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Shear Induced Coagulation

R. W. O'BRIEN
Department of Applied Mathematics, Institute of Advanced Studies, Research School of Physical Sciences,
Australian National University

SUMMARY The rate at which colloidal particles coagulate in a suspension may be increased by stirring the suspension. This phenomenon is known as shear induced coagulation. In this paper we study the coagulation of a dilute suspension of spherical particles in a steady shear flow. The rate at which single particles come together to form doublets per unit volume of suspension is calculated for "high" shear rates at which the Van der Waals attraction between the particles only affects the nearly-touching pairs.

1 INTRODUCTION

The addition of salt to a colloidal suspension reduces the electrical repulsive forces between the suspended particles, and if sufficient salt is added the particles may coagulate under the influence of the Van der Waals forces of attraction. The ease with which colloidal particles may be removed from the suspension increases with particle size, and thus the processes for the removal of colloidal impurities from a liquid begin with the addition of salt to the suspension. For most of the industrial purification processes, the liquid is stirred after the addition of the salt, for the stirring increases the rate at which particles coagulate.

In this paper we study the shear induced coagulation phenomenon for the case of a dilute suspension of spherical particles in steady shear flow. The particles have uniform radius a and we assume that the electrical forces between the particles are negligible.

In the initial stages of the process, most of the coagulation takes place between single particles which unite to form "doublets". Our aim is to derive an expression for the "coagulation rate" C defined as the number of doublets formed in unit volume of suspension per unit time.

2 THE FACTORS WHICH AFFECT THE COAGULATION RATE

In order to describe the coagulation process in a suspension, it is convenient to introduce the concept of a "pair space". Each pair of spheres in a chosen unit volume of the suspension is represented by two points (x_1,x_2,x_3) and $(-x_1,-x_2,-x_3)$ in pair space, where x_1,x_2 and x_3 are the cartesian components of the vector which passes from the centre of one member of the pair to the centre of the other. The points in pair space are obtained by placing the axes shown in figure 1 at the centre of each sphere in turn and noting the coordinates of every other sphere in the volume. If n denotes the number of particles in the volume, there are n(n-1) points in pair space.

The points which correspond to coagulated pairs lie on a sphere of radius 2a, centred on the origin in pair space. This sphere will be referred to as the "central sphere". The number of points which move onto the central sphere in unit time is double the coagulation rate, since each pair of spheres is counted twice.

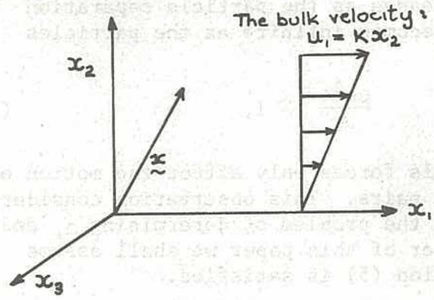

Figure 1 The cartesian coordinate system

The density of points in pair space is denoted by $\rho(\underset{\sim}{x})$. In the absence of any long range order in the suspension we have

$$\rho(\underset{\sim}{x}) \rightarrow n^2 \tag{1}$$

as $|\underset{\sim}{x}| \rightarrow \infty$. In other words, the fact that there is a sphere at the origin does not affect the probability of there being another sphere in the unit volume about $\underset{\sim}{x}$, provided $|\underset{\sim}{x}|$ is sufficiently large.

We assume that the system is in a quasi steady state, i.e.

$$\frac{\partial\rho}{\partial t} \approx 0.$$

Although the number n of single spheres decreases with time, we assume that the time over which n changes appreciably is much longer than the time required to achieve steady-state conditions.

As mentioned earlier, the coagulation rate C is equal to half the number of points which move onto the central sphere in unit time, and since $\frac{\partial\rho}{\partial t} = 0$, C is given by

$$C = \frac{1}{2}\oint_{s} \underset{\sim}{i}(\underset{\sim}{x}).\hat{\underset{\sim}{n}}(\underset{\sim}{x})dA \tag{2}$$

where $\underset{\sim}{i}$ is the flux density of the points $\underset{\sim}{x}$, s is a closed surface surrounding the the central sphere, and $\hat{n}$ denotes the unit normal directed into the volume enclosed by s. The flux density $\underset{\sim}{i}$ may be written as

$$\underset{\sim}{i} = \underset{\sim}{i}_B + \rho(\underset{\sim}{V}' + \underset{\sim}{V}''), \tag{3}$$

where $\underset{\sim}{i}_B$ is the flux density due to the Brownian motion of the particles, $\underset{\sim}{V}'$ is the velocity of the points due to shear flow (i.e. the velocity of the centre of one member of a force free sphere pair relative to the centre of the other sphere), and $\underset{\sim}{V}''$ is the velocity due to the Van der Waals force.

