0$ μm were used to demonstrate the presence of aggregates. The dilute dispersion (volume fraction of silica $\Phi = 0.00011$) was first made by mixing the powder with water, ultrasonicating using a high-intensity ultrasonic processor (Sonics & Materials Inc, USA), adjusting the pH to 9.6 with concentrated ammonia, filtering through a 10 μm mesh, then sedimenting to remove any remaining large particles. The dispersion was tested with the Multisizer at 293 K using a 200 μm orifice. Only a few counts were observed because all the particles were below the detection limit of 4 μm. The principle of this measurement is shown in Figure 1a where it is seen that sufficiently small particles cannot be detected by a large orifice because many particles occupy the orifice at any time.

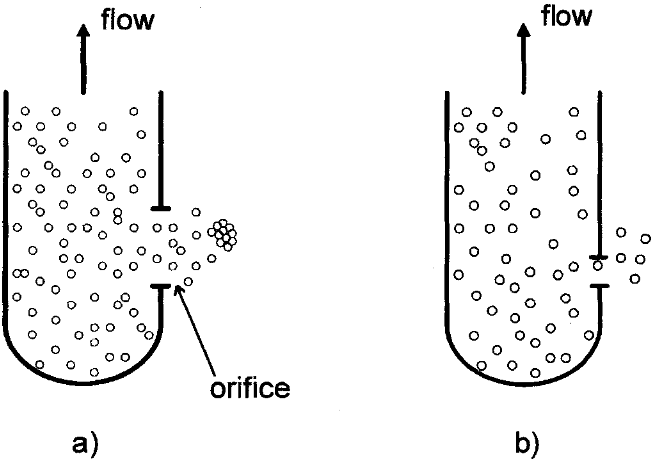

FIGURE 1 a) Schematic picture of particles traversing a large orifice in the Coulter counter. Many particles occupy the orifice at one time, such that no net signal is produced, unless a large aggregate passes through. b) Schematic showing the normal operation. One particle occupies the orifice to give an electrical blockage which can be counted.

Normally, the Coulter instrument detects single particles as they pass individually through a smaller orifice (Fig. 1b).

However, the presence of the 1.0 μm peak was confirmed and measured by the use of the Malvern Mastersizer which operates by light scattering at low volume fraction giving the result which is shown in Figure 2, left-hand peak. This peak is also detected at low volume fraction, $\sim 10^{-5}$, by the Coulter Counter with a 50 μm orifice. At this volume fraction the Coulter Counter also detects a doublet peak at 25% larger diameter. This doublet peak is typically a hundred times less in volume than the primary peak.

Then the silica concentration was increased to $\Phi = 0.011$ by centrifuging and the measurements repeated. The Multisizer with the 200 μm orifice then detected a distinct peak of aggregates with a mean size of 9 μm, this peak remaining steady with time. The right hand peak in Figure 2 represents this measurement of the large multiplets at a much higher volume fraction; the depleted singlet and doublet peaks

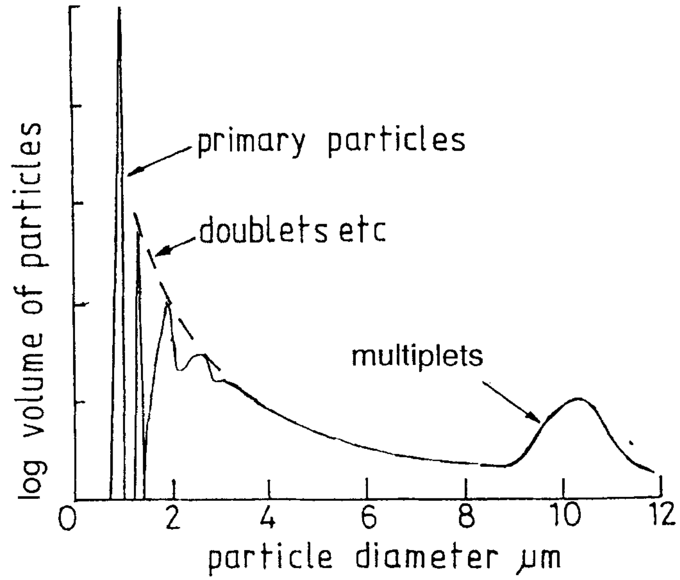

FIGURE 2 Schematic particle size distribution for silica spheres in water ($D = 1$ μm, $\Phi = 0.011$). The left-hand peak is the singlet particles, but one can also find small numbers of doublets and larger aggregates which we call multiplets (right-hand peak). The multiplet volume was typically 10000 times less than the primary particle volume.

