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Elastic properties of networks of fractal clusters

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Abstract: Elastic properties of casein gels were followed by dynamic measurements for various volume fractions of casein micelles far above the percolation threshold. Elastic and loss storage moduli versus volume fractions obey a power law with an exponent close to 3. The previous theoretical models for networks made of a homogeneous packing of fractal flocs do not predict the observed behavior. A model is proposed to estimate the vectorial contribution to the network elasticity. This model is in agreement with our experimental results. The value of the fractal dimension of the flocs derived from this analysis is discussed as a function of the volume fraction of primary particles.

Key words: Colloidal gels – fractal clusters

Introduction

Aggregation of colloidal particles is involved in many industrial processes. Prediction of the mechanical properties of such flocculated structures is of great interest for many applications in food industry, cosmetics, and soil science. The structures resulting from aggregation strongly depend on the volume fraction of particles in suspension. At low volume fractions Φ ($\Phi \ll 1$) aggregation leads to clusters with finite size [1]. Both simulations and experimental studies on model colloids established the fractal nature of these clusters [2, 3]. The fractal dimensions range from 1.78 to 2.04 depending on the aggregation conditions. The flocculated suspensions are commonly viscoelastic, with the viscosity depending on the deformation rates [4].

With increasing volume fractions, an infinite cluster appears that ensures particle interconnection throughout the whole suspension. At the percolation threshold ($\Phi \cong \Phi_g$) aggregation leads to disordered networks characterized by a large distribution of cluster size. The percolation theory predicts that the fractal dimension of the network is 2.52 at any scale. Two models for the network elasticity are known: the scalar elasticity attributed to the compression of bonds between particles seen as springs and the vectorial elasticity which accounts for their angular deformation. The elastic modulus of the permanent cross-linked network obeys a power law $G \sim (\Phi - \Phi_g)^t$ with $t = 2$ for scalar elasticity and $t = 4$ for vectorial elasticity [5].

When the particle volume fraction is increased far above the percolation threshold ($\Phi \gg \Phi_g$), aggregation leads to a homogeneous network. By analogy with polymer gels, the structure of a colloidal gel has been described as a homogeneous packing of monodisperse fractal flocs, the gel being homogeneous at large scales [1, 6–11]. Light-scattering studies on silica particle gels have evidenced a characteristic length R, which depends on the volume fraction of particles [1]. The experiments have pointed out that i) the gels have a fractal structure for length scales shorter than R, the fractal dimension being apparently characteristic of the aggregation process, and ii) the gels behave like a collection of nearly randomly distributed scattering centers for length scales greater than R.

In this paper, we are concerned with the mechanical properties of colloidal gels far above the percolation threshold. We performed rheological measurements on enzyme-induced casein gels at different volume fractions and determined the volume fraction dependence of the elastic modulus. Our experimental results are not in agreement with previous theoretical predictions. A brief statement of theoretical models is made. We propose a new model which allows to estimate the vectorial contribution to the gel elasticity far above the percolation threshold.

Experimental

The high stability of the casein micelle suspensions is not only due to electric repulsions between micelles, but also to a steric effect ascribed to the protuberant glycomacropeptide of the κ casein surrounding the micelles [12]. The cleavage of the macropeptide under enzyme action leads to the formation of a homogeneous network [13]. Numerous experimental investigations have been performed on the coagulation kinetics and on the rheological behavior of casein gels [11, 14–21]. However, there are significant discrepancies between reports, especially concerning the volume fraction dependence of the complex dynamical moduli of the gels. We performed dynamic measurements in the linear regime of deformation of casein gels.

Milk samples were reconstituted by a standard procedure using distilled water containing 0.03% of NaN_3 as an antibacterial. The skimmed milk powder was provided from N.I.Z.O. (Ede, Netherlands). Samples were stored for 16 h at 30 °C to ensure complete hydration of casein micelles. Casein concentration was varied between 2.13 and 6.67% with appropriate amount of milk powder. The pH and the conductivity of suspensions were measured. The volume fraction Φ was derived from relative viscosity measurements performed with a Low Shear 30 Contraves at 30 °C, they whey being obtained by centrifugation after a fast coagulation following the addition of a large amount of enzyme.

