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## Evolution of the sedimentation equilibrium in an interacting colloidal suspension

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**Abstract.** The evolution of the sedimentation equilibrium from the initial state of the uniform distribution of particles in a column of aqueous suspension of interacting polystyrene particles is investigated. An analytic expression for the particle concentration is obtained as a function of the height in the column and of the time from the initial state. The difference between the gravitational force and the elastic restoring force on a particle in the suspension is equated to the viscous drag force on the particle. The drift velocity of the particle is modelled in order to investigate the evolution of the sedimentation equilibrium. The calculation based on the present theory agrees very well with the reported experimental evolution of the particle concentration in colloidal liquid.

### 1. Introduction

Aqueous suspensions of polystyrene particles are known to exhibit many interesting features. They develop different kinds of ordering, like gas, liquid, crystalline and glass, as in the case of a condensed matter system (Pieranski 1983, Arora *et al* 1988, Kesavamoorthy *et al* 1988, 1989). Since the density of the polystyrene particle ( $1.05 \text{ g cm}^{-3}$ ) is higher than that of water ( $1 \text{ g cm}^{-3}$ ) there is a certain amount of gravitational force on the particle. Gravity causes the particle concentration to be higher at the bottom than at the top of a column of colloidal suspension. The extent to which the particle concentration varies along the height of the column depends on the strength of interparticle interaction (Kesavamoorthy and Arora 1985). The observed smooth variation of the particle concentration down the length of the column has been used to determine Young's modulus of the colloidal crystal (Crandall and Williams 1977) and the bulk modulus of the colloidal liquid (Kesavamoorthy and Arora 1985) by angle-resolved polarised light scattering techniques.

One does not always observe a smoothly varying particle concentration down the column. Arora *et al* (1988) have reported that a homogeneous colloidal gas phase separates into a dense phase (particle-rich) and a rare phase (particle-poor) on decreasing the impurity concentration,  $c$ . At the boundary between these phases, the particle concentration decreases discontinuously. On reducing  $c$  further, they noticed that the boundary disappears resulting in a smoothly varying particle concentration down the column. Siano (1979) has observed layered sedimentation in colloidal suspensions having a gradient in  $c$  down the column, in which the particle concentration has shown

many discontinuities. It is now fairly clear that the particle concentration in a column varies continuously or discontinuously depending on  $c$ , the gradient in  $c$  and the average particle concentration,  $\bar{n}$ . Spinodal decomposition has been invoked to explain the observed features of layered sedimentation (Siano 1979) whereas Barker and Grimson (1987) have used a solitary wave model to explain the above features. Jansen *et al* (1986) have studied the phase separation and sedimentation in sterically stabilised silica dispersions.

It is known that the non-interacting colloidal particles of diameter  $\sim 0.1 \mu\text{m}$  in aqueous suspension take about 1.2 years to drift a distance of 1 cm under gravity (Pieranski 1983). This implies that the colloidal gas of  $\sim 0.1 \mu\text{m}$  particles remains practically homogeneous over time, due to the fluctuations in temperature, vibration of the floor, etc. However, when these particles start interacting, as in a colloidal liquid, the particle concentration at different heights varies and attains sedimentation equilibrium in  $\approx 3$  h (Kesavamoorthy and Arora 1985). Kesavamoorthy and Arora (1985) have developed a formalism that describes the equilibrium particle concentration as a function of height of the column of polystyrene colloidal liquid. They shook the cylindrical cell containing the suspension in order to prepare the initial state of uniform distribution of particles and measured the particle concentration at the top of the column as a function of time; the particle concentration was found to decrease and attain the sedimentation equilibrium in  $\approx 3$  h. At equilibrium, they equated the gravitational force to the elastic restoring force and explained the equilibrium properties. A number of investigations have been reported on the evolution of sedimentation equilibrium in non-interacting colloids. Chandrasekar (1943) has investigated the evolution of the distribution of non-interacting colloidal particles theoretically in a cylindrical container on the basis of a delta function distribution by considering the gravity and the diffusion. Huang and Somasundaram (1988) have recently studied by computer simulation the evolution of the particle concentration at any height in a cylindrical column of non-interacting colloid from a uniform distribution. However, the evolution of the sedimentation equilibrium in an interacting colloid has not, to my knowledge, been investigated. In the present work, such an investigation is reported. In a column of colloidal liquid, the difference between the gravitational force and the elastic restoring force on a particle at any height and time is equated to the viscous drag force on the particle. The drift velocity is modelled according to the initial conditions, the boundary conditions and the asymptotic value. An analytic expression for the particle concentration is obtained as a function of height and time. The calculated time variation of the particle concentration at the top of the column is shown to fit well with the reported data (Kesavamoorthy and Arora 1985).

