

Compressive yield stress of depletion gels with variable interaction strength^(*)

E. LATTUADA⁽¹⁾⁽²⁾

⁽¹⁾ *Dipartimento di Chimica, Materiali e Ingegneria Chimica, Politecnico di Milano - Milano, Italy*

⁽²⁾ *Dipartimento di Fisica, Sapienza Università di Roma - Roma, Italy*

received 22 February 2019

Summary. — We studied the stationary sedimentation profiles of colloidal gels in which the arrested phase separation process is driven by depletion forces, obtained by compressing the samples by either natural or artificial gravity in the range between $6g$ and $2300g$. We found that the rheological properties of these gels display a drastic change when the particle volume fraction ϕ exceeds a value ϕ_c which barely depends on the strength of the attractive forces. The compressive yield stress $\Pi(\phi)$, in fact, first grows as a power law of ϕ for $\phi \lesssim \phi_c$ and, then, displays a diverging behavior for larger values of the gel volume fraction, with an asymptotic value similar to the random close packing value for hard spheres. The evidence we collected suggests that ϕ_c essentially coincides with the colloid-rich liquid branch of the metastable coexistence line, rather than with an attractive glass line penetrating inside the coexistence region, for which lower ϕ values, also dependent on the strength of the interactions, are expected.

1. – Introduction

The phase diagram of systems of colloidal particles interacting via a short-ranged attractive potential, as happens, for example, for particles interacting through depletion forces or for certain systems of globular proteins, displays a metastable coexistence gap, which is analogous to the gas-liquid transition for a pure fluid [1]. When a system is quenched inside this gap by increasing the strength of the attractions, it starts undergoing phase separation into a colloid-poor and a colloid-rich phase. The phase separation, however, does not reach completion (except for very shallow quenches) and the system

^(*) This communication was awarded at the SIF National Congress of Trento, 2017, but it is herewith published with the communications awarded in 2018.

gets arrested into a disordered gel phase [2]. Since the coexistence line is rather flat, the binodal and the spinodal lines are pretty close, so that the phase separation proceeds in a way similar to a spinodal decomposition, even when the particle volume fraction is lower than the critical point value. Therefore, while undergoing phase separation, clusters progressively grow up, with a size which is smaller as the quench into the coexistence gap gets deeper [3]. It was also shown [4] that these clusters are much more compact than the ones obtained in the irreversible aggregation of very dilute colloidal suspensions. Therefore, gels forming by arrested spinodal decomposition are constituted by a network of rather compact clusters linked by relatively weak intercluster bonds. These gels usually collapse or compress under the effect of gravitational stress, unless the densities of the particles and the solvent match, with a behavior which depends on the initial particle concentration and on the depth of the quench [5-7]. Thus, the clusters progressively consolidate and possibly merge (at least partially) forming a less heterogeneous network. Which is, however, the typical value of the particle volume fraction ϕ_c of the clusters that form initially?

Two distinct statistical methods used to analyze the confocal microscope images of clusters of depletion gels, obtained for suspensions of large spherical particles (with a size in the hundred of nanometers range), suggest that $\phi_c \simeq 0.55\text{--}0.60$ and that it barely depends on the strength of the attractive interactions and on the initial particle concentration, basically coinciding with the liquid branch of the coexistence line [4, 8]. Simulations of depletion gels [9] also showed that the cluster radial density profile increases towards the center of the cluster up to values close to the random close packing of hard spheres $\phi_{\text{rcp}} \simeq 0.64$, although the average cluster volume fraction is comparable to the values found in refs. [4, 8].

