FRACTURE OF ADHESIVE BONDS BETWEEN COLLOIDAL SPHERES

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ABSTRACT

When a good dispersion of fine particles is observed in water, adhesive bonds may be seen forming between some of the particles to build doublets, triplets and larger aggregates ie multiplets. In this paper we report the observation of doublets in suspensions of polymer latex. By concentrating the slurries, more doublets were formed, whereas by dilution the doublets were fractured and disappeared. The mechanism of such colloidal bonding and fracture processes was addressed by measuring doublets in several particulate suspensions, showing that the adhesion and fracture phenomena could be followed over a wide range of experimental conditions. In particular, the results showed that the doublets existed at small concentrations even in ostensibly perfect dispersions. A model of colloidal adhesion and fracture was proposed to fit the experimental observations. Doublets formed as a consequence of small adhesion forces between particles immersed in liquid, then fractured by energetic collisions with other particles. A nearly linear dependence of doublets on particle volume fraction was predicted and observed experimentally

KEYWORDS

Fracture of colloids, adhesion between spheres

INTRODUCTION

An important question in the colloid industries relates to the forces needed to break adhesive joints between colloidal particles dispersed in liquids. Such fracture processes are usually performed by shearing or milling slurries of particles. However, there are two major problems in understanding these systems. The mechanism of fracture is not known; and the particles tend to stick together again after the shearing stops.

This paper considers a dispersion which has been made by suspending fine polymer latex particles in 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 (Everett,1988; Kendall, 1994). However, when the colloid is altered in some way, for example by increasing the number of particles in the dispersion, the particles stick together to form solid aggregates of particles, evidently held together by adhesion (Kendall,1989, 1987; Poon et al 1996). Here we consider the adhesion necessary to form doublets of particles and study the process of fracture of such doublets.

Several important problems are related to this colloidal adhesion and fracture question. One is the condensation of gas molecules which solidify as the temperature is reduced, thereby

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defining the gas/solid phase change (Liebowitz, 1988). Another problem is that of nucleation, in which molecules must overcome an energy barrier to grow into large solid crystals from a solution (Strickland-Constable, 1968). These questions are formally similar to those of aggregation in colloids (Pusey, 1991). 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 by comminution and grinding processes (McKay, 1994). Aggregates can generally be found in the products, causing defects which limit performance (Kendall,1989a,b, 1987).

The purpose of this paper is to describe new experimental and theoretical studies of the adhesion and fracture of colloidal particle doublets. First, methods are presented for detecting small numbers of doublets within a particulate dispersion (Kendall and Liang, 1996), using microscopic observation and particle size measurements. Then a model based on molecular dynamics is used to interpret the results. The model uses a square well interaction potential to show that adhesion around 2kT causes particles to stick together, once three body collisions have occurred. These doublets are fractured by collisions with other particles, leading to a dynamic equilibrium between adhesion and fracture, and an equilibrium number of doublets in the suspension. The fracture mechanism and the equilibrium concentration of doublets are described in detail.

METHODS FOR DETECTING DOUBLETS

Two methods have been used to measure the doublets in the dispersion. The first method was microcopic observation and counting of the doublet numbers. For example, figure 1 shows a doublet formed in an aqueous dispersion of polystyrene latex, volume fraction 0.000625. The second method (Kendall and Liang, Kendall et al, 1996,1997) made use of a Coulter Multisizer II instrument. This instrument operates by sensing the blockage of an electrical field across an aperture through which the particles are pumped. Doublets are detected as larger particles, giving a distinct peak in the particle size distribution, as shown in figure 2.
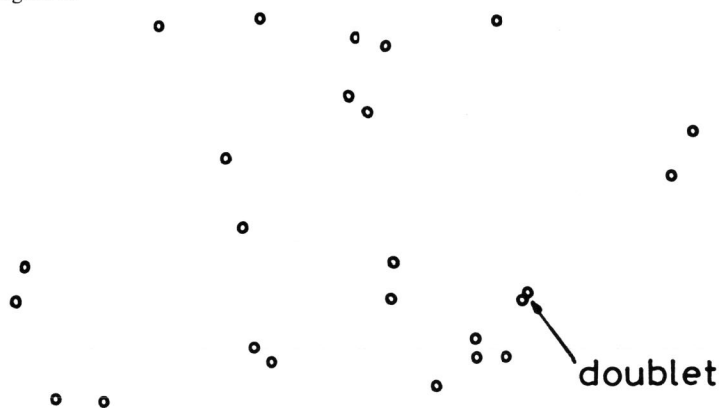
Figure 1 Micrograph of 0.97 μm polystyrene latex particles in water showing a doublet