## 2. Theory

Consider a column of height  $h$  of aqueous suspension of interacting colloidal particles of diameter  $2a$ , with the average particle concentration,  $\bar{n}$ . Let  $g$  be the acceleration due to gravity acting along the  $z$  axis, and  $n(z, t)$  be the particle concentration at the height  $z$  and time  $t$ . The difference between the gravitational force on a layer at the height  $z$  and that at  $z + dz$  is given as (Kesavamoorthy and Arora 1985)

$$F_1 = \frac{4}{3} \pi a^3 \Delta\rho g A n(z, t) dz$$

where  $A$  is the area of cross section of the column and  $\Delta\rho$  is the difference in density

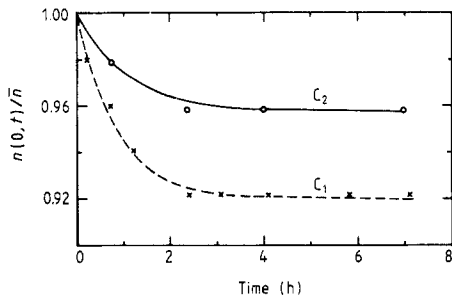
between the particle and water. The cross sectional area of a particle is  $\pi a^2$  and hence the difference between the gravitational force on a particle at  $z$  and that at  $z + dz$  is

$$F_g = F_1 \pi a^2 / A = \frac{4}{3} \pi^2 a^5 \Delta \rho g n(z, t) dz. \quad (1)$$

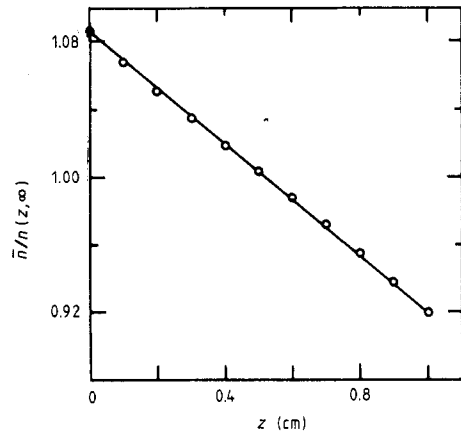
The difference between the elastic restoring force on a layer at  $z$  and that at  $z + dz$  is given as (Kesavamoorthy and Arora 1985)

$$F_2 = -BA \Delta V / V$$

where  $B$  is the bulk modulus of the colloidal liquid,  $V$  is the volume of the suspension per particle and  $\Delta V$  is the change in  $V$ . The value of  $B$  depends on the impurity concentration and the average particle concentration (Kesavamoorthy and Arora 1985).  $B$  is a constant for a suspension that has attained the deionisation equilibrium. The above equation for  $F_2$  is the equilibrium equation for  $B$ . Due to the anelastic behaviour of the system,  $F_2$  would be high initially and relax to the equilibrium value,  $-BA \Delta V / V$ . This relaxation time is less than 0.1 s at room temperature for a metallic crystal. For the colloidal liquid of interest here, this time would be still smaller. The evolution of the sedimentation equilibrium extends to more than three hours (figure 1). Since this time



**Figure 1.** The variation of the particle concentration at the top of the interacting colloidal column with time.  $\bar{n} = 4.76 \times 10^{12} \text{ cm}^{-3}$ ;  $2a = 0.091 \mu\text{m}$ .  $\times$ : experimental value for the three-day-old suspension ( $B = 0.55 \text{ dyn cm}^{-2}$ );  $\circ$ : experimental value for the month-old suspension ( $B = 0.86 \text{ dyn cm}^{-2}$ ). Curves  $C_1$  (---) and  $C_2$  (—) are the corresponding theoretical fits obtained using equation (16).