in the figure are scaled appropriately. The volume of particles in this cluster peak was about 10000 times less than that in the main peak, as shown by the logarithmic scale. Such a small volume fraction of aggregates explains why this phenomenon has not been observed before. These aggregates have been called multiplets because they were not like normal flocs caused by destabilisation. The multiplets seemed to form naturally within a fully-stable dispersed system. They were also reduced in size and number as the slurry was diluted, until a dilution beyond the machine's detection limit was reached.

In order to demonstrate that the measurement of multiplets was a real effect, a sample of standard calibration latex (poly(styrene-co-divinylbenzene); $D = 17.6\,\mu m$, $\Phi = 0.0000057$) was added to the Coulter counter sample of silica ($\Phi = 0.011$) for comparison (Fig. 3). The calibration peak is shown to the right and the silica multiplet peak to the left (the singlet and doublet particles were not measured because they were not detected with the 200 mm orifice). This verified the presence of multiplets and allowed the calculation of their diameter, $8.37\,\mu m$, and volume fraction, $\Phi_C = 0.0000152$. The multiplets comprised 0.138% of the silica in the dispersion. When the dispersion was rediluted, the multiplets were again reduced in size and number.

The effect of concentrating the particles was then tested. As the silica concentration was increased, the size of the multiplets increased,

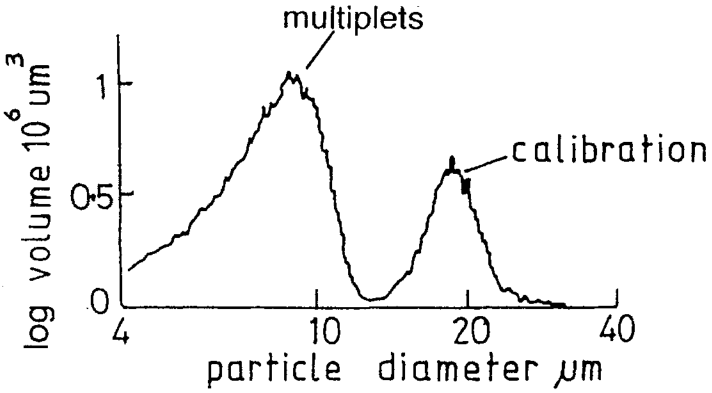

FIGURE 3 Coulter measurement of large multiplets after addition of calibration latex (17.6 µm, $\Phi = 0.0000057$).

and so did the volume fraction of multiplet material. Figure 4a shows the Coulter results giving the multiplet peak for increasing silica concentrations. Figure 4b indicates that the plot of log multiplet volume against log silica concentration was a straight line.

Other colloidal particles were found to behave in the same manner as the silica particles. For example, a dispersion of monosize polystyrene particles displayed multiplets which also increased in size as the particles were concentrated (Fig. 5, lower curve). The theoretical line is given by [13, 14]:

$$S = \frac{36D}{1 + \dfrac{\mathrm{kT}\ln(0.74/\Phi)}{0.47E}} \tag{1}$$

The equation is arrived at by consideration of the compacting energy required to form a close-packed multiplet of size, S, in terms of the energy of adhesion, E, between particles in the bulk of the cluster and those in the surface of the multiplet, and the work required to condense each particle against the osmotic pressure. The total free energy of a multiplet can be obtained; the stationary point in the free energy leads to a result for the diameter of the most stable multiplets.