Rennet powder was obtained from Hansen laboratory (Saint-Germain les Arpajons, France). The powder contains 4438 mg of active Chymosin and 63 mg of bovine pepsin per kg. Rennet solutions were prepared shortly before required in 0.5 M acetate buffer pH 5.5 and 0.1% of bovine serum albumin. For all experiments the ratio E/C, E being expressed in mg of chymosin per liter of the total solution and C in mg casein per liter, was kept constant. In these conditions it has been shown by Tokita et al. [15] that the time variations of the elastic modulus can be merged into a master curve by a simple shift along G axis. With a ratio of 2.1×10^{-5} the aggregation of micelles starts about 15 min following the addition of the enzyme. This latent time corresponds to the enzymatic hydrolysis since 90% of a micelle's κ-casein has to be hydrolyzed before the aggregation can start [22, 23].

Dynamic measurements were carried out using a Weissenberg rheogoniometer with cone/plate geometry. A sinusoidal rotating movement was applied to the lower plate and the movement of the upper cone was recorded. The frequency range was 0.0015 to 1.5 Hz and the imposed strain was limited to 2% to allow a linear regime of deformation.

Milk and rennet were mixed together by gently stirring for 30 s and poured into the apparatus between the cone and the plate at time $t = 0$. A thin film of paraffin was added to minimize evaporation. Temperature was controlled at 30 °C ± 0.1 °C. The first measurement was made after 30 min in order to avoid disturbing the network formation. Then, the complex modulus was measured versus time at a fixed frequency of 0.1582 Hz. The frequency dependence of the moduli were examined for the coagulum aged for 360 min.

Experimental results

Characterization of the casein suspensions

Both the pH and the conductivity of the casein suspensions vary with the amount of casein, as represented in Fig. 1. The Newtonian relative viscosity μ_R of the suspension versus the casein concentration is plotted in Fig. 2. Various empirical viscosity laws have been applied to describe the viscosity of a suspension of casein micelles [24]. Eilers equation requires that the voluminosity does not depend on the casein content. Since this hypothesis is not trivial [12], we applied the viscosity law valid for hard spheres in concentrated suspension interacting hydrodynamically [4]. This law was in a good agreement with experimental results on red cell suspensions [25]. The volume fraction of a casein micelle suspension containing 2.67% of casein was found at 0.108.

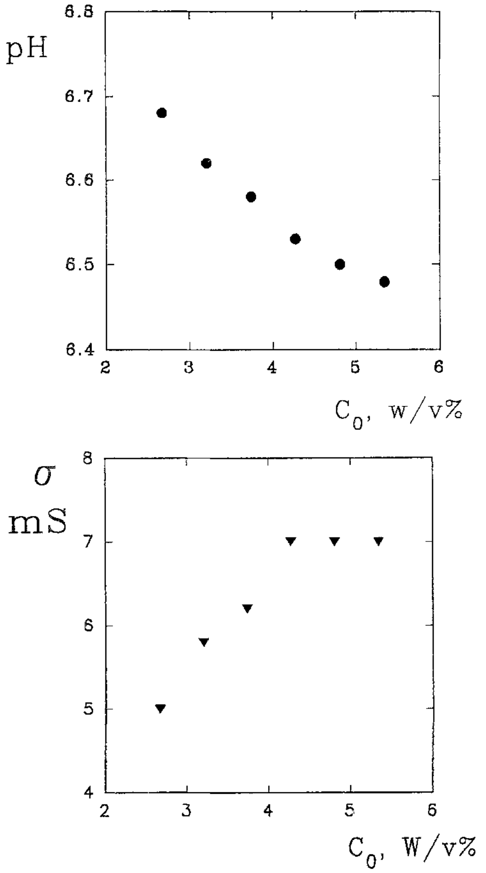

Fig. 1. Effect of the casein concentration C (% w/v) on the pH (a), and on the conductivity (b) of the milk powder suspensions measured at 30 °C. Casein concentrations were altered by varying the amount of skimmed milk powder.