**Figure 2.** The variation of the inverse of the particle concentration with the height of the column of interacting colloidal suspension as  $t \rightarrow \infty$ .  $\bar{n} = 4.76 \times 10^{12} \text{ cm}^{-3}$ ;  $2a = 0.091 \mu\text{m}$ ;  $B = 0.86 \text{ dyn cm}^{-2}$ .  $\circ$ : obtained from equation (17); —: obtained from equation (6).

scale is much larger than the relaxation time, one can apply the above equation for  $F_2$  to the sedimentation process. Since  $\Delta V / V = -dn(z, t) / n(z, t)$  the difference between the elastic restoring force on a particle at  $z$  and that at  $z + dz$  is

$$F_e = F_2 \pi a^2 / A = \pi a^2 B dn(z, t) / n(z, t). \quad (2)$$

If the forces  $F_g$  and  $F_e$  are equal, the particles at  $z$  and  $z + dz$  will not move with respect

to each other. Otherwise  $F_g - F_e$  will be equal to the difference between the viscous force on a particle at  $z$  and that at  $z + dz$ . Hence,

$$F_g - F_e = 6\pi\eta a \, dv(z, t) \quad (3)$$

where  $\eta$  is the viscosity of water and  $dv(z, t)$  is the difference between the drift velocities of particles at  $z + dz$  and  $z$ . Substituting equations (1) and (2) in (3), one gets

$$Cn(z, t) - (D/n(z, t)) \, dn(z, t)/dz = dv(z, t)/dz \quad (4a)$$

where

$$C = 2\pi a^4 \Delta\rho g/9\eta \quad (4b)$$

$$D = Ba/6\eta. \quad (4c)$$

Consider the aqueous suspension of sub-micrometre polystyrene particles contained in a cylindrical cell from  $z = 0$  to  $h$ . Let the suspension have uniform particle concentration throughout the column at  $t = 0$  (achieved by shaking) and leave it undisturbed thereafter. The particles will drift according to equation (4), and as  $t \rightarrow \infty$  the suspension will approach sedimentation equilibrium with

$$dv(z, \infty)/dz = 0.$$

Hence equation (4) reduces to

$$Cn(z, \infty) - (D/n(z, \infty)) \, dn(z, \infty)/dz = 0.$$

Writing  $n(z, \infty)^{-1} = u(z, \infty)$ , the above equation becomes

$$C + D \, du(z, \infty)/dz = 0. \quad (5)$$

Equation (5) is exactly the same as equation (4) in Kesavamoorthy and Arora (1985) and its solution is given by

$$u(z, \infty) = -Cz/D + u(0, \infty). \quad (6)$$

Kesavamoorthy and Arora (1985) have reported that this solution fits very well to their experimentally determined particle concentration at various heights of the colloidal liquid at sedimentation equilibrium.

As has been said earlier, this work is concerned with the evolution of the particle concentration at various heights. Let the drift velocity and the particle concentration at the height  $z$  be  $v$  and  $n$  while those at  $z + dz$  are  $v + dv$  and  $n + dn$  respectively. Let  $dN/dt$  be the net rate of increase in the number of particles in the cylindrical disc bounded by the layers  $z$  and  $z + dz$  with area  $A$ . Then

$$dN/dt = A \, dz \, dn/dt = Anv - A(n + dn)(v + dv).$$

On simplifying the above equation, one gets

$$dz \, dn/dt = -n \, dv - v \, dn - dv \, dn. \quad (7)$$

Neglecting the term  $dv \, dn$  in comparison with other terms and rearranging, equation (7) becomes