Human red blood cells, 5 µm diameter, also showed reversible multiplets as shown in the upper curve of Figure 5. These multiplets

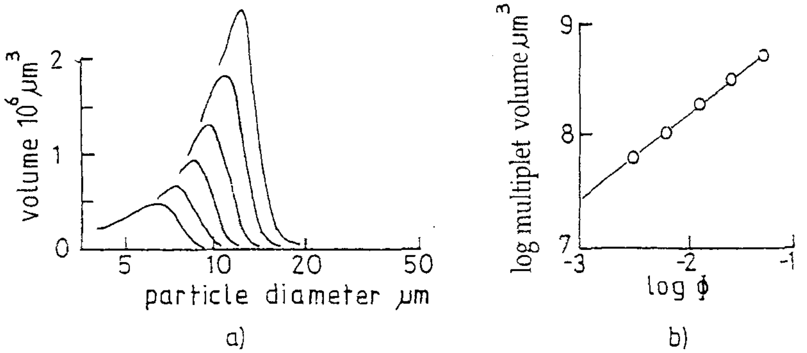

FIGURE 4 a) As the volume fraction of dispersed particles was increased, the large multiplets also increased in volume and diameter. b) Log (multiplet volume) was found to be almost linearly related to Log (particle volume).

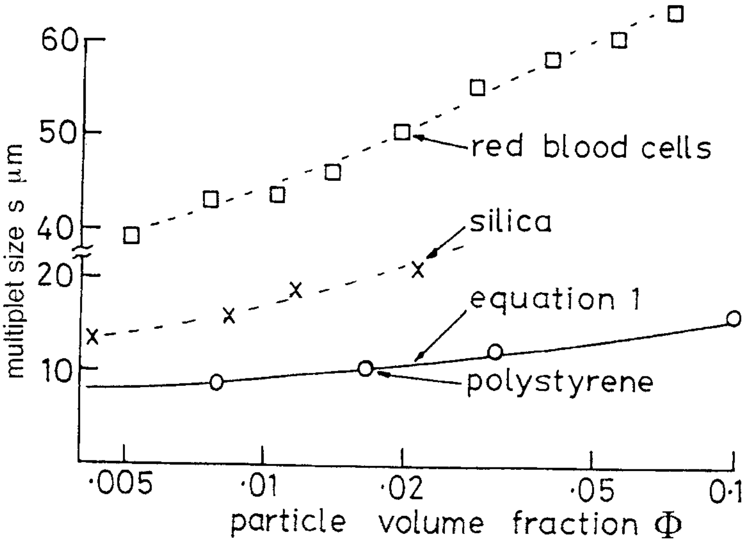

FIGURE 5 Large multiplets were found in all dispersions studied, including silica, polystyrene, blood and oil/water emulsions. The size S was given by Eq. (1).

were 70 μm in size at a volume fraction of 0.18. Such results suggest that the clumping observed in these experiments is a general phenomenon to be found in a wide range of particle systems, dependent on particle adhesion.

3. THEORY

The experiments described above show that a very dilute suspension of silica particles in water ($\Phi = 0.0001$ at pH 9.6) behaved as a perfectly-dispersed colloid, with all the particles separated and in continuous Brownian motion. However, when the particles were packed more closely, to 0.01 volume fraction, some of the particles clumped together to form larger aggregates, leaving the remainder of the particles in their dispersed state. As this suspension was diluted back to its original condition, the multiplets gradually disappeared. A molecular dynamics model using a very short range attraction(adhesion) between particles reproduced this effect.

4. HARD SPHERE WITH ADHESION

There are several options for simulating colloids suspended in a solvent, the most complex of which is Brownian Dynamics which may take into account the Brownian collisions, the hydrodynamics of the solvent and interparticle forces. The simplest choice (see [15]) represents the colloidal particle as a hard sphere undergoing elastic collisions on contact with neighbouring spheres; the solvent is neglected entirely. Despite the different levels of approximation in these simulations, it has been demonstrated that there is an equivalence between them, at least in terms of osmotic pressure and structure factors [16]. The theoretical basis for this equivalence is given in [17].

