

SEDIMENTATION AND COMPACTION OF CALCIUM CARBONATE AGGREGATING SUSPENSIONS: SCALING ANALYSIS OF THE EQUILIBRIUM

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SÉDIMENTATION ET COMPACTION DE SUSPENSIONS
AGRÉGÉES DE CARBONATE DE CALCIUM: ANALYSE
EN LOI D'ÉCHELLE DE L'ÉQUILIBRE

Les suspensions agrégées se divisent généralement en un surnageant transparent et un sédiment gélifié volumineux. La suspension demeure homogène (gel stable sous l'effet de la gravité) seulement quand la fraction volumique des particules dépasse une valeur donnée Φ^{**} . La présente étude porte sur le calcul de Φ^{**} . Un modèle simplifié décrivant l'équilibre du gel a été mis au point et sa validité est vérifiée en comparant de ses prédictions avec des mesures systématiques du volume du sédiment effectuées sur des suspensions de carbonate de calcium. Si nous appliquons ce modèle à la prédiction de Φ^{**} , nous démontrons que Φ^{**} n'est pas une caractéristique du système physicochimique mais qu'il dépend de la hauteur de l'échantillon, de son rapport d'aspect et des frottements entre le gel et la paroi. Pour les grands (respectivement petits) rapports d'aspect, nous montrons que Φ^{**} est une fonction en loi de puissance de la largeur (respectivement la hauteur) de l'échantillon comportant un exposant $1/(k - 1)$ qui est relié à la dépendance du seuil d'écoulement avec la fraction volumique de la suspension.

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CARBONATE AGGREGATING SUSPENSIONS:
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Aggregating suspensions generally separate into a clear supernatant and a voluminous gelled sediment. The suspension remains homogeneous (i.e. a gel stable under gravity forms) only when the volume fraction of particles exceeds a given value Φ^{**} . The present study is devoted to the determination of Φ^{**} . A simplified model describing the gel equilibrium has been developed and its validity is checked comparing its predictions to systematic measurements of the sediment volume performed on calcium carbonate suspensions. Applying this model to the prediction of Φ^{**} , we show that Φ^{**} is not a characteristic of the physico-chemical system but depends on the height of the sample, its aspect ratio and friction between the gel and the side wall. For large (respectively small) aspect ratios, we find that Φ^{**} is a power law function of the width (respectively the height) of the sample involving an exponent $1/(k - 1)$ which is related to the dependence of the yield stress on the volume fraction of the suspension.

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SEDIMENTACIÓN Y COMPACTACIÓN DE
SUSPENSIONES DE AGREGADOS DE CALCIO :
ANÁLISIS DE ESCALA DES EQUILIBRIO

Las suspensiones agregadas se dividen, por lo general, en una fracción transparente que sobrenada y un sedimento geleficado voluminoso. La suspensión quedarse homogénea (gel estable sobre el efecto de la gravedad) únicamente cuando la fracción de volumen de partículas sobrepasa un valor determinado Φ^{**} . El presente estudio presenta un al cálculo de Φ^{**} . Se ha desarrollado un modelo simplificado que describe el estado de equilibrio del gel, cuya validez esta verificado mediante una comparación de sus predicciones con mediciones sistemáticas del volumen de sedimento debajo de suspensiones de carbonato de calcio. Si se aplica este modelo para la predicción de Φ^{**} , se demuestra que Φ^{**} no constituye una característica del sistema fisicoquímico pero que, en cambio depende de la altura de la muestra, de su relación de tamaño y de las fricciones entre el gel y la pared. Para los grandes (respectivamente, pequeños) relaciones de tamaño, se mostra que Φ^{**} esta siguiendo una ley de potencia de la anchura (respectivamente, la altura) de la muestra con un exponente $1/(\kappa - 1)$ que guarda relación con la dependencia del límite de flujo con fracción volumétrica de la suspensión.

INTRODUCTION

The stability of colloidal suspensions under gravity is of great importance in many practical applications. Various processes involve the separation of the fine solids from a fluid by destabilization and settling. On the contrary, separation should be avoided in other situations as drilling operations. In the past decade, many works have been devoted to the understanding of aggregation phenomena in colloidal suspension from a fundamental point of view [1 - 4]. By contrast, only few studies have considered the coupling between aggregation and sedimentation which is particularly important when the particle density is large compared to 1 [5 - 8]. In that case, suspension separation is avoided only if the suspension gels very rapidly and does not collapse under its own weight.

