Layer Formation of Dilute Colloidal Suspensions as a Result of a Concentration-Dependent Sedimentation Velocity: Some Simple Considerations and Suggestions for Further Experiments.

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Abstract. – In a number of experiments on sedimentation in colloidal suspensions, the formation of a vertically layered structure in the concentration profile has been observed. We argue that this may be interpreted as the formation of shock fronts in the concentration profile due to the concentration dependence of the sedimentation velocity, a mechanism first identified by Kynch. We propose several experiments to test this suggestion, and draw attention to the possibility of observing anomalous diffusion in a sedimenting suspension with reversible aggregation.

For over a century[1], it has been known that suspensions often exhibit a stratified structure upon sedimentation. This stratification occurs in the form of the appearance of one or more horizontal bands, as sketched in fig. 1. Within each band, the suspension appears to be approximately homogeneous, but the concentration (volume fraction) of the suspension differs from one band to the other. Thus, a plot of the concentration *vs.* height shows a staircaselike structure, with the «interfaces» between the bands corresponding to the vertical positions where the concentration jumps.

As discussed by Siano[2], this stratification has been observed in a number of different suspensions, including clays, oil emulsions, gold sols[3], membrane vesicles[4] and polyballs[2]. For an extensive account of the various observations, we refer to the recent paper by Siano[2]. As he discusses, there is apparently no agreement on the origin of this effect. It has sometimes been suggested that the layering is due to the polydispersity of the suspended particles. However, one would rather expect polydispersity to give rise to the formation of streamers[5] (predominantly horizontal velocity and density modulations) than to vertical stratification. Moreover, the experiments of Siano[2] on monodisperse suspensions rule out this explanation. An alternative suggestion[6] has been that the layering should be viewed of as some kind of spinodal decomposition. Spinodal decomposition has in fact recently been observed in colloids with attractive interparticle forces[7], but as one would expect the patterns are isotropic and statistically homogeneous,
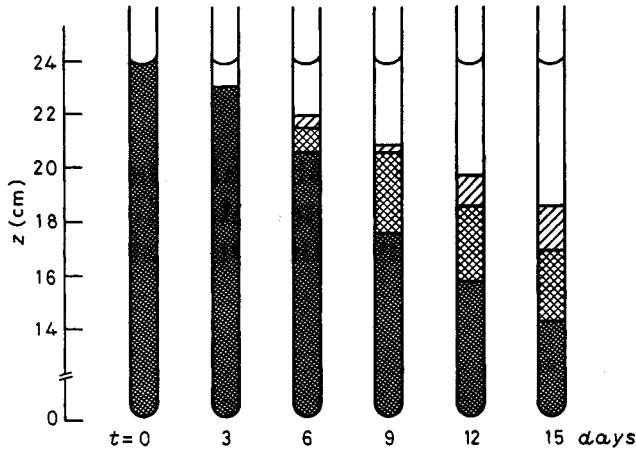
Fig. 1. – Schematic representation of the appearance of layers as a function of time in the experiments of Siano on an initially homogeneous suspension of 1.09 μm spheres at a volume fraction of 0.001. After Siano [2], fig. 2.

not layered on length scales of order centimeters. Moreover, there is no evidence for the existence of significant particle clustering through attractive forces in Siano's experiments [2].

The aim of this letter is to point out that it is natural, even for dilute suspensions, to attribute the stratification to the (nonlinear) concentration dependence of the sedimentation velocity [8]. We propose some simple experiments to test this idea in more detail.

For suspensions that are large enough that Brownian motion can be neglected, this idea is not at all new. It is well known that the sedimentation velocity $V(c)$ of a homogeneous suspension is a *decreasing* function of the concentration c. (This effect is sometimes called «hindered settling».) Back in 1952, Kynch [9] realized that according to the conservation equation for a suspension sedimenting in the $-z$ direction

$$\frac{\partial c}{\partial t} = \frac{\partial V(c)\, c}{\partial z}, \tag{1}$$

one should expect the development of shocks, *i.e.* interfacelike discontinuous jumps in the concentration c. These shocks arise from the concentration dependence of $V(c)$. One way in which this shows up is the «self-sharpening» of the interface at the top of a sedimenting suspension. Although some questions have remained [10] concerning the precise conditions at the shock discontinuity, the existence of shocks is well established—in fact a convenient way to determine the concentration dependence of $V(C)$ is by extracting it from the measured shock velocities [11-13].

