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## Gravitational compression in colloidal suspension

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**Abstract.** Gravitational effect in colloidal suspensions is examined both theoretically and experimentally by light scattering. In contrast to the previous theory the present theory predicts the cube of the nearest-neighbour distance to vary linearly as a function of height of the suspension. The position of the first peak in the static structure factor of the suspension having liquid-like order is used to obtain average nearest-neighbour distance. The experimental data fit well to the present theory. The bulk modulus of the liquid order estimated for the first time by this method is found to evolve as a function of time. The time taken for the colloidal suspension to reach gravitational equilibrium as well as deionisation equilibrium is obtained. The time to reach gravitational equilibrium is found to be much less than earlier theoretical estimates based on a simple model. A possible mechanism for this is proposed. Concentration dependence of the saturation bulk modulus is obtained and discussed.

### 1. Introduction

Aqueous suspensions of polystyrene particles are known to develop liquid or crystalline solid-like order depending on the extent of ionic purity (deionisation) (Pieranski 1983, Clark *et al* 1979). The particles interact predominantly via the screened Coulomb repulsion (Hess and Klein 1983, Maleki *et al* 1983). Since the density of polystyrene particles ( $1.05 \text{ g cm}^{-3}$ ) is not the same as that of water ( $1.0 \text{ g cm}^{-3}$ ) there is a certain amount of gravitational force on the particles. Because of the small size of the particles ( $\sim 0.1 \mu\text{m}$  diameter) the gravitational effects are small but still measurable. 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 concentration at the bottom and at the top of a column are different is governed by the elastic properties of the suspension (Crandall and Williams 1977) which in turn is determined by the strength and the range of the interaction between the particles. As the interparticle separation is of the same order ( $\sim 1 \mu\text{m}$ ) as the wavelength of light in the visible region, light scattering is the most convenient technique to probe the structure of the suspension (Grüner and Lehmann 1982). The time averaged first-order light scattered intensity is directly proportional to the static structure factor (Dhont 1983).

Crandall and Williams (1977) have derived a simple expression relating the height dependence of the lattice parameter in a column of colloidal crystals to its elastic modulus. Their simple theory predicts the nearest-neighbour ( $N_N$ ) distance to vary linearly as a function of the height in the suspension. However they have taken the particle concentration to be independent of the height of the suspension which is inconsistent as this would lead the  $N_N$  distance to also be independent of the height. In the present work a theory of the gravitational compression in colloidal suspension

is worked out which removes the inconsistency. The theory is presented in terms of NN distances so that it is applicable to a suspension with liquid order also. The present theory predicts the cube of the NN distance (which is proportional to the unit cell volume in the crystalline case and to the average volume occupied by each particle in the case of liquid order) to vary linearly as a function of the height of the suspension. To verify the theory the gravitational compressions are measured in colloidal suspensions having liquid-like order with different particle concentration by light scattering. The height dependence of the NN distance agrees very well with the present theory. The data when fitted to the linear dependence of Crandall and Williams (1977) does not yield a good fit. The evolution of the estimated bulk modulus of the liquid order as a function of time is examined and compared with other reported results. The time taken by the suspension to reach gravitational equilibrium is obtained and compared with the theoretical estimates. The concentration dependence of the saturation bulk modulus is also studied and discussed.

## 2. Theory

Consider a column of colloidal suspension of total height  $h$ . Because of gravitational force, the particle concentration ( $n_p$ ) and hence the NN distance ( $l$ ) changes continuously from the bottom to the top of the column. At any given height  $Z$  from the bottom, the particle concentration and the NN distance are related by