In a previous work, we have shown that the coupling between aggregation and sedimentation leads to three distinct behaviours depending on the volume fraction of particles in the suspension, Φ [7]. At small volume fractions, $\Phi < \Phi^*$, settling by cluster deposition is observed. At the beginning of the phenomenon, the aggregates are tiny and their displacement is mainly controlled by diffusion. When their size becomes large enough, their displacement is then controlled by sedimentation: they settle individually and deposit onto the cell bottom forming a voluminous sediment which compacts slowly until equilibrium. At larger volume fractions, $\Phi^* < \Phi < \Phi^{**}$, a collective behaviour is observed. The aggregates no more settle separately; a close packing of aggregates filling the whole cell (i.e. a gel) forms very rapidly and collapses under its own weight. A sharp interface separates the solvent clear of particles from the other part of suspension; it moves down until it reaches its equilibrium height. Finally, when $\Phi > \Phi^{**}$, the suspension is stable and does not separate under gravity. Experimental investigations performed on calcium carbonate suspensions have shown that the volume fraction Φ^* is $\approx 3 \times 10^{-3}$. This very low value has to be related to the fractal properties of the aggregates formed by irreversible growth. A scaling analysis based on the comparison between the gel time and the time corresponding to the cross-over from diffusive to settling displacement allows to predict Φ^* . A good agreement with the experimental value has been found [7].

The present work deals with the volume fraction Φ^{**} which separates settled suspensions from

stable suspensions. We have developed a simplified model describing the irreversible compaction and the equilibrium of a gel under its own weight. It allows to predict Φ^{**} and the relative volume occupied by the sediment ($\Omega = H_s/H$) when $\Phi < \Phi^{**}$ (H_s is the sediment height at equilibrium and H the sample height). To check the validity of our model, we have performed systematic experiments on calcium carbonate suspensions. Ω has been measured in a broad range of experimental conditions varying the volume fraction of the suspension, the height H , and the diameter D of the experimental cell. The paper is organised as follows. In section 1, we describe the preparation of the suspensions, and the method of measurement and its accuracy. Section 2 is devoted to the presentation of the experimental results. In section 3, we present our model describing the gel equilibrium and we discuss the predictions obtained for the sediment height in relation with the experimental results. Section 4 concerns to Φ^{**} ; a scaling analysis allows to determine the gel stability conditions and to predict the variation of Φ^{**} with the height and the width of the sample.

1 MATERIALS AND METHODS

1.1 Samples and preparation

The experiments were performed with aqueous dispersions of calcium carbonate (Socal U1 supplied commercially by *Solvay Co*). This system has been chosen because of the large density of the particles ($\rho = 2.7 \text{ g/cm}^3$). Thus settling takes place rapidly and gravity influence is expected to be large. The particles of Socal U1 are prepared by precipitation. This ensures a good chemical purity and an almost spherical shape. Their radius (a) is equal to 35 nm. In water, the surface charge of the particles is controlled by the concentration of calcium and carbonate ions in the suspending medium. Under our experimental conditions, (free atmosphere, $[\text{Ca}^{2+}] \approx 10^{-4} \text{ mol/L}$, pH ranging between 8.7 and 9.2), the charge borne by the surface of each particle is very small ($\psi_s < 10 \text{ mV}$) [6]. The colloidal interaction is given by the Van der Waals attraction without electrostatic repulsion.

The samples are prepared by adding a weighed amount of calcium carbonate under powder form to deionized water (quality Milli- μ). In order to well

disperse the particles, a strong stirring is applied for at least 100 h and all the manipulations and storage are performed under continuous stirring. Previous observations done by optical and electronic microscopy for $\Phi \leq 5 \times 10^{-3}$ had checked the efficiency and the reproducibility of the dispersion state obtained following this protocol; no cluster having a diameter larger than about 0.1 μm can be found in the suspension [6].

1.2 Measurement of the relative volume occupied by the sediment, Ω

The experiments were carried out in cylindrical cells made from *Plexiglas*. A broad range of height and diameter was investigated: H was varied from 2 to 320 mm, and D from 7 to 44 mm. Volume fractions ranging from 10^{-4} to 1.2×10^{-2} were investigated. Note that since $\Phi^* \approx 3 \times 10^{-3}$, the studied samples belong both to the dilute and semi-dilute regimes ($\Phi < \Phi^*$ and $\Phi > \Phi^*$). The experimental results show no change in the variations of Ω for $\Phi \approx \Phi^*$.