This value is consistent with other experimental data. For a fixed casein concentration (2.67% w/v), we found that the volume fraction of micelles derived from relative viscosity depends on the pH and varies by addition of the appropriate amount of HCl (see Fig. 3). For casein suspensions a linear relationship between the volume fraction Φ and the casein concentration was obtained from volume fractions up to 0.30. For $\Phi > 0.30$, The Newtonian plateau could not be measured for the lowest available shear rates [12]. This behavior is due to the subtle balance of the salt and casein distribution between the aqueous phase and the casein micelles.

Elastic properties of casein gels

For very low volume fractions ($\Phi < 0.03$) a homogeneous network was obtained under enzyme action, but it did not sustain the rheological measurements without disturbance. Thus, our investigations were confined to the range $0.1 < \Phi < 0.30$.

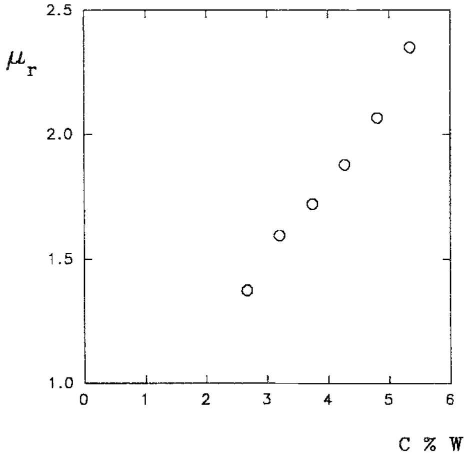

Fig. 2. Relative viscosity measured with a Low Shear 30 Contraves at 30 °C versus the casein concentration of suspensions. Casein concentrations were altered by varying the amount of skimmed milk powder.

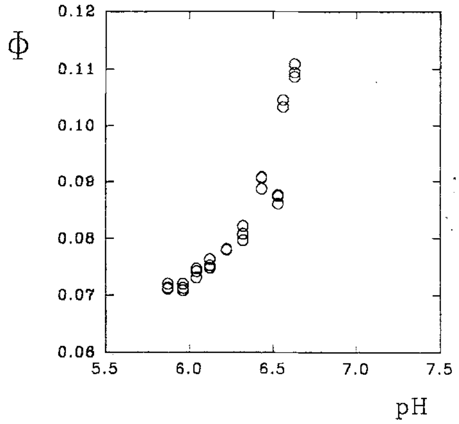

Fig. 3. The volume fraction Φ of the casein micelles as a function of the pH. The pH was varied by adding the appropriate amount of HCl. The casein concentration was 2.67% w/v. Φ was derived from the relative viscosity of milk at 30 °C by applying a viscosity law [4].

The elastic modulus G' of the gels tends to reach a plateau for times greater than 200 min as represented in Fig. 4a for different volume fractions. A closer examination shows a slight increase of G' versus time for long aging times ($t > 300$ min), the rate of increase depending on the volume fraction. For all volume fractions, the