The interesting question therefore becomes: is the stratification observed in dilute colloidal suspensions another manifestation of the same physics? The most important effect on going towards small particle sizes is that Brownian motion becomes significant. A convenient way to express the importance of the sedimentation relative to the effects of Brownian motion for a dilute monodisperse suspension is through the Péclet number P

$$P = \frac{2a\, V_0}{D_0}, \tag{2}$$

defined so that Brownian motion becomes more important with decreasing P. Here a is the particle radius, and V_0 and D_0 are the sedimentation velocity and the diffusion coefficient of a single sphere, respectively. Since

$$V_0 \frac{(4/3)\,\pi a^3 g\,\Delta\rho}{6\pi\eta a}, \tag{3}$$

$$D_0 = \frac{k_B T}{6\pi\eta a}, \tag{4}$$

with g the gravitational acceleration, $\Delta\rho$ the density difference between the particles and the liquid and η the viscosity of the liquid, we get

$$P = \frac{8}{3}\frac{\pi a^4 g\,\Delta\rho}{k_B T}. \tag{5}$$

Thus, the importance of fluctuations and diffusion rapidly increases with decreasing sphere size. Usually, Brownian motion becomes important for particles smaller than a few μm. Siano used polystyrene particles in the range $2a = 0.109\,\mu$m ($P = 2 \cdot 10^{-5}$) to $2a = 1.09\,\mu$m ($P = 0.2$), and polyvinyltoluene particles with diameter $2.02\,\mu$m and $P \simeq 1.6$.

For dilute systems—Siano [2] used concentration up to about 0.5 volume percent—we can approximate $V(c) \simeq V_0(1 - kc + ...)$, where $k = 6.55$ for hard spheres [14, 15]; since the concentration-dependence of the (collective) diffusion coefficient [16, 17] $D(c)$ is unimportant for the effects discussed here[1], we will neglect it and consider for dilute colloidal suspensions the generalization [19] of eq. (1)

$$\frac{\partial c}{\partial t} = V_0\frac{\partial c}{\partial z} - 2V_0 kc\frac{\partial c}{\partial z} + D_0\nabla^2 c + \xi. \tag{6}$$

Here ξ is a fluctuating noise term; for a system with a conserved number of particles that obeys the fluctuation dissipation theorem, its correlations are [20]

$$\langle \xi(r,t)\,\xi(r',t')\rangle = \frac{8}{3}\pi a^3 c D_0\nabla^2\delta(r-r')\,\delta(t-t').$$

For $\xi = 0$ and one-dimensional profiles $c(z,t)$, eq. (6) reduces to

$$\frac{\partial c}{\partial t} = V_0\frac{\partial c}{\partial z} - 2kV_0 c\frac{\partial c}{\partial z} + D_0\frac{\partial^2 c}{\partial z^2}. \tag{7}$$