Before each experimental run, the cells are carefully cleaned to ensure a good reproducibility of the surface properties which govern the friction between the gel and the vertical wall of the cell. They are first left in an ultrasonic bath for about 30 min, then they are rinsed with deionized water and dried using a special paper. No cleaning liquids or organic solvents were used. To avoid that a meniscus forms at the top of the suspension, the cells are first filled up to a level above the final height and then closed with perforated plugs which allow the air and the excess of suspension to go out. The cells being completely filled of suspension, the sample volume and its height can be accurately defined.

The measurements were performed with a cathetometer having a resolution of $5 \times 10^{-2} \text{ mm}$. The reproducibility on the determination of the relative sediment height Ω is good, $\Delta\Omega = 0.01$, for runs performed with a same suspension. However, larger irreducibilities are observed from one sample to another: typically for $\Phi = 0.05$, $\Delta\Omega = 0.05$. This is due to the difficulty to prepare well dispersed aggregating suspensions. Ω was measured 24 h and 48 h after the suspension has been poured in the cell. If a difference is observed between the two determinations, showing that the equilibrium has not been reached after 24 h, new measurements are done later.

2 RESULTS OF THE SEDIMENT VOLUME MEASUREMENTS

Figure 1 presents the variation of the relative sediment volume Ω as a function of the volume fraction of particles in the suspension Φ . Even for low values of Φ , Ω is large i.e. the sediment is very voluminous, and the increase of Ω versus Φ is not linear. This differs from the case of usual non colloidal suspensions. Then, the sediment is formed by a close packing of particles which does not deform under its own weight. The volume fraction in the sediment is uniform and is about $\Phi_{cp} \approx 0.63$ for random close packing of beads. Setting the conservation of the total volume of the particles, Ω_{nc} (for a non colloidal suspension) expresses as:

$$\Omega_{nc} = \frac{H_s}{H} = \frac{\Phi}{\Phi_{cp}} \quad (1)$$

The values of Ω_{nc} calculated from (1) ($\Omega_{nc} \approx 0.008$ for $\Phi = 0.5 \times 10^{-2}$) differs by about two orders of magnitude from the value observed with calcium

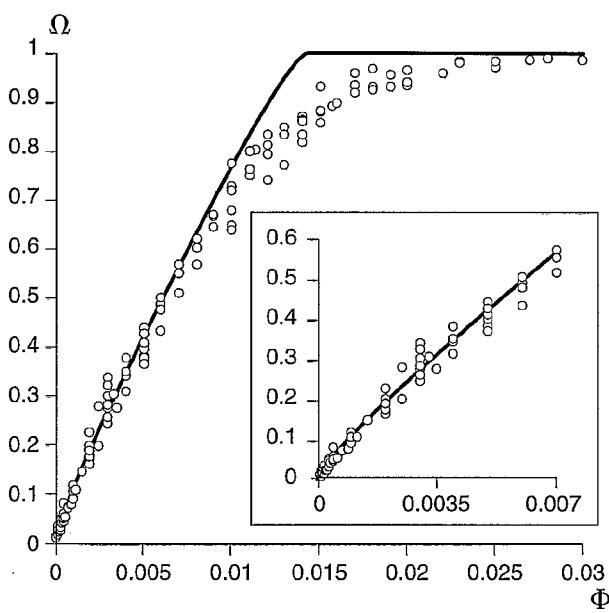


Figure 1

Relative sediment volume Ω versus particle volume fraction Φ . The sample is $H = 70$ mm height and its diameter is $D = 12$ mm. The lines drawn in full correspond to the predictions of the simplified model described in section 3. Inset: detail of the variation observed for low values of Φ .

carbonate suspensions. Furthermore, Ω does not increase linearly contrary to that expected from (1).

The variation of Ω versus the sample height H is shown in Figure 2. A large decrease with H is observed, up to a factor 2 for H varying from 2 to 320 mm. This observation reveals the compaction of the gel under its own weight. Indeed, when the sediment is incompressible as in non colloidal suspensions, Ω is independent of H (equation (1)). Here, for increasing H , the stress at the bottom of the sample increases and the local value of the volume fraction, φ , becomes larger. Then, since the sediment is more concentrated, its relative volume is lower.