We have treated the colloidal suspension as a perturbation on the hard sphere molecular dynamics problem. The model results for hard spheres, representing an ideal stable dispersion, are well-known [18], being distinguished by an order-disorder transition occurring between volume fractions 0.5 and 0.55. The simplest possible adhesion model,

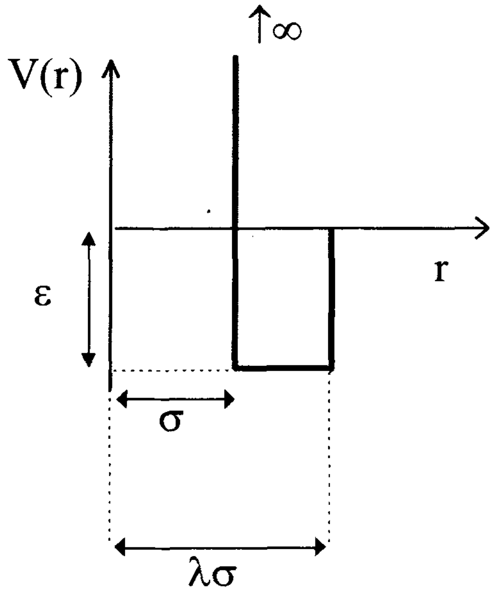

FIGURE 6a Square well potential $V(r)$ *Versus* r, where r is the separation between particle centres, to give adhesion energy, ε, over a range σ to $\lambda\sigma$.

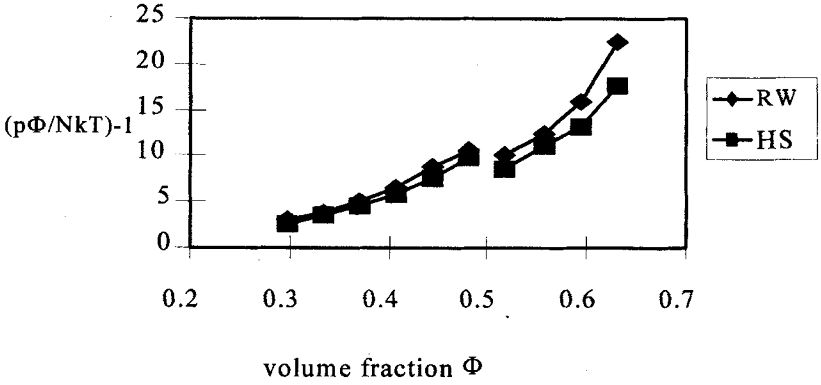

FIGURE 6b Pressure in hard sphere model computed for 500 particles with (RW) and without (HS) adhesion, showing the order/disorder transition in both systems at the same volume fraction.

the square well interaction (Fig. 6a), was introduced with a small well depth of $\varepsilon = 2\,kT$ and a range, λ, of 1.001. Such an adhesion model permits rapid numerical solution which is detailed in Ref. [19]. This perturbation on the hard sphere model preserves this main order/disorder transition, as is shown in Figure 6b., while permitting the formation of multiplets. The square well attraction is formally similar to the adhesiveness parameter, τ, used for the purposes of a statistical mechanical theory, the adhesive excluded shell model, discussed in Ref. [15]. The square well potential parameters can be related to τ by equating the second virial coefficients in the equations of state for each model.

We are aware of square well simulations by Alder *et al.* [20], Michels *et al.* [21, 22] and the work in Refs. [23, 24]. In each of these simulations the range of λ was chosen to be around 1.5 in keeping with a desire to use the square well to approximate a related interatomic Lennard-Jones potential.

In our simulation we set in motion 500 particles, initially set up in a face-centred cubic array, at various volume fractions. The particles interacted with the square well adhesion parameters above and periodic boundary conditions were applied. In order to simulate a system in the canonical ensemble a constant temperature constraint was imposed by frequent rescaling of all the particle velocities. We went on to determine whether this square well system, with almost identical properties to the ideal hard sphere system, reproduced any of the experimental observations. The two effects required in the simulation were the increase in multiplet volume and increase in multiplet size with volume fraction of particles.

The interesting feature of the square well adhesion model was that it began to generate doublets, triplets and higher aggregates, *i.e.* multiplets. Simulations were then performed for a number of volume fractions and a number of values of adhesion energy, ε. Every 10,000 collisions the 500 particles were examined and singlet particles were tested for contact with a second particle. Then the doublets were tested to find triplets and so on up to the nth multiplet. The results, showing multiplet content after a fixed number of collisions, are presented in Figure 7 as a function of ϕ/ϕ_{fcc}, the particle packing relative to a close-packed, face-centred cubic system. At low relative packing, below $\phi/\phi_{fcc} = 0.001$, only a few doublets were found. However, as the relative packing increased to 0.4, 30 doublets appeared, together with higher multiplets. The volume of multiplets increased with particle packing as shown in Figure 7b, slightly reminiscent of the results obtained by the Coulter Counter measurements, although clearly not with the same scaling properties. More multiplets also formed as the adhesion energy, ε, and the range of attraction, λ, were increased, implying that a better choice of ε and λ would yield a better agreement with the experimental observations.