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[1] Note that although we consider, for simplicity, dilute suspensions in arriving at eq. (6), this equation is valid more generally for small concentration jumps in nondilute suspensions if c is reinterpreted as the deviation of the particle concentration from its mean value c_m and V_0 and D_0 are reinterpreted as the velocity and diffusion coefficient at $c = c_m$. In this case, $k = -V_0^{-1}\,dV(c)/dc|_{c_m}$. Moreover, the concentration dependence of $D(c)$ can straightforwardly be incorporated. The layering arises from the behavior of eq. (6) on scales much larger than the interface width W (defined in eq. (9)) and so is driven by the convective term given in (1). As a result, a strong concentration dependence $D(c)$ only effects the «interface structure». For weak concentration jumps that satisfy $D^{-1} \cdot (dD/dc)\Delta c \ll 1$ the concentration dependence can indeed be neglected and the internal shock structure is that given by Whitham, ref. [18].
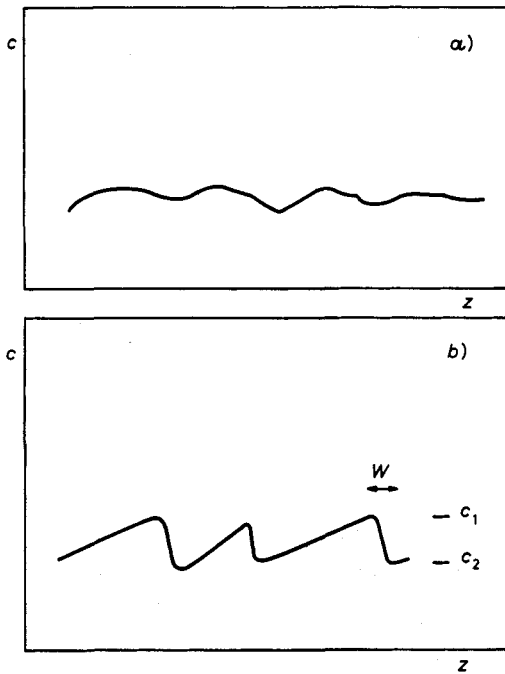
Fig. 2.   Fig. 3.

Fig. 2. – Sketch of the dynamics implied by the Burgers equation for small D_0. a) The initial profile at $t = 0$. b) The profile after long times.
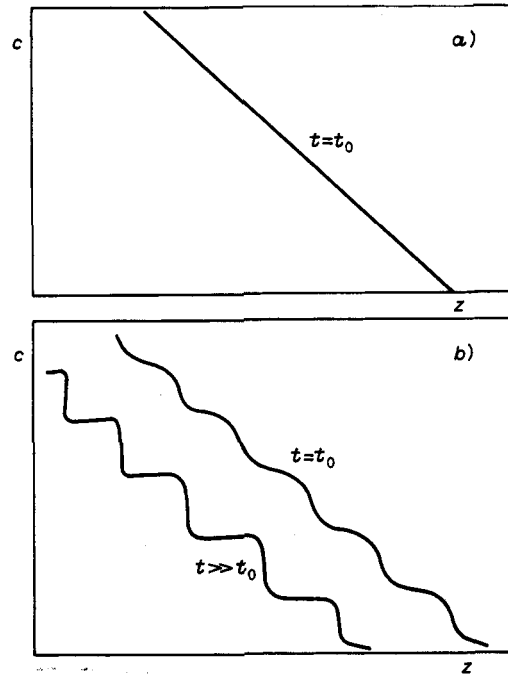
Fig. 3. – a) Initial concentration profile as hypothesized by Siano and Hagan and Cohen. b) Illustration of the fact that if the initial concentration profile has a smoothed steplike character, the dynamics dictated by the Burgers equation would correspond mainly to a sharpening of the steps.

Since the $V_0 \partial c/\partial z$ term can be transformed away by going to a frame moving with velocity $-V_0$, this equation is equivalent to the Burgers equation [18] whose dynamics is well understood [18] (the equation is exactly solvable). The effect of adding noise to this equation in one and more dimensions has been under active investigation in the last few years. We will come back to this below.