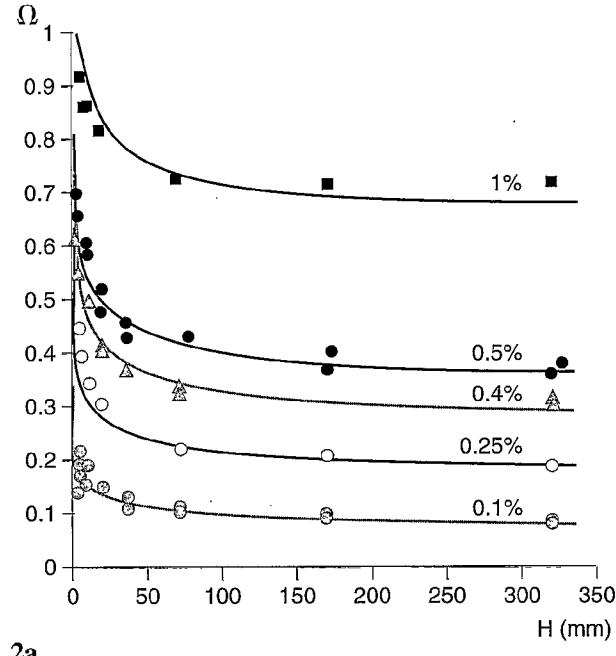
Figure 3 presents the variation of Ω as a function of the cell diameter D . Here again, contrary to the case of non colloidal suspensions, Ω varies with D . For large values of D , Ω is constant; as D decreases, Ω increases. This is due to the existence of a friction between the gel and the vertical cell side. This friction hinders gel compaction and so leads to larger value of the sediment volume.

3 IRREVERSIBLE COMPACTION

To model the equilibrium of the sediment, we use a simplified description of the gel mechanical properties. Firstly, we assume that elastic deformations are negligible and that under a compressive stress σ exceeding the yield stress σ^Y , the gel collapses, i.e. its local volume fraction φ increases until $\sigma^Y(\varphi)$ exactly balances the stress σ . Secondly, σ^Y is assumed to depend solely on φ and to follow a power law variation:

$$\sigma^Y(\varphi) = \sigma_0 \varphi^\kappa \quad (2)$$

σ_0 represents the prefactor and is related to the interaction potential between two particles [9]. The exponent κ is known to be very large. Rheological investigations and measurements done either under centrifugal acceleration or pressure filtration have shown that κ is of the order of 4 to 5 [10, 11, 12]. Finally, we assume that friction between the gel and the cell side is at the origin of a wall stress σ_w equal to $\sigma_w = \mu \alpha \sigma$ where μ is the usual friction coefficient involved in law of Amonton and α is a constant which relates the radial stress to σ . Note that, although this description of friction is exact for usual solids, for a compacted gel, $\mu \alpha$ may depend on σ , φ or on the



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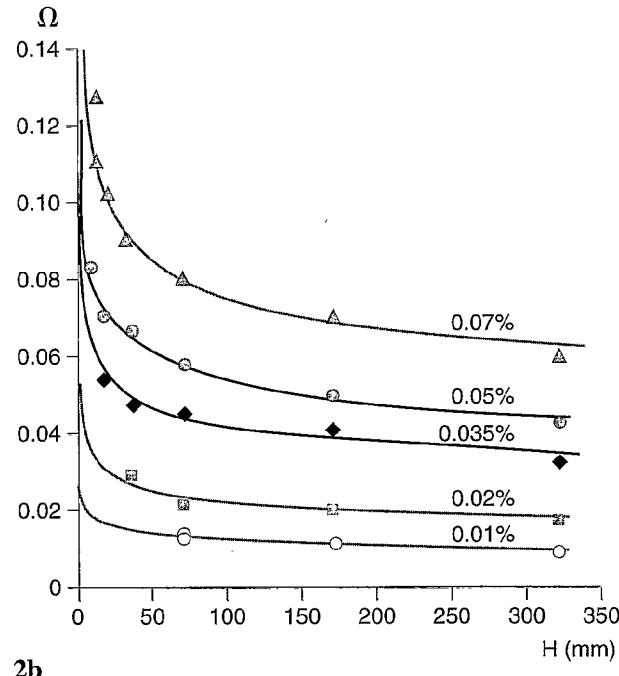


Figure 2

Relative sediment volume Ω versus the sample height H for different values of the particle volume fraction Φ :
a: $\Phi \geq 0.001$, b: $\Phi < 0.001$.
The diameter is $D = 12$ mm. The lines drawn in full correspond to the predictions of the simplified model described in section 3.