$$n_p(Z) = A/l^3(Z) \quad (1)$$

where the constant  $A$  has a value  $3\sqrt{3}/4$  for a BCC solid and  $\sqrt{2}$  for a FCC solid. However, for liquids one can define only an average NN distance; consequently the value of  $A$  is not uniquely defined and one needs to be careful when choosing a value for  $A$ . The difference in the value of the NN distance at  $Z+dZ$  and  $Z$  arises due to the pressure exerted on plane  $Z$  by the particles in the region between  $Z$  and  $Z+dZ$ . If the suspension has a liquid-like order, the pressure at any plane  $Z$  will be hydrostatic (isotropic) in nature. The situation concerning a crystalline suspension is more complicated. Usually the time taken by a suspension to reach gravitational equilibrium (of the order of a few hours (present work)) is much shorter than that for crystallisation to occur (of the order of a few days (Crandall and Williams 1977, present work)) and hence in such cases one can also expect the pressure to be hydrostatic because the crystals would then grow under the environment of hydrostatic pressure. However, if crystallisation occurs much earlier (say, after shaking the sample) than the gravitational equilibrium, then the pressure at any plane would have both uniaxial and hydrostatic components because the lateral dimensions of the suspension are bounded by the cell walls. The relative magnitudes of hydrostatic and uniaxial stresses in this case would be determined by the ratio of the gravitational stress to the shear modulus of the crystalline order. However, a purely uniaxial stress is not possible. The uniaxial component of the stress may also lead to anisotropy of the NN distance in both horizontal and vertical directions. Hence in such samples the unambiguous observation of the gravitational effect would be more difficult and its interpretation would be more complicated. Crandall and Williams' (1977) observations (shaking the suspension during the crystallisation led to permanent mechanical distortions in the crystals which masked the effect they were trying to measure) also support the present arguments.

Consider a colloidal suspension having crystalline or liquid-like order in which the gravitational stress is hydrostatic in nature. If  $B$  is the bulk modulus of the suspension, then equating the gravitational force to the elastic restoring force one can write

$$\left(\frac{\pi D^3}{6} n_p(Z) \rho_{\text{eff}}\right) g \, dZ = \frac{l^3(Z+dZ) - l^3(Z)}{l^3(Z)} B \quad (2)$$

where  $D$  is the particle diameter,  $\rho_{\text{eff}} = \rho_{\text{particle}} - \rho_{\text{water}}$  is the effective density of the particle and  $g$  is the acceleration due to gravity. It may be noted that  $l^3$  is proportional to the volume available for each particle. For comparison it is pertinent to give the equation used by Crandall and Williams (1977) which is

$$\frac{\pi D^3}{6} \bar{n}_p \rho_{\text{eff}} g \, dZ = \frac{l(Z_m+dZ) - l(Z_m)}{l(Z_m)} E \quad (2a)$$

where  $\bar{n}_p$  is the average concentration in the suspension,  $Z_m$  is the mean height of the suspension and they call the proportionality constant  $E$  Young's modulus. Equation (2a) represents a pure uniaxial stress which is not possible as we have already discussed. However, it should be pointed out that the samples used by Crandall and Williams (1977) took several days for crystallisation and hence the gravitational stress must be hydrostatic rather than uniaxial. Equation (2) can be written as

$$d(l^3(Z)) = \left(\frac{\pi D^3 \rho_{\text{eff}} g}{6B}\right) n_p(Z) l^3(Z) \, dZ. \quad (3)$$

Substituting equation (1) in equation (3) one obtains

$$d(l^3(Z)) = \left(\frac{\pi D^3 \rho_{\text{eff}} g A}{6B}\right) dZ. \quad (4)$$

In the above equation the dependence of  $B$  on the height  $Z$  (due to variation in the concentration with  $Z$ ) has not been explicitly put in. If  $B$  strongly depends on  $Z$ , any treatment that takes  $B$  to be independent of height will be limited in its validity to small variations in the  $z$  distance. Hence the height dependence of  $B$  is discussed in the following paragraph.

The elastic constants of a colloidal suspension (either crystalline or liquid) are known to depend on concentration of particles (Crandall and Williams 1977, Grüner and Lehmann 1982, Lindsay and Chaikin 1982). Grüner and Lehmann (1982) have reported a quadratic dependence of  $B$  in the case of liquid-like order and a linear dependence for crystalline order. Crandall and Williams (1977) have got a concentration dependence of Young's modulus of crystalline order which is weaker than linear whereas Lindsay and Chaikin (1982) have obtained a concentration dependence of shear modulus which is in between linear and quadratic. The theoretical estimates of bulk and shear moduli (Arora and Kesavamoorthy 1984) based on the simple model of Lindsay and Chaikin (1982) show that these elastic constants depend also on concentration of impurity ions and no unique power law can be obtained. It must be pointed out that the experimental concentration dependence of elastic moduli have been obtained from samples of different average concentrations and represent average macroscopic elastic moduli for that average concentration. Though the concentration may vary from top to bottom within a single sample due to gravitational effects, in equilibrium it is reasonable to expect the entire suspension to have a single unique macroscopic average elastic modulus as various regions (top, middle and bottom) of