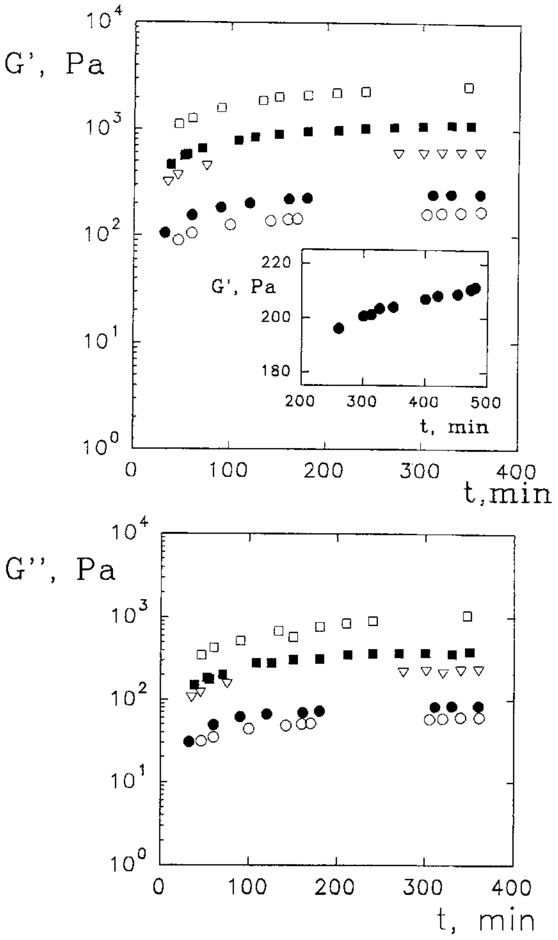

Fig. 4. Time (t) variations of the elastic moduli G' (a) and the loss moduli G'' (b) at different volume fraction (○ 0.10; ● 0.13, ▽ 0.17; ■ 0.25, □ 0.30) in a semi-logarithmic scale. The time zero corresponds to addition of the enzyme; temperature was 30 °C, the enzyme and casein concentration ratio was $E/C = 2.15 \times 10^{-5}$, frequency was 0.158 Hz. The insert in figure a shows the linear variation of the elastic moduli G' for the volume fraction $\Phi = 0.13$ for times longer than 350 min.

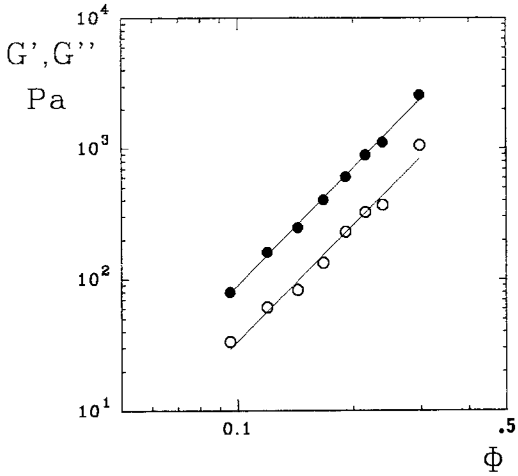

Fig. 5. Storage modulus G' (●) and loss modulus G'' (○) measured at 360 min as a function of the volume fraction (Φ) plotted using double logarithmic scales; temperature was 30 °C, the enzyme/casein concentration ratio, $E/C = 2.15 \times 10^{-5}$, frequency was 0.158 Hz.

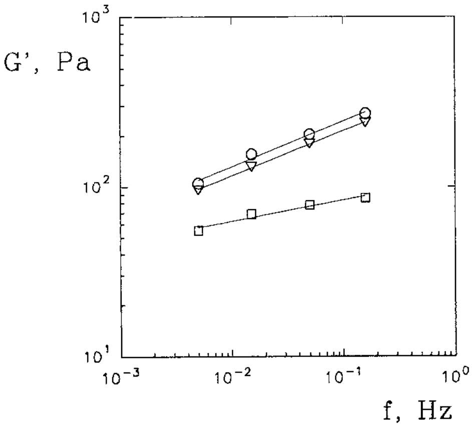

Fig. 6. Storage modulus G' at 360 min (▽) and at 1440 min (○) and loss modulus G'' at 360 min (□) as a function of the frequency f. The volume fraction of the casein gel was $\Phi = 0.10$, temperature was 30 °C, the enzyme/casein concentration ratio, $E/C = 2.15 \times 10^{-5}$.

loss moduli G'' were less than one order of magnitude below the storage moduli and showed a similar time dependence (Fig. 4b).

The volume fraction dependence of the elastic moduli G' and G'' was recorded at a fixed time $t = 360$ min. Assuming a power law, the regression gave $G' \propto \Phi^3$ and $G'' \propto \Phi^{2.7}$ with regression coefficients respectively equal to 0.996 and 0.982 (Fig. 5). Figure 6 illustrates the frequency dependence of the elastic moduli. No permanent elasticity can be evidenced. Such a relaxation was observed for all casein concentrations and also for longer aging times (1440 min). A linear regression gave the following frequency ω dependence of the elastic moduli at 360 min: $G' \propto \omega^{0.2}$ and $G'' \propto \omega^{0.15}$. This behavior was previously observed by numerous investigators [16, 10, 26]; it is also consistent with relaxation experiments performed by Johnston [14].