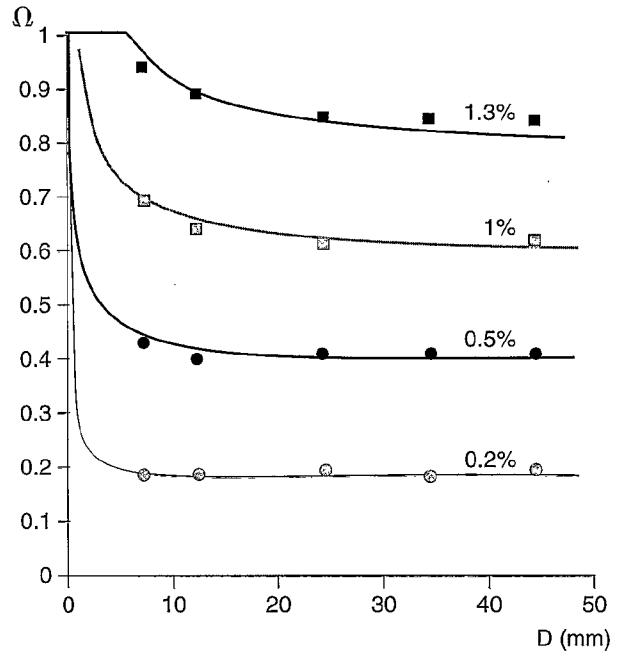


Figure 3

Relative sediment volume Ω versus the sample diameter D for different values of the particle volume fraction Φ , $H = 70$ mm. The lines drawn in full correspond to the predictions of the simplified model described in section 3.

history of compaction. In the following, we do not consider such effects and we assume that $\mu\alpha$ is constant.

With these assumptions, the balance of the forces on a volume element gives (see Fig. 4):

$$-\Delta\rho g\varphi = \frac{\partial\sigma}{\partial\varphi} \frac{d\varphi}{dz} - \frac{4\mu\alpha}{D} \sigma \quad (3)$$

where $\Delta\rho$ is the difference between the density of the particles and that of the solvent and g is the acceleration of gravity. z axis is oriented upwards (Fig. 4). The resolution of this equation allows to calculate the variations of σ and φ versus the height z in the sample. Ω can be found from the conservation of the total particle volume [13].

To check the validity of this simplified description, we have compared its predictions to systematic measurements of Ω performed on calcium carbonate suspensions (see section 2). The full line drawn on figures 1, 2 and 3 correspond to the predicted values for Ω setting $\sigma_0 = 5 \times 10^{10}$ Pa, $\kappa = 5.5$ and $\mu\alpha = 0.2$ [9].

The values of σ_0 and κ have first been determined fitting the data in the domains where friction is negligible. Then, $\mu\alpha$ has been determined from the entire dependence of Ω on H and D . On the whole, a good agreement with the experimental data is observed, although some discrepancies are observed in particular, in the dependence of Ω versus Φ at large values of Φ . In practice, above $\Phi \approx 0.01$, a good dispersion of the suspensions is difficult to ensure. By increasing the size of the elementary units, this decreases the effective volume of the clusters and leads to smaller values of Ω . The observed discrepancies may also be related to a poor description of the friction between the gel and the vertical cell side. Calculations including a dependence of $\mu\alpha$ on φ and/or compaction state are under progress.

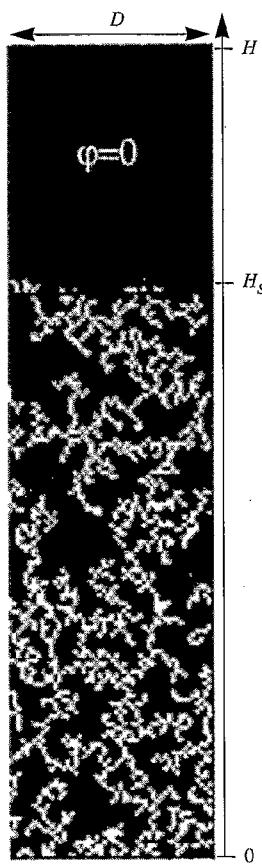


Figure 4

Schematic illustration of a sediment equilibrium. The picture comes from a simulation of cluster-cluster aggregation in the presence of gravity.