the sample are not isolated but are in real physical contact with each other and must be in equilibrium with each other. However this point can be experimentally verified and is discussed in the forthcoming sections. For the sake of completeness, the concentration dependence of  $B$  is explicitly considered in the appendix and complete expressions are worked out. But for the present  $B$  is taken not to vary with the height of the suspension. Equation (4) can be integrated to yield  $Z$  dependence of the  $NN$  distance as

$$l^3(Z) = l_0^3 + \left( \frac{\pi D^3 \rho_{\text{eff}} g A}{6B} \right) Z \quad (5)$$

where  $l_0$  is the  $NN$  distance at  $Z = 0$ . Equation (5) can be rewritten in a more convenient form as

$$(l(Z)/l_0)^3 = 1 + (bn_p(0)/B)Z \quad (6)$$

where  $b = \pi D^3 g \rho_{\text{eff}}/6$  and  $n_p(0)$  is the particle concentration at  $Z = 0$ . However  $l$  and  $n_p(0)$  can be related to the average particle concentration ( $\bar{n}_p$ ) if one considers the conservation of total number of particles ( $N$ ) in the suspension. This leads to

$$Sh\bar{n}_p = N = S \int_0^h n_p(Z) dZ \quad (7)$$

where  $S$  is the area of cross section of the column. Equation (7) when integrated and simplified gives

$$bn_p(0)h/B = \exp(b\bar{n}_ph/B) - 1. \quad (8)$$

Equation (6) allows one to estimate the bulk modulus  $B$  of a crystalline phase of suspension in a straightforward manner as one can measure  $l$  and  $n_p$  experimentally from the light diffraction (for example in the BCC phase  $l = (2\pi/K_{110})\sqrt{3}/2$  and  $n_p = (K_{110}/2\pi)^3/\sqrt{2}$  where  $K_{110}$  is the wavevector corresponding to diffraction from [110] planes). In a liquid phase it is not simple to write such expressions for  $l$  and  $n_p$ , however, the following experimental facts allow one to relate the average  $NN$  distance ( $l$ ) to wavevector ( $K_p$ ) corresponding to the first peak in the structure factor,  $S(K)$ . (a) The density (and hence the packing) does not change by more than two per cent across any liquid-solid interface (Warren 1969) implying that average  $l$  (liquid)  $\approx l$  (solid). (b) The first peak in  $S(K)$  appears at the same position as the first diffraction peak in the corresponding solid phase (e.g.  $K_{110}$  in the BCC phase) (Warren 1969, Grüner and Lehmann 1982) i.e.  $K_p = K_{110}$ . This implies that the local structure (at least the coordination in the first shell) in the liquid phase is not drastically different from that for the crystalline phase. Hence in analogy with the crystalline solid it is reasonable to take the average  $NN$  distance in liquid as

$$l \propto K_p^{-1}. \quad (9)$$

Hence in the case of liquid order one can estimate  $n_p(0)/B$  from equation (6) and then  $B$  can be estimated from equation (8) as  $\bar{n}_p$  is known independently. It is important to point out that equation (2a) predicting  $l(Z)$  varying linearly in  $Z$  used by Crandall and Williams (1977) to analyse their data is only the derivative equation for  $l(Z)$ . The equation (2a) when integrated gives the  $Z$  dependence of  $l(Z)$  as the exponential

$$l(Z) = l_0 \exp\left(\frac{\pi D^3 \bar{n}_p \rho_{\text{eff}} g}{6E} Z\right). \quad (10)$$

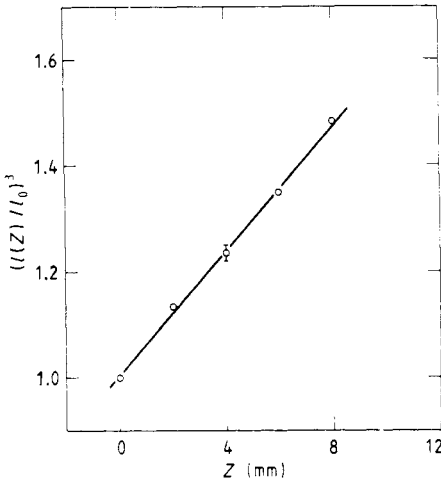
Equation (10) can be approximated to be linear in  $Z$  only within certain limits. When the concentration dependence of the bulk modulus is explicitly taken into account (as derived in the appendix) the predicted  $Z$  dependence is a power law and one can fit the data to equation (13) to experimentally determine the concentration dependence of the bulk modulus.