$$dv/dz = -n^{-1} \, dn/dt - (v/n) \, dn/dz. \quad (8)$$

On combining equation (8) and equation (4) and using  $n^{-1} = u$ , one gets

$$C + D \, du/dz = u \, dv/dz = du/dt + v \, du/dz. \quad (9)$$

Eliminating  $du/dz$  from equation (9) one gets

$$D \, du/dt = u(D - v) \, dv/dz + vC. \quad (10)$$

Consider the suspension in which the particle concentration varies down the column

continuously with finite particle concentrations at the top and bottom. This is possible because the interparticle separation happens to be smaller than the position of the minimum in the pair potential (Kesavamoorthy *et al* 1989). In this situation the structural stability is achieved via the repulsive pair potential and the excluded volume effect. If  $v \neq 0$  at the top surface,  $z = 0$ , then a particle-free region will appear at the top; this is not the situation considered here. Hence,  $v = 0$  at the top surface, and at the bottom of the container,  $z = h$ ,  $v$  is zero at any time because of the boundary. The particle concentration is the same at all points in a horizontal layer. As  $t \rightarrow \infty$ , the drift velocity at all heights should be zero. Let us model the drift velocity by factorising the dependences of  $z$  and  $t$  for simplicity. As far as the  $z$  dependency is concerned, a triangular function (linear in  $z$ ) is not suitable since its derivative has a discontinuity at  $z = h/2$ . Hence, let us choose a parabolic function of  $z$ . For the time dependency let us choose an exponentially decreasing function. Hence the drift velocity is assumed to be of the form

$$v = v_0 z(h - z) \exp(-kt) \quad (11)$$

where  $v_0$  and  $k$  are constants. Substituting equation (11) in equation (10) one gets

$$\begin{aligned} du/dt = uv_0(h - 2z)[1 - v_0 z(h - z) \exp(-kt)/D] \exp(-kt) \\ + v_0 Cz(h - z) \exp(-kt)/D. \end{aligned} \quad (12)$$

Writing  $u = U \exp(-kt)$ , equation (12) becomes

$$dU/dt = pU + q \quad (13)$$

where

$$\begin{aligned} p &= k + (h - 2z)[v_0 \exp(-kt) - v_0^2 z(h - z) \exp(-2kt)/D] \\ q &= v_0 Cz(h - z)/D. \end{aligned}$$

The solution of equation (13) is given by

$$U \exp(f(t)) = q \int_0^t \exp(f(t')) dt' + S = u \exp(f(t) + kt) \quad (14a)$$

where

$$f(t) = - \int p dt = -kt + (h - 2z)[v_0 \exp(-kt)/k - v_0^2 z(h - z) \exp(-2kt)/2kD] \quad (14b)$$

and  $S$  is a constant which can be determined from the initial conditions. Let us consider the case where the suspension is shaken at  $t = 0$  and left undisturbed thereafter. At  $t = 0$  the particle concentration is uniform throughout the column:

$$u(z, 0) = \bar{n}^{-1}.$$

Hence, equation (14a) gives

$$S = \exp(f_0)/\bar{n} \quad (14c)$$

where  $f_0$  is the value of  $f(t)$  at  $t = 0$ , given by

$$f_0 = (h - 2z)[v_0/k - v_0^2 z(h - z)/2kD]. \quad (14d)$$

Substituting equation (14c) into (14a) and recalling that  $u = n^{-1}$ , one gets

$$n(z, t) = \exp(f(t) + kt) / \left( q \int_0^t \exp(f(t')) dt' + \exp(f_0)/\bar{n} \right). \quad (15)$$

Equation (15) describes the evolution of sedimentation equilibrium in a colloidal liquid.