4 SCALING PROPERTIES OF Φ^{**}

The stability of gelled suspensions under gravity involves two different characteristic lengths: one vertical and another horizontal. Let us first consider Λ the vertical characteristic length which is the sole involved in the absence of friction with the vertical cell side ($\mu\alpha \rightarrow 0, D \rightarrow \infty$). For a stable homogeneous gel, the maximum of the compressive stress, which is observed in $z = 0$, is equal to $\Delta\rho g H \Phi$. Comparing this value to the yield stress $\sigma^Y(\Phi)$ leads to define:

$$\Lambda = \frac{\sigma^Y(\Phi)}{\Delta\rho g \Phi} = \frac{\sigma_0 \Phi^{\kappa-1}}{\Delta\rho g} = \Lambda_0 \Phi^{\kappa-1} \quad (4)$$

Then, the gel stability under gravity expresses as:

$$\begin{aligned} H \leq \Lambda & \quad \text{stable} \\ H > \Lambda & \quad \text{unstable} \end{aligned} \quad (5)$$

It is to note that, as Λ is an increasing function of Φ , the stability condition $H = \Lambda$ takes place for a value of H which is not a constant and increases with Φ . Another way to express the inequalities (5) is:

$$\begin{aligned} \Phi \geq \Phi^{**} & \quad \text{stable} \\ \Phi < \Phi^{**} & \quad \text{unstable} \end{aligned} \quad (6)$$

with:

$$\Phi^{**} = \left(\frac{H}{\Lambda_0} \right)^{1/(\kappa-1)} \quad (7)$$

This demonstrates that the volume fraction Φ^{**} is not an intrinsic property of the suspension but depends on the sample height. For example, for calcium carbonate suspensions $\Lambda_0 = 3 \times 10^6$ m, we find $\Phi^{**} = 0.02$ for $H = 10$ cm, and $\Phi^{**} = 0.036$ for $H = 100$ cm.

Let us now consider the other limit where the equilibrium is only controlled by the friction with the side wall. Then, the stress is independent of z and equal to $(1/4\mu\alpha)D\Delta\rho g \Phi$. Comparing this value to the yield stress leads to introduce Γ , the horizontal characteristic length scale:

$$\begin{aligned} \Gamma &= \frac{\sigma^Y(\Phi)}{(1/4\mu\alpha)D\Delta\rho g \Phi} = \frac{4\mu\alpha\sigma_0\Phi^\kappa}{\Delta\rho g \Phi} \\ &= \Gamma_0 \Phi^{\kappa-1} = 4\mu\alpha\Lambda = 4\mu\alpha\Lambda_0 \Phi^{\kappa-1} \end{aligned} \quad (8)$$

The gel stability then expresses as:

$$\begin{aligned} D \leq \Gamma & \quad \text{stable} \\ D > \Gamma & \quad \text{unstable} \end{aligned} \quad (9)$$

As previously, we find that the cross-over $D = \Gamma$ takes place for a value of D which increases when Φ increases. The inequalities (9) can also be expressed as (6), Φ^{**} being now given by:

$$\Phi^{**} = \left(\frac{D}{\Gamma_0}\right)^{1/(\kappa-1)} = \left(\frac{D}{4\mu\alpha\Lambda_0}\right)^{1/(\kappa-1)} \quad (10)$$

Finally, let us consider the general case where the gel equilibrium involves at the same time compressive stress and friction i.e. where both Λ and Γ are involved. Different cases can be distinguished following the aspect ratio of the cell. If the ratio H/D is larger than $\Lambda/\Gamma = 1/(4\mu\alpha)$ the compressive stresses are dominant and the gel stability is controlled by (6) and (7). On the contrary, if H/D is smaller than Λ/Γ then friction is dominant and the gel stability is controlled by (6) and (10). Typically, the value of $4\mu\alpha$ is expected to be of the order of 1 ($\mu\alpha \approx 0.2-0.3$) thus, the cross-over between compressive stress to friction dominant cases corresponds to $H \approx D$ (when $H \gg D$, friction is dominant while when $H \ll D$, compressive stress is dominant). This last remark shows the importance of taking account of the aspect ratio before to change scale