### 3. Experimental

Aqueous suspensions of polystyrene spheres of  $0.091 \mu\text{m}$  diameter (from M/s Serva Feinbiochemica GmbH, FRG) were prepared in deionised water (conductivity  $\approx 2 \mu\text{mho cm}^{-1}$ ) at different particle concentrations ranging from  $3.2 \times 10^{12} \text{ cm}^{-3}$  to  $9.5 \times 10^{12} \text{ cm}^{-3}$  by diluting the stock suspension. The samples were in a cylindrical glass scattering cell (diameter 1 cm, height 2.5 cm) that also contained a mixed bed of ion exchange resin at its bottom (cation: Dowex; anion: Duolite A 161C). The resin to sample ratio was 1:5. The cells were closed using teflon stoppers. In concentrated samples crystallisation occurred in the region close to the resin after one or two days. One could easily distinguish the crystalline order from the liquid order by its opalescence and Bragg diffraction of a laser beam. Crystallites were found typically up to 2 to 3 mm above the resin. On top of the crystalline region liquid order was observed. The interface between crystalline and liquid order was plane and horizontal. In many cases crystallisation occurred first close to the walls of the lower region of the cell indicating that leaching of small ions from the walls was not significant. Due to gravitational compression the concentration of particles at the bottom is higher than that at the top. As the crystalline to liquid-order transition is of first order (Williams *et al* 1976), depending on the charge on the particle and the level of ionic impurities there exists a critical particle concentration beyond which a crystalline order can be seen. Hence one can expect the crystallites at the bottom and the liquid order at the top. The dilute samples had only liquid order. The scattering cell was immersed in a cylindrical glycerine bath (diameter 6 cm, height 6 cm) which acted as an index matching liquid as well as a constant temperature bath. The polarised  $VV$  ( $V$ : vertical) light scattering was measured in the suspension in the region having liquid-like order as a function of scattering vector using a set-up described earlier (Arora 1984). A He-Ne laser (power 10 mW) was used as a source. The scattering cell along with the bath was positioned using a  $XYZ$  translation stage and measurements were made at different heights in the scattering cell to obtain the scattering vector  $K_p$  corresponding to the first peak in the structure factor  $S(K)$  of the liquid-like order. The average particle concentration  $\bar{n}_p$  was obtained by finding the total weight of polystyrene spheres after carefully drying a sample of known weight (Udo and de Souza 1980).

### 4. Results and discussions

Figure 1 shows the cube of the estimated average  $NN$  distance as a function of the height of the colloidal suspension. The straight line is a least squares fit of the experimental points to equation (6). For the sake of comparison the same data were also least squares fitted to (a) linear, (b) exponential and (c) power law dependencies. The results of fittings are shown in table 1. One can see from figure 1 and table 1 that equation (6) fits best to the experimental data. If the bulk modulus had varied as a



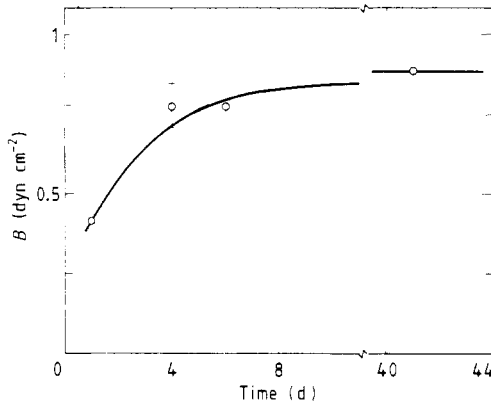
**Figure 1.**  $[l(Z)/l_0]^3$  ( $l(Z)$ : estimated average NN distance at height  $Z$ ) as a function of height  $Z$  in the suspension having liquid-like order. Straight line is a least squares fit to the data points. The slope of the line is used to obtain the bulk modulus of the suspension as described in the theory.  $\bar{n}_p = 4.76 \times 10^{12} \text{ cm}^{-3}$ .