The ratio $|\underset{\sim}{i}_B(\underset{\sim}{x})|/|\rho(\underset{\sim}{x})\underset{\sim}{V}'(\underset{\sim}{x})|$ is proportional to $kT/\mu a^3\kappa$, where k is Boltzmann's constant, T is the absolute temperature of the system, μ is the solvent viscosity, a is the particle radius and κ is the shear rate. If $kT/\mu a^3\kappa << 1$, the Brownian motion of the particles may be neglected and the expression (2) for the coagulation rate becomes

$$c = \frac{1}{2}\oint_{\mathcal{S}} \rho(\underset{\sim}{x})\left(\underset{\sim}{V}'(\underset{\sim}{x}) + \underset{\sim}{V}''(\underset{\sim}{x})\right).\underset{\sim}{n}dA. \qquad (4)$$

In the work that follows the Brownian motion of the particles will be neglected.

The ratio $|\underset{\sim}{V}'(\underset{\sim}{x})|/|\underset{\sim}{V}''(\underset{\sim}{x})|$ is proportional to $\mu a^3\kappa/A$, where A is the Hamaker constant, a parameter which appears in the expression for the Van der Waals force. This force increases as the particle separation decreases and becomes infinite as the particles touch. Thus if

$$\frac{\mu a^3\kappa}{A} >> 1, \qquad (5)$$

the Van der Waals forces only affect the motion of nearly touching pairs. This observation considerably simplifies the problem of determining c, and for the remainder of this paper we shall assume that the condition (5) is satisfied.

Thus the Van der Waals forces only affect the motion of pairs which lie in a thin layer surrounding the central sphere. We let L denote this layer.

Pairs which lie outside L move as force free pairs. The motion of such pairs has been thoroughly investigated by Batchelor and Green (1972a). In the following section we shall briefly describe the relevant results of their work and in §4 we show how the coagulation rate c may be obtained by combining Batchelor and Greens results with expressions for the relative trajectories of the nearly touching pairs which are affected by Van der Waals forces.

3 THE MOTION OF FORCE FREE PAIRS

Batchelor and Green obtained expressions for the relative trajectories of sphere pairs in shear flows. Some of the trajectories of pairs which lie in the plane of the shear flow (x_3=0) are illustrated in figure 2.

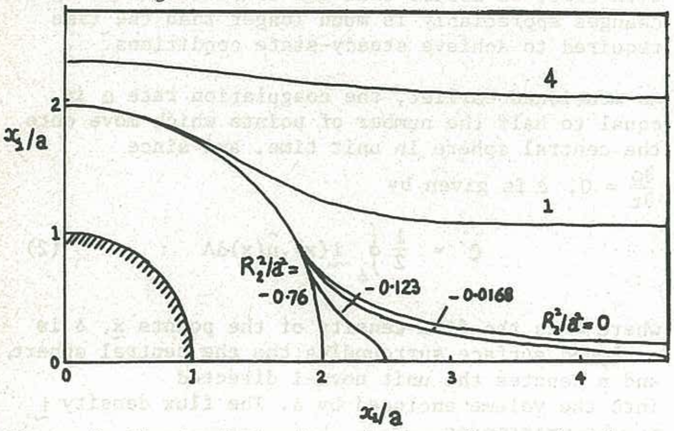

Figure 2 The trajectories of force-free pairs in the plane of the shear flow

The quantity R_2 which appears in this figure is the x_2 coordinate of the trajectory at points far from the central sphere. From figure 2 it can be seen that trajectories are "squeezed together" near the top of the central sphere; pairs which move along trajectories such as the $R_2/a = 1$ trajectory shown in figure 2 pass very near to the central sphere and only a slight force of attraction is required to cause these pairs to coagulate.

Also from figure 2 it can be seen that there is a region of closed trajectories surrounding the central sphere. The quantity R_2 associated with trajectories in this region is imaginary, and pairs which move on these trajectories execute closed orbits about each other.

4 CALCULATING THE COAGULATION RATE

If $A/\mu a^3\kappa$ is small (but non zero), pairs move through pair space on trajectories such as those shown in figure 2 until they pass into the region L in which the Van der Waals forces are significant. While moving through L each pair is drawn closer to the central sphere. If a pair does not coagulate on passing through L it leaves on a different force-free trajectory to the one on which it entered L. Those pairs which leave L on a closed trajectory will eventually coagulate, for they will be drawn closer to the central sphere each time they pass through L.

We have assumed that the density of points in pair space does not vary with time, and therefore the coagulation rate is equal to the number of pairs which enter L from outside the region of closed trajectories in the half space $x_2 > 0$ and eventually become attached to the central sphere.

To translate this into a mathematical expression we take the surface $\mathcal{S}$ which appears in the expression (4) for c to be that part of the surface L which lies outside the region of closed trajectories together with the part of the boundary of the region of closed trajectories which lies outside L. This surface is illustrated in figure 3.