### 3. Results and discussion

The relevant features of the reported experimental work (Kesavamoorthy and Arora 1985) have been given here. Aqueous suspensions of polystyrene spheres of diameter  $0.091 \mu\text{m}$  (Serva Feinbiochemica GmbH, FRG) were prepared at the average particle concentration,  $\bar{n}$ , of  $4.76 \times 10^{12} \text{ cm}^{-3}$ .  $\bar{n}$  was determined by an evaporation technique (Udo and de Souza 1980). The suspension was held in a closed cylindrical glass scattering cell (diameter 1 cm, height 2.5 cm) that also contained a mixed bed of ion-exchange resins at the bottom (cation : Dowex; anion : Duolite A 161C). The suspension was found to separate into phases initially for about a day, after which no boundary was seen in the suspension due to the re-entrant phenomena (Arora *et al* 1988). The suspension was left for two more days. The angle-resolved, polarised, static light scattering intensity from this homogeneous liquid-like ordered suspension was recorded at various heights and at different times after shaking the suspension. The structure factor thus measured was fitted to the calculated one using a rescaled mean-sphere approximation (Tata *et al* 1987) and the particle concentration at various heights and at different times was obtained from the best fit. The suspension was left in the cell for about a month. It was shaken again, the structure factor was measured at different times and at various heights, and the corresponding concentrations were obtained. The data on a three-day-old suspension (Kesavamoorthy and Arora 1985) and those on a month-old suspension (not reported earlier) have been analysed here.

The impurity concentration in the suspension decreases due to the action of resins and comes to an equilibrium value in about a week (Kesavamoorthy and Arora 1985, Okubo 1987). The evolution of the bulk modulus,  $B$ , of the suspension during this time has been observed (Kesavamoorthy and Arora 1985).  $B$  increases monotonically and saturates in about a week implying that the interparticle interaction increases for a week and becomes steady. At two different values of  $B$ , the particle concentration at the top of the column of the suspension was measured and is shown in figure 1. It is observed from figure 1 that the particle concentration in the three-day-old suspension (the points on the curve  $C_1$ ) decreases to a greater extent than that in the month-old suspension (the points on the curve  $C_2$ ). In view of the fact that  $B$  saturates in about a week, the value of  $B$  is a constant in the month-old suspension as assumed in the present theory (equation (2)). Figure 1 indicates that the particle concentration comes to an equilibrium in about 3 hours and the measurement has been taken up to 7 hours. During this period of 7 hours, the value of  $B$  has increased by less than 1% in the three-day-old sample (Kesavamoorthy and Arora 1985). Hence, the present theory might be suitable for a three-day-old sample also.

The theory is compared with the experiment. For  $z = 0$ , equation (15) reduces to

$$n(0, t) = \bar{n} \exp[-v_0 h(1 - \exp(-kt)/k)]. \quad (16)$$

The best fit to the experimental data obtained using the above expression is shown in figure 1 as the curves  $C_1$  and  $C_2$ . It is clear that the fit is very good. The fit gives  $k = 3 \times 10^{-4} \text{ s}^{-1}$  and  $v_0 = 2.5 \times 10^{-5} \text{ cm}^{-1} \text{ s}^{-1}$  for the three day-old sample (curve  $C_1$ ). The maximum drift velocity of the particle according to the present model is realised at  $t = 0$  and at  $z = 0.5$ , with the value  $6.25 \times 10^{-6} \text{ cm s}^{-1}$ . Assuming a body-centred cubic type of coordination in the colloidal liquid with  $\bar{n} = 4.76 \times 10^{12} \text{ cm}^{-3}$  (Lindsay and Chaikin 1982), the nearest neighbour distance,  $l$ , comes out as  $0.65 \mu\text{m}$ . Hence, the particle would move a distance of the order of  $0.1 l$  with this maximum drift velocity in one second. The free Stokes sedimentation velocity,  $v_s = 2a^2 \Delta\rho g / 9\eta$ , for this suspension

works out to be  $2.29 \times 10^{-8} \text{ cm s}^{-1}$  which is 273 times smaller than the maximum drift velocity. According to equation (11), the drift velocity at  $z = 0.5$  becomes  $v_s$  at  $t = 5.2 \text{ h}$ . It is important to note that the sedimentation equilibrium is reached in about 3 h which implies that throughout the duration of the experiment the particle drifts with velocity greater than  $v_s$ . This becomes possible because of the interparticle interaction. The best fit to the data for the month-old suspension (curve  $C_2$  in figure 1) gives  $k = 1.46 \times 10^{-2} \text{ s}^{-1}$  and  $v_0 = 6.42 \times 10^{-4} \text{ cm}^{-1} \text{ s}^{-1}$ . Comparing the values of  $k$  obtained for curves  $C_1$  and  $C_2$  it is clear that as the interparticle interaction increases, the suspension reaches the sedimentation equilibrium more quickly. It is also clear from the values of  $v$  that in order to reach the equilibrium more quickly the particles must drift faster. Since the fits for the three-day-old sample and the month-old sample are equally good, the 1% variation of  $B$  during the 7 h of the experiment in the three-day-old sample is not serious enough to affect the solution given by equation (15).