**Table 1.** Summary of the least squares fitting of the experimental data to various functions.

Function fitted	Fitted parameters		Residual sum of squares $\times 10^5$	
	$A_1$	$A_2$		
Power law	$y = (l + A_1 Z)^{A_2}$	$0.064 \pm 0.025$	$0.318 \pm 0.107$	2.15
Equation (6)	$y = (l + A_1 Z)^{1/3}$	$0.0600 \pm 0.0008$	—	2.16
Linear	$y = (l + A_1 Z)$	$0.0178 \pm 0.0003$	—	5.1
Exponential	$y = \exp(A_1 Z)$	$0.0168 \pm 0.0004$	—	8.7

function of height then the plot of  $(l(Z)/l_0)^3$  against  $Z$  (figure 1) would show a departure from straight line. Hence experimental data as shown in figure 1 confirms that the entire suspension had a single unique bulk modulus. It may be noted that the data when fitted to power law (two parameters) also gives the same residual sum of squares as that for equation (6); however the error bars of the fitted parameters are large because of the larger number of parameters. The value of  $q$  obtained from the parameter  $A_2$  has the value  $0.04 \pm 0.2$  which also supports a height independent bulk modulus. It is worth mentioning that the data of Crandall and Williams (1977) (sample in  $\text{H}_2\text{O}$ ) when fitted to these four expressions gives the best fit for the equation (6).

Deionisation of the colloidal suspensions by ion-exchange resin is known to be a slow process. We have obtained the time taken to reach deionisation equilibrium for the first time by light scattering measurements. Time evolution of the bulk modulus in a colloidal suspension after the addition of ion-exchange resin is shown in figure 2. The bulk modulus increases monotonically and reaches its saturation value typically in ten days. Other particle concentrations also show a similar behaviour. The observed time evolution can be understood in the following way. Initially the concentration of

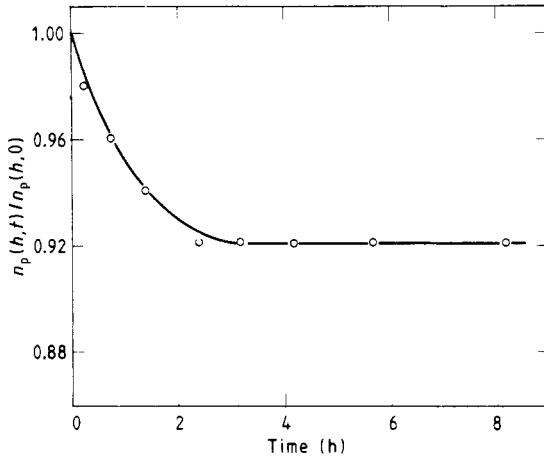


**Figure 2.** Time evolution of the bulk modulus of the colloidal suspension after the addition of ion-exchange resin.  $\bar{n}_p = 4.76 \times 10^{12} \text{ cm}^{-3}$ .

impurity ions is fairly large and the Coulomb interaction between particles is effectively screened. The ion-exchange resin removes the impurity ions slowly (Williams *et al* 1976) (because of the small volume of the sample, however, it was not possible to determine the time evolution of the concentration of the impurity ions) and consequently the range of the screened Coulomb interaction increases gradually causing a liquid-like order to develop. It is observed that in the beginning the peaks in the structure factor (characteristic of the liquid-like order) are not very pronounced indicating a weak liquid-like order; the corresponding bulk modulus is low. As the extent of deionisation of water increases gradually, the structure factor develops strong peaks indicative of a strongly interacting liquid and correspondingly its bulk modulus is also found to have increased. The observed evolution of the structure factor is similar to the one reported by Brown *et al* (1975). Increase of shear modulus with decreasing impurity ion concentration (similar to the one observed here) has been reported both theoretically and experimentally in the case of crystalline order also (Lindsay and Chaikin 1982). However the time evolution was not investigated.

As the particle size is very small, gravitational drag on the particle is small and it may take a long time to reach gravitational equilibrium. A simpleminded estimate (Pieranski 1983) of the time taken by a column of 1 cm height (particle diameter  $0.1 \mu\text{m}$ ) to reach *sedimentation* (gravitational) *equilibrium* is of the order of  $10^7$  s which is the time taken by a particle to drift from the top to bottom. However the changes in the particle concentration over the height of the suspension due to gravitational effect is expected to come about by small and local movement (over a few  $\lambda_D$  distance) of particles and the time taken for this is expected to be much smaller than estimated previously (Pieranski 1983). To confirm this, a sample that had reached steady state of deionisation was shaken to make the particle concentration uniform throughout the column and then the time evolution of the particle concentration ( $n_p \propto K_p^{-3}$ ) at the top of the suspension was monitored by recording the structure factor at different times. Figure 3 shows such a time evolution for a suspension with particle concentration of  $4.76 \times 10^{12} \text{ cm}^{-3}$ . One can see that at the top of the suspension the particle concentration slowly reduces and it takes typically 3 h ( $\sim 10^4$  s) to reach the gravitational equilibrium confirming the present arguments. The estimated maximum distance drifted by a particle during this time turns out to be of the order of  $3 \mu\text{m}$  which appears reasonable.