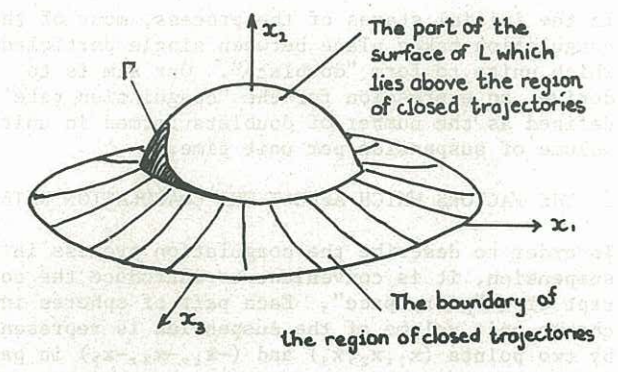

Figure 3 The surface $\mathcal{S}$

The pairs which lie outside L are approximately force-free and therefore pairs cannot cross $\mathcal{S}$ through the part of the surface formed by the boundary of the region of closed trajectories.

Those pairs which coagulate enter $\mathcal{S}$ through a portion of the surface denoted by Γ. This region is shown in figure 3. The pairs which cross Γ either become attached to the central sphere (corresponding to pairs which coagulate on their first encounter), or they pass out of L and into the region of closed trajectories.

The coagulation rate is equal to the rate at which pairs pass through Γ, i.e.

$$c = \int_{\Gamma} \rho \underset{\sim}{V}'.\hat{n}dA. \qquad (6)$$

The distribution function ρ at a point in pair space is determined by the history of the motion of the pairs which arrive at that point. Pairs which cross Γ come from a region in which the Van der Waals forces are insignificant and thus we may use Batchelor and Green's (1972b) expression in (6) for the density of force-free pairs in shear flow.

We are free to choose any shape for L, provided that the surface $\mathcal{S}$ (of which L forms a part) encloses the region in which the Van der Waals forces are significant. It proves convenient to choose L to be the volume which lies between the central sphere and a concentric sphere of radius $2a + \Delta$.

It can be shown that if

$$\Delta = a\sqrt{A/\mu a^3 \kappa}\ ,$$

$\mathcal{S}$ encloses the region in which the Van der Waals forces are significant. This value of Δ was used in calculating the coagulation rate.

To determine c from (6) we require expressions for the curves which form the boundary of Γ. One part of that boundary, formed by the intersection of L with the boundary of the region of closed trajectories is easily determined. Pairs which pass through the other part of the Γ-boundary pass out of L on trajectories which lie on the boundary of the region of closed trajectories. Thus to determine this part of the Γ boundary, we require expressions for the trajectories of pairs in L.

The expressions for the relative velocity of pairs in L are greatly simplified by the fact that the pairs are nearly touching and hence there are large lubrication stresses generated in the thin layer of liquid between the spheres. By integrating these equations in a straightforward manner we obtain the required expression for the trajectories of the pairs in L.

With the aid of these expressions we can calculate the coordinates of points of the Γ-boundary by finding the point of entrance into L of pairs which leave L and move along the boundary of the region of closed trajectories. By repeating this procedure a large number of times and performing the integration in (6) numerically, we obtain the value of c.

The results of these calculations are shown in figure 4. From that figure it can be seen that the slope of the coagulation rate curve decreases as the shear rate increases, and at very high shear rates the coagulation rate approaches the limiting value $2.04 \times 10^5 (n^2 A/\mu)$.

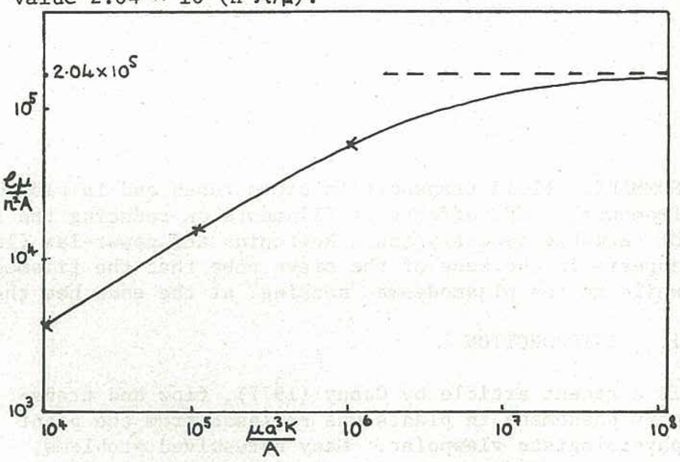

Figure 4 The computed values of non-dimensional coagulation rate $C\mu/n^2H$

5 ACKNOWLEDGEMENT

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