Clearly, there is a fundamental problem in finding very large multiplets in this model because of the limited number of particles. Simulation of this experimental effect would require many more particles in the model. The effects of potential shape, kinetic effects and the influence of inelastic collision between particles also remain to be investigated. A major improvement would involve a more realistic simulation representation of the repulsive and attractive forces between particles, perhaps employing a DLVO potential with primary and secondary minima, which would help shed more light on the cause of these multiplets. However, in the case of sterically-stabilised latex in an aqueous system we believe that the secondary minimum is extremely shallow ($\leq 0.5\,\mathrm{kT}$) and yet large multiplet formation is still observed under the microscope, suggesting a more general adhesion is present.

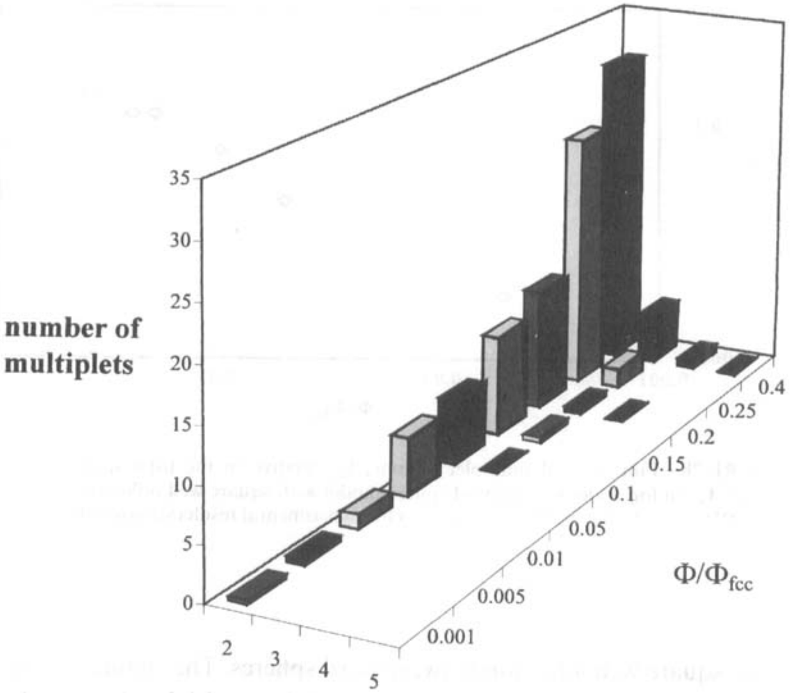

FIGURE 7a Histogram showing the number of doublets, triplets and higher multiplets increasing as the particle packing increased ($\varepsilon = 2\,kT$ $\lambda = 1.001$).

5. CONCLUSIONS

A general colloid phenomenon, that large multiplets co-exist with single particles, has been observed by studying concentrated dispersions in a desensitised Coulter Counter. Large clumps were detected, some ten times larger than the primary particles, even though the suspension was well dispersed. These peculiar aggregates were called multiplets to distinguish them from flocs formed by destabilising the suspension. The size and volume of the multiplets increased with particle packing.