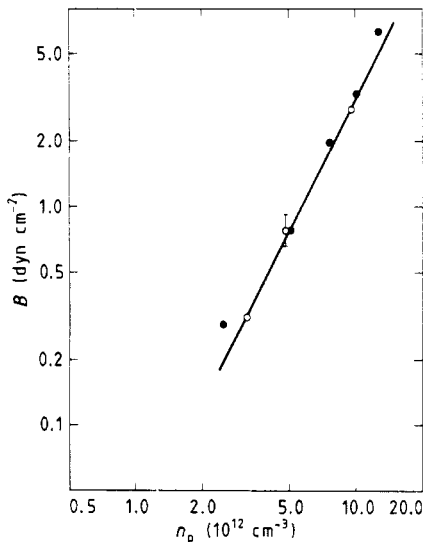




**Figure 3.** Time evolution of the estimated particle concentration at the top of the suspension after a deionised sample was shaken and left undisturbed. Time taken to reach gravitational equilibrium is typically 3 h.  $n_p(Z, 0) = 4.76 \times 10^{12} \text{ cm}^{-3}$ .

It may be noted that the time taken to reach the gravitational equilibrium is much shorter than that for the deionisation equilibrium.

As discussed earlier elastic constants of a colloidal suspension depend on the particle concentration. The present measurements of the saturation bulk moduli for different concentrations are shown in figure 4. It is important to note that the bulk modulus goes like the square of the particle concentration. Gr $\ddot{u}$ ner and Lehmann (1982) have estimated the bulk modulus from the value of the static structure factor in the hydrodynamic limit ( $k = 0$ ). They pointed out that because of errors involved



**Figure 4.** Concentration dependence of saturation bulk modulus (O). Data of Gr $\ddot{u}$ ner and Lehmann (1982) (●) is also shown for comparison. The slope of the full line drawn through the points is  $2.0 \pm 0.2$ .

in the extrapolation such estimated bulk moduli may have systematic errors of  $-50\%$  to  $+150\%$ ; however the concentration dependence is unaffected. Their estimated bulk moduli are also shown in figure 4 for the sake of comparison. It can be seen from figure 4 that the data of Grüner and Lehmann (1982) agree very well with the present more direct and accurate measurements. It is worth emphasising that measurements of the elastic constants in the case of crystalline order yield the concentration dependence different from the quadratic (Grüner and Lehmann 1982, Crandall and Williams 1977, Lindsay and Chaikin 1982). A simple theory similar to that of Lindsay and Chaikin (1982) is not really adequate. This aspect requires rigorous theoretical consideration.

## 5. Conclusion

The present theoretical and experimental investigations of gravitational compression in colloidal suspensions show that the cube of the nearest-neighbour distance varies linearly with the height of the suspension. The estimated bulk modulus is found to increase slowly as the ion-exchange resin deionises the water. The time taken for the system to reach gravitational equilibrium is found to be much less than previously estimated. The present more accurate concentration dependence of saturation bulk modulus shows a quadratic behaviour.

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## Appendix

Let the concentration dependence of  $B$  be given as some power law

$$B = Pn_p^q \quad (\text{A1})$$

where  $P$  is the constant of proportionality. Substituting equations (A1) and (1) in equation (4) and after simplifying one gets

$$l(Z)^{2-3q} dl(Z) = \frac{\pi D^3 \rho_{\text{eff}} g A^{1-q}}{18P} dZ. \quad (\text{A2})$$

Equation (A2) when integrated with appropriate boundary conditions gives

$$\left(\frac{l(Z)}{l_0}\right)^{3(1-q)} = 1 + \left(\frac{(1-q)\pi D^3 \rho_{\text{eff}} g A^{1-q}}{6Pl_0^{3(1-q)}}\right)Z \quad \text{for } q \neq 1. \quad (\text{A3})$$

If  $q = 1$ , equation (A2) when integrated gives an exponential behaviour similar to that of equation (10).

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