Discussion

Many rheological experiments, including relaxation, creep techniques, and oscillatory shear, show the liquid-like behavior of enzyme-induced casein gels at long time. This long time behavior can be compared to the behavior of concentrated silica suspensions and silica gels considered as model systems [27]. It is usually ascribed to the finite lifetime of links involved in the network and is shared by many physical colloidal gels. In the linear regime of deformation, the network elasticity can be characterized either by the storage modulus measured at a constant and low frequency, or by the instantaneous modulus measured by creep and corresponding to the high-frequency limit. The volume fraction dependence of the elastic moduli (either storage or instantaneous moduli) appears to be dependent on the suspension and on the experimental procedure. In the next section, we summarize the theoretical models which predict scaling behavior of network elasticity and examine their agreement with our experimental study.

Previous experiments and theoretical models

Our discussion deals with colloidal gels well above the gelation threshold which are not described by the percolation theory. The 3D network structure is seen as a homogeneous packing of fractal flocs. The characteristic size R of flocs refers to the maximum length on which the fractal behavior survives. For a given volume fraction of particles Φ, R is given by

$$\frac{R}{a} = \Phi^{\frac{1}{D-3}} \quad R \gg a\,, \tag{1}$$

where a is the radius of the elementary particles and D the fractal dimension inside the flocs which may be assimilated to the fractal dimension of the primary aggregates.

From the elasticity of individual flocs, Ball and Brown predicted that the shear modulus of the gel should scale like:

$$G \propto \Phi^{\mu} \quad \text{with} \quad \mu = \frac{3 - d_{\text{chem}}}{3 - D}\,, \tag{2}$$

where d_{chem} is the so-called chemical length exponent [28]. For chemically limited aggregation ($D = 2.04$) the theoretical power-law index is $\mu = 4.5$ and for diffusion limited aggregation, ($D = 1.78$) $\mu = 3.5$. Buscall et al. studied both the influence of the volume fraction Φ and the size of the particles a on the instantaneous elastic modulus of various colloidal gels [8, 29–32]. Experimental results were consistent with the theoretical predictions of Ball and Brown: a strong volume fraction dependence is observed with an exponent $\mu \approx 4$ over the volume fraction range $0.05 < \Phi < 0.3$ for latex particles with radii between 0.16 and 0.5 μm. A much stronger dependence is observed ($\mu \approx 10$) for either lower or higher radii (0.085, 0.03, 2.1 μm) of latex particles [32]. For small particles this is attributed to more compact floc structures, as revealed by electron microscopic studies. An exponent $\mu \approx 3$ can be found by fitting data on latex particles of radii 38 nm in the volume fraction range 0.146 to 0.303 [30]. Buscall et al. did not clearly observe a power law behavior for attapulgite clays [32]. No scaling exponent could be derived either from experiments performed with silica gels at very low volume fractions ($0.05 < \Phi < 0.07$) [32].

More recently, Shih et al. assumed that the elasticity of individual flocs was dominated by their "effective backbone", which was approximated to a linear chain of springs [7]. A spring represents a bond between two adjacent particles in a floc. Shih et al. introduced the fractal dimension x of the backbones which could be different from the fractal dimension of the floc D. Assuming that the bending constant between two neighboring springs is independent of particle concentration and considering that the bending contribution dominates the elastic behavior of a long chain, compared to the stretching contribution, they found that the elastic constant of individual flocs rapidly decreases with increasing size R of the flocs. As a consequence, they distinguished two regimes: i) in the strong-interfloc-link regime, corresponding to a moderate volume fraction range, the links between flocs have a higher elastic constant that those of the flocs. The network elasticity is dominated by the behavior of the elastic constant of the individual flocs. The shear modulus of the gels then scales like:

$$G \propto \Phi^{\frac{3+x}{3-D}} \quad \text{with } 1 < x < D\,. \tag{3}$$

If $D \approx 2$, the scaling exponent varies from 1 to 2.

ii) in the weak-interfloc-link regime, corresponding to higher volume fraction range, the elasticity of the network is dominated by the elastic constant of interfloc links. In this case, Shih et al. derived the scaling law:

$$G \propto \Phi^{\frac{1}{3-D}} . \tag{4}$$

If $D \approx 2$ the elastic modulus is then proportional to the volume fraction.