In view of the experimental observation that the layering is only in the z-direction, we will first consider z-dependent profiles $c(z, t)$ and compare to what extent the experimental results agree with what one would expect theoretically on the basis of eq. (7). As illustrated in fig. 2 and discussed in detail by Whitham [18], according to eq. (7) an initial profile $c(z, t_0)$ will develop into a saw-tooth–like profile. Clearly, it is tempting to associate this with the formation of layers or bands seen experimentally. Let us therefore make a more detailed comparison of the experimental observations and prediction of this model, and propose a number of experiments that would provide a better test of these ideas.

i) Because of the sign of the $c(\partial c/\partial z)$ term in (7), regions with $\partial c/\partial z$ negative tend to develop interfaces («shocks»), while regions where $\partial c/\partial z > 0$ do not. As a result, according to the Burgers equation one will typically find a positive gradient $\partial c/\partial z$ within the bands. Siano [2] remarks that although, to the eye, each layer appears to be of nearly constant concentration, there could perhaps be a slight «reverse gradient», in other words, c

increases with height. Clearly, measurements of whether the concentration in the bands does indeed show this expected reverse gradient effect would be extremely valuable.

ii) According to the Burgers equation, the velocity of an interface between two bands is [18]

$$V_0[-1 + k(c_1 + c_2)],$$ (8)

where c_1 and c_2 are the concentration on both sides of the interface as sketched in fig. 2b). Similarly, the interface width W is of order

$$W \simeq \frac{2D_0}{V_0 k (c_1 - c_2)}.$$ (9)

Again, measurements of the concentration in the bands would provide definite tests of these predictions, essentially without adjustable parameters. In fact, Hagan and Cohen [6], on the basis of a private communication by Siano, mention that the transition zone between the layers was of the order of $(8 \div 20)\%$ of the layer width, say $(1 \div 2)$ mm. If this number refers to the 1.09 μm particles, it would be consistent with the estimate (9) if we arbitrarily take $c_1 - c_2$ of the order of 10^{-3}. For spheres of diameter 0.1 μm, on the other hand, it is difficult to understand on the basis of (9) how one could ever get such sharp interfaces with concentration jumps that are less than 0.5%.

iii) One of the main conclusions of Siano [2] is that the layering depends on the initial concentration profile. In one set of experiments, he starts with a homogeneous profile $c(z, t = 0) =$ constant. In experiments of this type with 1.09 μm spheres, bands form with a rather irregular spacing, while the 0.109 μm spheres apparently did not show any evidence towards stratification [2, 6]. In another set of experiments, Siano prepared an initial profile with an approximately constant negative gradient, so that c decreased with height. In this case, spheres of both sizes gave rise to layering. Moreover, bands appeared much sooner and were more regularly spaced. While Siano [2] and Hagan and Cohen [6] conclude from these observations that a strictly *linear* initial profile $c(z, t = 0) = b_0 - b_1 z$ as sketched in fig. 3a) facilitates the formation of striations, we note that these findings are completely consistent with the dynamics of the deterministic one-dimensional Burgers equation if one assumes that the initial profile was not linear but actually looked more like the smoothed out steplike profile of fig. 3b). As indicated in this figure, the dynamics dictated by the Burgers equation would show a sharpening in time of the initial homogeneities. That this is the proper explanation appears plausible to us in view of the fact that these «linear» profiles were prepared by mixing two solutions, one, A, with a given concentration of the colloid and the other one, B, without any particles. The initial concentration profile was then made [2] «by first adding enough of A to give a depth of about 10 cm in the tube. Then, for example, 2 drops of B were added and then 18 drops of A, 4 drops of B, 16 drops of A, etc., until the last addition was 20 drops of B». Since the time for the 1.09 μm particles to diffuse 1 cm is of the order of two months, it is unlikely that the initial concentration profile ever becomes accurately linear, as was assumed. It would clearly be interesting to systematically investigate our suggestion that the late time concentration profile is indeed a sharpened «image» of the initial profile. In particular, by preparing a number of different well-charact-erized initial concentration profiles, it should be possible to test qualitatively as well as quantitatively the accuracy of the Burgers equation for the concentration dynamics, and hence the origin of the formation of bands.