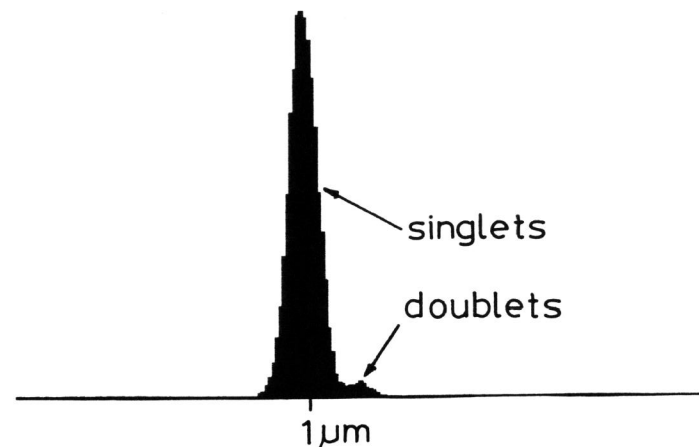Figure 2 Coulter Multisizer results for doublets

A typical experiment involved polystyrene latex particles, 0.97μm diameter, obtained from Zeneca . As the suspension was concentrated the number of doublets increased relative to the number of primary particles. On diluting the dispersion, the number of doublets fell along the same curve. At higher concentrations, triplets and multiplets were seen.

Other colloidal particles were found to behave in the same manner as the polystyrene particles. For example, a dispersion of monosize silica particles displayed doublets which also increased in number as the particles were concentrated. Human red blood cells, 5 mm diameter, also showed reversible doublets. Such results suggest that the formation of doublets observed in these experiments is a general phenomenon to be found in a wide range of particle systems, dependent on particle adhesion.

THEORY

The experiments described above show that even in a dilute and perfectly dispersed colloid, with all the particles apparently separated and in continuous Brownian motion, doublets can form. When the particles are packed more closely, as volume fraction increases, more of the particles clump together to form doublets, leaving the remainder of the particles in their perfectly dispersed state. When this suspension is diluted back to its original condition, the doublets disappear by a fracture process. At larger concentrations of particles, triplets and higher multiplets began to appear. Other dispersions of silica and blood also show these effects. In order to model these phenomena, the colloids were represented in a molecular dynamics computer simulation as hard spheres interacting via a small adhesive attraction.

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,

some aspects of the solvent hydrodynamics, and interparticle forces. We have taken the simplest choice which represents the colloidal particle as a hard sphere undergoing successive elastic collisions on contact with neighbouring particles, neglecting the effects of the solvent entirely. It has been demonstrated that there is an equivalence, at least in terms of osmotic pressure and structure factors (TeGrotenhuis et al, 1994), between the two vastly different approaches. The theoretical basis for this equivalence has been supplied by Brady (1993).

The model results for hard spheres are well-known (Snook et al, 1991). We have modified this model to include attractions between the particles. The simplest conceivable model which incorporates adhesion between spheres is that of the square well interaction (Fig 3) in which the hard core character of the particles at radius r is retained, but with an adhesion energy ε acting from the particle surface to a distance λr. Outside this latter range, the particles behave as hard spheres travelling in straight lines at constant velocity, allowing rapid numerical solution of their motion between interactions as detailed in Alder and Wainwright (1959).
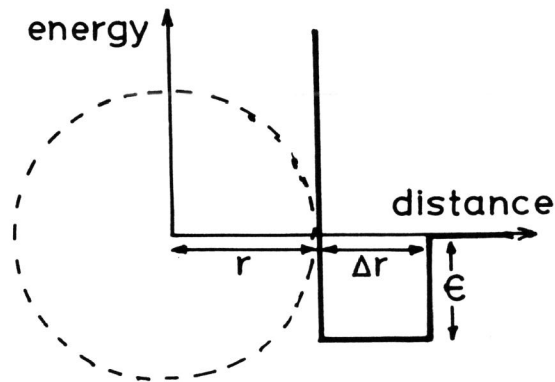

Figure 3 Square well adhesion of depth ε and range $\lambda = (\Delta r + r)/r$ used in hard sphere computer model

This type of potential, in molecular dynamics modelling, appears to have had relatively little use. The only dynamical simulations we are aware of are those by Alder et al (1959,1972) who conceived the method, and Michels et al (1980,1988). In each case the work was directed at deducing properties of a molecular fluid for which it was thought that a square well interaction with a range $\lambda = 1.5$ would provide a reasonable approximation. Here we adopt a much smaller λ to simulate short-range adhesion of colloids.