The storage moduli of two boehmite alumina gels (Catapal and Dispal) obtained by addition of an excess of electrolytes were measured at various oscillating strain amplitudes with low angular frequencies (0.7 rad/s for Catapal gels and 1 rad/s for Dispal gels). The storage modulus G' was constant with strain amplitude at small strain. The Catapal gel was studied at constant pH, while the Dispal gel was studied at a constant electrolyte concentration. The particle volume fraction ranged from 0.03 to 0.1, the gel threshold being $\Phi_g \approx 0.01$. These authors found, respectively, $G \sim \Phi^{4.1}$ and $G \sim \Phi^{4.2}$, with the two types of gels in good agreement with their theoretical predictions in the case of strong-link regime. The fractal dimension of the flocs $D = 1.95$ deduced from the rheological measurements is close to the value $D = 2.04$ obtained with static light-scattering experiments on dilute Dispal suspensions.

Neglecting entropy contribution, Bremer et al. suggested that the elastic modulus of a particle network could be written as [9, 10]:

$$G = NL\frac{\partial^2 A}{\partial x^2} , \tag{5}$$

where x is the direction of the external force applied to the gel; N is the number of stress carrying strands per unit area in a cross-section perpendicular to the x direction; ∂A is the change in the Gibbs energy when the particles in the strands are moved apart a distance ∂x, and L is a characteristic length determined by the geometry of the network which relates the deformation of the strands in the gel and the macroscopic shear strain. Bremer et al. [9] have shown that L is independent of the volume fraction Φ, but varies with the elementary particle size.

For scale invariant flocs N is given by:

$$N = \frac{n}{a^2}\Phi^{\frac{2}{3-D}} , \tag{6}$$

where n is the effective number of bonds between flocs.

Assuming that n is constant and considering the *scalar* elastic contribution associated with the stretching of strands, they predicted two power-laws for rigid or curved strands:

$$G = \Phi^{\frac{2}{3-D}} \quad \text{for rigid strands} \tag{7a}$$

$$G = \Phi^{\frac{3}{3-D}} \quad \text{for curved strands ,} \tag{7b}$$

with D being fixed to 2, the elastic modulus scales respectively like $G \sim \Phi^2$ (Eq. 7a) and $G \sim \Phi$ (Eq. (7b)).

Two types of acid casein gels were made from Na caseinate suspensions i) at constant pH = 4.6 by warming solutions from 4 to 30 °C (type 1) and ii) at constant NaCl concentration of 0.14M by varying the pH from 6.7 to 4.6 at 30 °C (type 2) [10, 19]. The angular frequency of the oscillation was kept at 1 rad/s and the deformation was smaller than 2% [19, 10]. Elastic moduli versus caseinate concentration gave an exponent of 2.6 for type (1) gels and 4.6 for type (2) gels. The fractal dimension $D = 2.24$ was derived for type 1 gels using Eq. (7a) and $D = 2.35$ for type 2 using Eq. (7b). It was pointed out by Bremer et al. that the voluminosity (the volume occupied by one g of dried casein in solution) of casein micelles depends both on temperature and on PH. As a consequence, the volume fraction of particles in type 1 gels is higher than the volume fraction of particles in type 2 gels at the same casein concentration [10].

The relation between the dynamic moduli of rennet-induced skimmed milk gels and the casein concentration was investigated with varying the casein concentration by ultrafiltration of the milk, using a constant amount of rennet and measuring the moduli after a long aging time [19]. An exponent of 2.4 was obtained versus the casein concentration, which gave a fractal dimension D of 2.17 [9, 19].