If our interpretation is correct, the noise in the experiments on the 1.09 μm spheres is

still small enough that most experimental observations can be understood in terms of the deterministic Burgers equation without noise. However, as we mentioned earlier, the diffusion coefficient and the relative strength of the fluctuations rapidly increase with decreasing particle size. According to our present understanding, we expect no anomalous behavior of the correlation functions in this fluctuation-dominated regime: as shown by Janssen and Schmittmann [21], $d_c = 2$ is the upper critical dimension for eq. (6) with conservative noise (relevant to the case considered here), and in three dimensions, the nonlinear sedimentation term only leads to long time tail correction terms [22] [2]. (Apparently [23], the structure of the equation does not give any reason to believe that there exists a nontrivial strong-coupling fixed point, as happens [24] in the case of an isotropic flux in dimensions $d > d_c = 3$.) However, if the noise were nonconserved ($\langle \xi\xi \rangle \propto$ $\propto \delta(r - r') \delta(t - t')$ in (6)), concentration correlations should have nontrivial scaling exponents [23]. It may be interesting to explore whether such a situation can be realized in a suspension in which reversible aggregation takes place [25], so that the effective number of sedimenting particles is nonconserved and fluctuates. Such a situation can occur [25] if the interaction potential of the colloidal particles has a minimum of order $k_B T$. In order to perform such an experiment, it would probably be advisable to choose the system such that the strength of the nonlinearity and the diffusion in (6) is of the same order of magnitude on scales of the interparticle distance $R \equiv ac_m^{-1/3}$, where c_m is the mean particle concentration. This requires [3] that the Péclet number $P = O(1/kc_m^{2/3})$. For concentrations of about 1%, this yields $P = O(3)$. According to the renormalization group analysis [23], the density correlation function in such an experiment should then exhibit anomalous exponents on long time and length scales, in particular superdiffusive spreading of density fluctuations. For this collective diffusion effect [4], the long-wavelength behavior needs to be probed. The μm particle size dictated by the above requirement might pose difficulties to probe this regime. Nevertheless, with a system in which a majority of the particles is index matched [26], this might become feasible.

In conclusion, we have argued that even the layering of colloidal suspensions of μm spheres can be attributed to the mechanism of shock formation identified by Kynch [9]. If the experiments that we have suggested do confirm our suggestion, the physics of band formation is related to the Burgers equation, which governs a number of related phenomena in physics, such as e.g. step-bunching during crystal growth [27, 28] and the anomalous roughness of an interface in a $2 - d$ Ising model with random interactions [29]. If systems with nonconserved noise can be created, these might yield interesting examples on which to test the recent prediction that the scaling exponents are nontrivial [23].

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[2] The following likely scenario indicates why one nevertheless sees sharp bands and interfaces in the experiments of ref. [2-4, 10-12]. Presumably, eq. (6) has a deterministic ($\xi = 0$) fixed point which is unstable to any amount of noise, so that the renormalization group flow is towards the noise-driven fixed point. For small D_0 and thus small ξ, the system starts extremely close to the deterministic fixed point and thus acts essentially deterministically for a long initial time period. From the renormalization group equations it should be possible to estimate the scaling of the crossover time (and associated lengths) from this deterministic regime to the long-time stochastic behavior.

[3] If we measure distances in units of R, times in units of R^2/D_0 and concentrations in units of c_m, eq. (6) becomes in a comoving frame $\partial\tilde{c}/\partial\tilde{t} = -Pkc_m^{2/3}\tilde{c}\,\partial\tilde{c}/\partial\tilde{z} + \bar{\nabla}^2\tilde{c} + \tilde{\xi}$. Here the dimensionless quantities are indicated by a tilde and, for the case of conserved noise, $\langle \tilde{\xi}(\tilde{r}, \tilde{t})\ \tilde{\xi}(\tilde{r}', \tilde{t}') \rangle =$ $= 8\pi/3\bar{\nabla}^2 \delta(\tilde{r} - \tilde{r}') \delta(\tilde{t} - \tilde{t}')$. Thus, in order that the strength of the nonlinear term is comparable to the diffusion term on the scale of the interparticle distance R, we need $Pkc_m^{2/3} = O(1)$.

[4] In an earlier version of this paper, we mentioned photobleaching as a possible way to study the effect. However, photobleaching probes self-diffusion, not the collective diffusion of interest here.

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