The solution given by equation (15) is approximate since the higher-order term in equation (7) has been neglected. In order to check its validity, the asymptotic form of equation (15) is compared with equation (6) which is exact. As  $t \rightarrow \infty$ , equation (15) becomes

$$u(z, \infty) = \exp(f_0)/\bar{n} + q \int_0^\infty \exp(f(t')) dt'.$$

On simplifying, it becomes

$$u(z, \infty) = \exp(f_0)/\bar{n} + (q/k) \exp(-\alpha^2/4\beta) \int_{-\alpha/2\beta}^{1-\alpha/2\beta} \exp(\beta\omega^2) d\omega \quad (17)$$

where

$$\alpha = v_0(2z - h)/k \quad \beta = v_0^2 z(h - z)(2z - h)/2kD \quad \omega = \exp(-kt) - \alpha/2\beta.$$

The values of  $v_0$  and  $k$  are taken from the fit to the data in figure 1 (curve  $C_1$ ). Taking the experimental value of  $B$  ( $0.55 \text{ dyn cm}^{-2}$ ),  $D$  is calculated from equation (4c) and found to be  $4.2 \times 10^{-5} \text{ dyn cm}^{-1} \text{ P}^{-1}$ . Figure 2 shows the inverse of the particle concentration at various heights of the three-day-old suspension as  $t \rightarrow \infty$ . The points in this figure were obtained graphically using equation (17). The straight line was obtained using equation (6) for which  $u(0, \infty)$  was taken from figure 1 (curve  $C_1$ ) and  $C$  was calculated using equation (4b). From the closeness of these points to the straight line it is clear that equation (15) representing the evolution of particle concentration at various height is quite valid.

It may be surprising to note that the simple-minded approach outlined in this paper to determine the evolution of the interacting colloidal suspension works very well. In this approach, the diffusion of interacting particles is not considered. The boundary conditions for the column of colloidal suspension (Chandrasekar 1943) are also not considered here. Still, this approach is good enough because of the appropriate modelling of the drift velocity. The boundary conditions are taken into consideration indirectly by modelling the drift velocity as becoming zero at  $z = 0$  and  $h$ , and also as  $t \rightarrow \infty$ . Similarly, the effect of diffusion has been incorporated in the values of the constants  $v_0$  and  $k$ . The values of  $v_0$ ,  $k$  and  $D$  depend on the strength of interaction. The present formalism can be applied to a situation where the particle concentration varies smoothly along one axis and it has been demonstrated that it is applicable to a colloidal liquid that has a smoothly varying concentration along  $z$ . However, it cannot account for the layered sedimentation (Siano 1979) in its present form. Siano (1979) obtained the layered



sedimentation in a colloidal suspension that had a tailor-made gradient in the impurity concentration. Hence, the inter-particle interaction would have been different at different heights in the suspension due to the variation in the impurity concentration. Probably the drift velocity in this case should be modelled in such a way that the functions of  $z$  and  $t$  differ in different segments of the column, so as to describe the observed evolution of the sedimentation equilibrium.

#### 4. Conclusion

The present investigation describes the evolution of the sedimentation equilibrium in an aqueous suspension of interacting polystyrene particles. The difference between the gravitational force and the elastic restoring force on a particle is equated to the viscous drag force on the particle. In a column of the suspension contained in a cylindrical cell, the drift velocity of the particle is modelled as a decreasing exponential in time and a parabola in height. It is shown that results obtained from the calculation using the present theory agree well with the reported experimental evolution of the particle concentration.

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