A molecular dynamics model has been used to demonstrate that aggregates can also arise in seemingly ideal systems using a very short

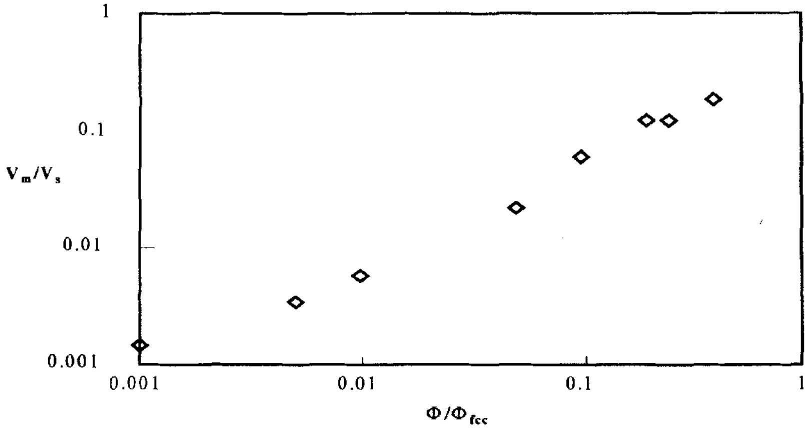

FIGURE 7b Plot of total multiplet volume, V_m, relative to the total single particle volume, V_s, on log scales for the hard sphere model with square well adhesion ($\varepsilon = 2\,kT$ $\lambda = 1.001$), showing the similar behaviour to the experimental results shown in Figure 4b.

range square well adhesion between hard spheres. The simulation also showed that these doublets, triplets and higher multiplets increased in size and in volume as the particle packing was raised, in qualitative agreement with the experimental observations.

References

[1] Everett, D. H., *Basic Principles of Colloid Science* (Royal Society of Chemistry, Letchworth, 1988), Chap. 9.

[2] Kendall, K., *Science* **263**, 1720-5 (1994).

[3] Kendall, K., *Powder Technology* **58**, 151–161 (1989).

[4] Kendall, K., Alford, N. McN. and Birchall, J. D., *Proc. Roy. Soc. Lond.* **A412**, 264-283 (1987).

[5] Poon, W., Pusey, P. N. and Lekkerkerker, H., *Physics World* **9**, 27–32 (1996).

[6] *Phase Transitions*, 12, Liebowitz, J. L., Ed. (Academic Press, New York, 1988).

[7] Strickland-Constable, R. F., *Kinetics and Mechanism of Crystallisation* (Academic Press, New York, 1968).

[8] Pusey, P. N., in *Liquids, Freezing and the Glass Transition*, Les Houches Session LI, Levesque, Hansen and Zinn-Justin, Eds. (North Holland, Amsterdam, 1991), pp. 763–942.

[9] *Technological Applications of Dispersions*, ***Surfactant Science Series***, Vol. 52, McKay R. B., Ed. (Marcel Dekker, New York, 1994).

[10] Kendall, K., Alford, N. McN., Clegg, W. J. and Birchall, J. D., *Nature* **339**, 130 (1989).

[11] Kendall, K., Alford, N. McN. and Birchall, J. D., *Nature* **325**, 794–796 (1987).

[12] Kendall, K., *Brit Ceram Proc* **42**, 81–90 (1989).

[13] Liang, W. and Kendall, K., submitted, *Colloids and Surfaces.*

[14] Kendall, K. and Liang, W., *Brit. Ceram. Trans.*, in press.

[15] Russel, W. B., Saville, D. A., Schowalter, W. R., Chapter 10 in *Colloidal Dispersions* (Cambridge University Press, 1989).

[16] TeGrotenhuis, W. E., Radke, C. J. and Denn, M. M., *AIChE Journal* **40**, 283 (1994).

[17] Brady, J. F., *J. Chem. Phys.* **98**, 3335 (1993).

[18] Snook, I., van Megen, I. and Pusey, P., *Phys. Rev.* **A43**, 6900 (1991).

[19] Alder, B. J. and Wainwright, T. E., *J. Chem. Phys.* **31**, 459 (1959).

[20] Alder, B. J., Young, D. A. and Mark, M. A., *J. Chem. Phys.* **56**, 3013 (1972).

[21] Michels, J. P. J. and Trappeniers, N. J., *Physica* **101A**, 156 (1980).

[22] Wilbertz, H., Michels, J., van Beijeren, H. and Leegwater, J. A., *J. Stat. Phys.* **53**, 6 (1988).

[23] de la Selva, S. M. T., Dickman, R., Schieve, W. C., Canestaro, C., *J. Chem. Phys.* **78**(11), 6885 (1972).

[24] Harrison, H. W. and Schieve, W. C., *J. Chem. Phys.* **58**(9), 3634 (1972).