For all the models proposed, a basic question remains about the domain of validity of the scaling behavior. According to Eq. (1), the size of the flocs determines the maximum length on which the network has a fractal structure. As a consequence, an upper limit of the volume fraction Φ_{crit} appears, above which the flocs cannot grow enough and do not have the fractal dimensions observed on dilute suspensions. For high volume fractions ($\Phi > \Phi_{\text{crit}}$) the fractal dimension of the flocs reveals the structure of the network for very short scales around the particle size a, which should be different from the fractal dimension characterizing highly branched aggregates. The review of microscopic studies on acid and rennet milk gels established that strands of casein micelles up to 10 particles long are observed in casein gels. If we assimilate this typical persistence length ($R \approx 10a$) to the maximum size of the flocs derived from Eq. (1) with $D \approx 2$, we find a critical volume fraction $\Phi_{\text{crit}} \approx 0.1$ for enzyme-induced casein gels. The volume fraction range corresponding to our experiments is 0.1 to 0.3. From electron microscopic images, we can assume that the strands of micelles are almost linear and rigid, then a fractal dimension close to 1 is expected. This assumption leads to a volume fraction dependence of $G \propto \Phi$ predicted in Bremer's model by Eq. (7a). However, we observe $G \propto \Phi^{2.7}$, so we have to derive an alternative model for the volume fraction dependence of the elastic moduli of gels made of rigid linear strands, in the regime $\Phi \gg \Phi_g$.

Our model

We consider a colloidal gel as a homogeneous packing of fractal flocs, and we derive the vectorial elasticity associated with the rotation of the cross-links between fractal flocs. Following Bremer et al., we assume that the elastic modulus of the gel obeys Eqs. (5) and (6), and we estimate the number of links between flocs n and the change of the free Gibbs energy associated with the angular deformation.

A simple dimensional analysis gives the probability p to have a particle of size a at the surface of a floc of size R:

$$p = \frac{\mathrm{d}W}{\mathrm{d}R}\,\frac{a^2}{R^2} = \frac{D(R/a)^{D-1}a^2}{a \cdot R^2}\,, \tag{8}$$

where W is number of particles inside a floc of size R, and D is the fractal dimension of the flocs. The number n of cross-links per flocs can be expressed as a function of R/a:

$$n \approx z_0 \cdot p^2 \pi R^2 \approx z_0 D^2 \left[\frac{R}{a}\right]^{2D-4}\,, \tag{9}$$

where z_0 is the coordinance of the network.

The deformation δx of the system submitted to a force δF in the direction x is approximated by:

$$\delta x \propto R\delta\vartheta = \frac{R^2}{k}\,\delta F\,, \tag{10}$$

where k is homogeneous to an energy and $\delta\vartheta$ the angular deformation. In the case of small deformations the change of the Gibbs energy is then derived by:

$$\frac{\partial^2 \delta A}{\partial x^2} \propto \frac{\delta F}{\delta x} \propto \frac{k}{R^2}\,. \tag{11}$$

Introducing expressions (9) and (11) in Eqs. (5) and (6), we obtain the volume fraction dependence of the elastic modulus, which is valid for volume fractions greater than Φ_g:

$$G \propto K\Phi^{\frac{8-2D}{3-D}} \quad \Phi \gg \Phi_g\,, \tag{12}$$

$$\text{with} \qquad K = \frac{z_0 D^2 kL}{a^4}\,.$$

Comparison with experimental results

Two ranges of volume fractions must be considered:

i) for high volume fractions $\Phi > \Phi_{\text{crit}}$ the local structure of the flocs constituting the network of *enzyme-induced casein gels* is almost linear. If we assume a fractal dimension $D \approx 1$, a power law index of 3 is derived from Eq. (12), in agreement with our experimental scaling. Our results are significantly different from other experiments on *acid and rennet gels* [9, 10, 19]. The rheological behavior of casein gels is very sensitive to the experimental procedure. The accurate comparison between experiments requires the measurements of the volume fraction Φ of casein micelles, which depends on casein concentration, pH, temperature and ionic strength. The different scalings observed for types (1) and (2) acid casein gels may correspond to different volume fraction ranges [9, 10, 19].

ii) For $\Phi < \Phi_{\text{crit}}$ the flocs are large enough and the fractal dimension of the flocs is close to the one observed in the dilute flocculated suspensions. In this intermediate volume fraction range the scaling exponent for the elastic modulus strongly depends on the fractal dimension D for