COMPARISON WITH RESULTS

λ was set to 1.01 to describe a short range adhesion force acting between colloidal particles. The strength of adhesion, represented by the well depth ε was in the first instance set to 2kT. The equations of motion for particles at various volume fractions were

then solved numerically over a period of time. Periodic boundary conditions with 1000 particles were used to represent an infinite system. After an initial period of equilibriation, the system was sampled at regular intervals, and the state of the particles was observed.

The interesting feature of this adhesion model was that it began to generate doublets and higher multiplets as a result of three (or more) body collisions between the particles. Consider a pair of approaching particles which interact through a square well potential. The particles are subject to an attractive impulse as they approach to a distance λr. This impulse leads to a mutual gain of ε in kinetic energy. Then, usually, the particles undergo a hard sphere elastic collision which reverses their direction and the particles separate. The influence of the hard sphere interaction comes into play again when their centres have receded to a distance λr apart, at which point the particles may continue with a mutual deceleration caused by energy loss ε. The only situation in which particles are trapped in the potential well occurs when a third particle has collided to reduce the particle kinetic energy below ε as it moves through the well. In the same way, a doublet can only be fractured by an energetic third body collision.

A typical picture of doublet fracture in a two dimensional version of the simulation allowed this three body mechanism to be studied (figure 4). In this picture, the doublet has been formed previously and is being broken as a particle impinges on the doublet and fractures it.
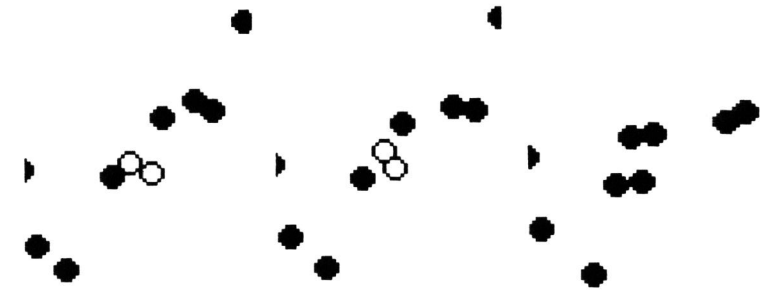

Figure 4 Sequence of computer pictures showing a three body collision leading to fracture of a doublet, shown in white. The impact starts on the left, and finishes on the right.

The simulations were repeated with systems at varying volume fractions. As the volume fraction of particles was increased, higher order multiplets were formed. The following statistics were gathered for a simulation of 1000 particles with a potential well depth of

ε = 2kT and a range of λ = 1.01 for volume fractions increasing from 0.00125 to 0.025.
The number of singlets is given as n_1, the number of doublets as n_2 and so on.

Table 1 Computer model calculations showing the increase in multiplet numbers with concentration of particles.

φ	n_1	n_2	n_3	n_4
0.025	972.18	13.368	0.34694	0.01
0.015	985.12	7.30928	0.07217	0.01
0.0025	998.65	0.67677	0	0
0.00125	999.54	0.23232	0	0

These calculations were compared with the experimental measurements in figure 5. It may be seen that both theory and experiment show an almost linear increase in doublets with particle volume fraction. Experimentally, the problem is to detect small numbers of doublets. Theoretically, the difficulty is to obtain calculated results at low volume fractions with 1000 particles, when three body collisions are rare.
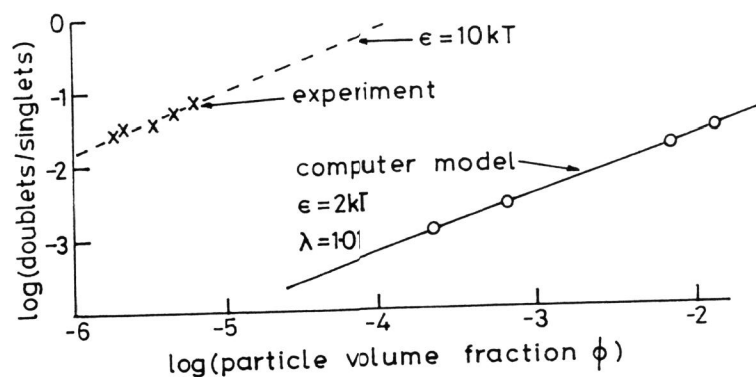

Figure 5 Plot of doublets against volume fraction of particles

CONCLUSIONS

The adhesion and fracture of bonds between colloidal particles suspended in water has been studied both experimentally and by molecular dynamics modelling. Doublets of particles are formed by three body collisions when adhesion forces act between spheres. These doublets can be broken by further collisions. The number of doublets increases almost in proportion to particle volume fraction as the packing of particles is raised, until triplets and higher multiplets are seen. The square well adhesion model allows values of adhesion energy and range to be determined.

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