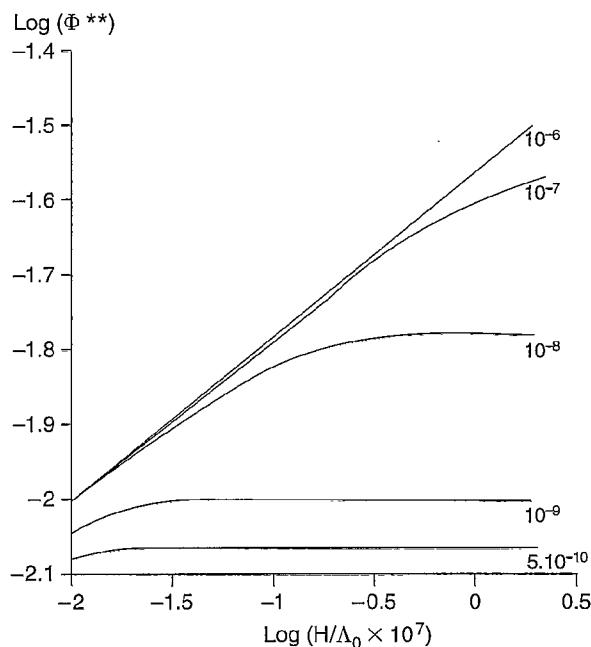


Figure 5

Log-Log plot of Φ^{**} versus the dimensionless height H/Λ_0 for different values of the dimensionless diameter D/Γ_0 .

length and generalise results obtained in laboratory to different situations.

Solving the whole equilibrium problem (see section 3), we can also calculate the dependence of Φ^{**} on H and D for different aspect ratios. Figure 5 shows the variation of Φ^{**} versus H/Λ_0 for different values of D/Γ_0 (the values of σ_0 , κ , and $\mu\alpha$ correspond to calcium carbonate suspensions). For small values of H/Λ_0 , the power law (7) is well verified since the influence of friction is negligible in that case. For large values of H/Λ_0 , Φ^{**} goes to a constant value as expected from (10). The cross-over between the two types of behaviour extends on about a factor 10 in H/Λ_0 ; for increasing D , i.e. decreasing the aspect ratio, its position moves toward larger values of H/Λ_0 as expected. A same type of behaviour is observed for the variation of Φ^{**} versus D .

CONCLUSIONS

Systematic measurements of the relative sediment volume have been performed on aggregating calcium carbonate suspensions. They have been used to establish the validity of a simplified model of the gelled sediment equilibrium. The study of the volume fraction Φ^{**} which separates stable from collapsed suspensions have shown that Φ^{**} is not a characteristic of the physicochemical system but depends on the height of the sample, its aspect ratio and the friction between the gel and the side wall. In the limit of small aspect ratios, Φ^{**} increases from 1.3×10^{-2} to 3.6×10^{-2} when the sample height is increased from 1 cm to 1 m. For large (respectively small) aspect ratios, we show that Φ^{**} is a power law function of D (respectively H) with an exponent $1/(\kappa-1)$ which is related to the dependence of the yield stress on the volume fraction of the suspension.

REFERENCES

- 1 Jullien R. (1992), *Croatica Chem. Acta*, **65**, p. 215.
- 2 Broide M.L. and R.J. Cohen (1990), *Phys. Rev. Lett.*, **64**, p. 2026.
- 3 Carpineti M., F. Ferri, M. Giglio, E. Paganini and U. Perini (1990), *Phys. Rev.*, **A42**, p. 7347.
- 4 Stoll S. and E. Pefferkorn (1992), *J. Colloid Interface Sci.*, **152**, p. 247.
- 5 Couch M. (1993), *Ph.D. Thesis*, Cambridge University.
- 6 Wafra M. (1994), *Ph.D. Thesis*, University of Paris XIII.

- 7 Allain C., M. Cloitre and M. Wafra (1995), *Phys. Rev. Lett.*, **74**, p. 1478.
- 8 Allain C., M. Cloitre and F. Parisse (1996), *J. Colloid Interface Sci.*, **178**, p. 411.
- 9 Senis D. and C. Allain, to be published.
- 10 Alderman N.J., G.H. Meeten and J.D. Sherwood (1991), *J. Non-Newtonian Fluids Mech.*, **39**, p. 291.
- 11 Buscall R., P.D.A. Mills, J.W. Goodwin and D.W. Larson (1988), *J. Chem. Soc., Faraday Trans. 1*, **84**, p. 4249.
- 12 Landman K.A. and W.B. Russel (1993), *Phys. Fluids A*, **5**, p. 550.
- 13 Senis D. and Allain C. (1996), in *Les Cahiers de Rhéologie XV*, p. 35.

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