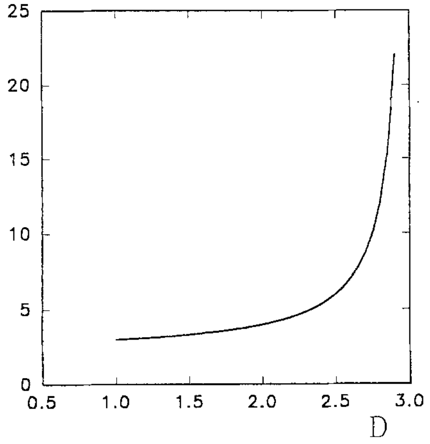

Fig. 7. Theoretical prediction (Eq. 12) of the scaling exponent of the elastic modulus of colloidal gels as a function of the fractal dimension D of the flocs.

$D > 2$, as represented in Fig. 7. The reaction-limited cluster–cluster aggregation model predicts a fractal dimension $D \approx 2$. A power law $G \propto \Phi^4$ can be deduced from Eq. (12) in the intermediate range $\Phi_g \ll \Phi < \Phi_{\mathrm{crit}}$. Restructuring motions available when the interactions between particles are weak may lead to more compact structures and may considerably increase the scaling exponent value. This behavior may explain the high exponent observed by Buscall et al. on small latex particle gels [32].

Still, in this same intermediate range, Buscall et al. [31] underlined that for low volume fractions, the length scale of heterogeneities R of the flocculated structures may be comparable to the annular gap of the couette in which the measurements are made. As a consequence, the measurements may considerably disturb the structure of the gels and produce large experimental variations.

In conclusion, we wish to point out that the length scale on which the structure heterogeneity is developed dramatically influences the mechanical properties of colloidal gels. As a consequence, the scaling behavior of such gels depends on the volume fraction range as summarized in Fig. 8. When the network is heterogenous at any scale, the percolation theory predicts scaling laws depending on the nature of the elasticity (scalar or vectorial). Above the percolation threshold the network is homogeneous at large scale and heterogeneous at a scale R (the mean size of the flocs).

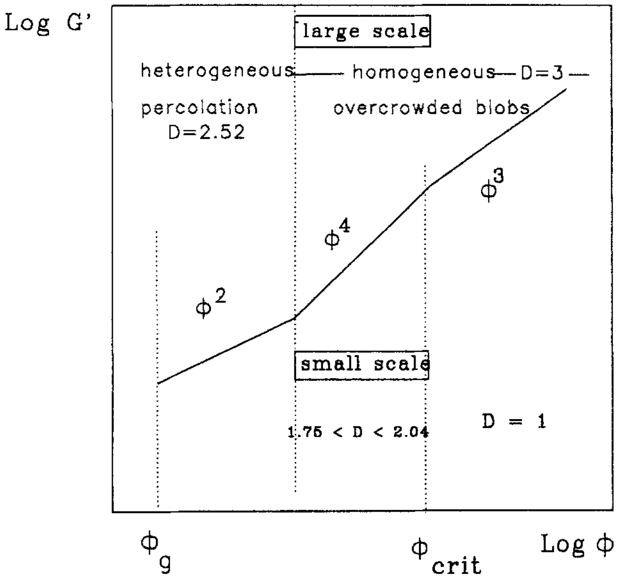

Fig. 8. Typical influence on the heterogenity scale on the scaling behavior of the elastic properties of a colloidal gel. At low volume fractions ($\Phi \approx \Phi_g$) the network is heterogeneous; gelatin is described by the percolation theory. At higher volume fractions, gelation leads to homogeneous networks described by overcrowded fractal clusters. At intermediate volume fraction, the fractal dimension D reveals the initial mechanism of aggregation. Above the critical volume fraction Φ_{crit}, the fractal dimension of the flocs reveals the network structure at very short scale (around the size of the particles). The fractal dimension should differ from the fractal dimension of the primary aggregates.

In moderately concentrated systems, rheological measurements are very sensitive to the fractal dimension D inside the flocs and may then provide a useful indirect determination of D. In more concentrated systems, the fractal dimension D of the flocs should differ from the fractal dimension of the aggregates obtained in dilute suspensions.

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