The results seem to be very different for aqueous solutions of small globular proteins, where gelation still takes place via an arrested gas-liquid phase separation, even if it is presumably driven by attractive forces caused by the presence of hydrophobic patches on the particle surface. An investigation of lysozyme gels using centrifugation methods showed [10], in fact, that the volume fraction of the protein dense phase is definitely smaller than the values found in refs. [4, 8], and that it decreases with increasing the strength of the attractive interactions, reaching values as small as $\phi_c \simeq 0.2$ for deep quenches inside the coexistence region. These values were obtained by observing that the gels cannot be further compressed when subjected to a centrifugal force as large as $2.3 \times 10^4 g$. The results suggest, therefore, that the gel dense phase that forms rather follows an attractive glass line penetrating inside the gas-liquid coexistence region.

The noticeable inconsistency of the two sets of results could be due either to the patchy and asymmetric nature of the interactions in lysozyme solutions or to the ambiguity of the method used to evaluate ϕ_c in ref. [4]. In fact, it is hard to state that the conclusions reached by the statistical analysis of cluster real-space images do not possess some degree of arbitrariness.

Here, I summarize the results we reported in ref. [11], where we showed that the investigation of the mechanical properties of colloidal gels subjected to gravitational stress (natural or forced, using a centrifuge), which are obtained by sedimentation measurements, can provide valuable and unambiguous information. We will show, in particular, that the yield stress of depletion gels drastically passes from a power-law dependence on the particle volume fraction ϕ to a rapidly increasing behavior around a volume fraction ϕ_c that barely depends on the strength of the attractive interactions, and which is quite close to the values obtained in refs. [4, 8].

2. – Materials and methods

2.1. Colloidal system. – We studied aqueous suspensions of monodisperse spherical particles with a radius $R = 90$ nm made of MFA, a polytetrafluoroethylene copolymer [12]. MFA colloids present some unique features when compared to other standard latex particles, making them particularly suitable for sedimentation studies. They have a high density ($\rho_p = 2.14$ g/cm³), which allows to accurately assess the volume fraction ϕ of the dispersed particles. In addition, due to the partial cristallinity of the material, the light scattered by MFA particles has a depolarized component which depends neither on the refractive index of the solvent n_s , nor on the particle interactions and is strictly proportional to the local particle concentration [12]. This component can be set apart by matching the refractive index of the solvent to the average refractive index of the particles $n_p = 1.355$, so to remove the polarized scattering contribution. In these conditions, the intensity of the scattered light can be used to measure the concentration profiles which are generated by gravity settling [13].

The particles are suspended in solutions of Triton X-100, a non-ionic surfactant which forms globular micelles with radius $a \simeq 3.5$ nm, acting as a depletant for the MFA particles. The system was fully characterized, in the past, in terms of equation of state and phase diagram, allowing a quantitative mapping of the suspension onto a model system of adhesive hard spheres [13]. All the samples were prepared in the presence of 250 mM NaCl to screen electrostatic interactions between the particles, which are stabilized by a monolayer of the same surfactant acting as depletant.

The solvent refractive index dependence on the amount of added surfactant was obtained using a high-precision Abbemat refractometer (Anton Paar GmbH), giving $n_s = 1.3355 + 1.467 \times 10^{-4} c_s$, where c_s is the surfactant concentration in g/l. Therefore, the index-matching condition is met for $c_s \simeq 132$ g/l.

The phase diagram of the colloidal system is displayed in fig. 1. The solid line is the representative curve obtained from the experimentally measured coexistence line, where the binodal and the spinodal lines basically coincide. The volume fraction of the lower gel phase (represented by the dashed line) which forms for $c_s \gtrsim 84$ g/l, measured just at the end of the first rapid settling, decreases with increasing the added surfactant (details can be found in ref. [11]). Although the gel phase seems to follow a kind of prolongation within the coexistence gap of the attractive glass line which is experimentally observed for depleted colloids at higher concentration, the characteristic structural length scale (*i.e.*, the cluster size) occurring in gels obtained by arrested spinodal decomposition is not expected in glasses.

Figure 1 also shows the composition of the samples under investigation. The full dots correspond to the samples prepared at fixed surfactant concentration $c_s = 132$ g/l, which coincides with the index-matching condition where the gel sedimentation volume fraction profiles can be obtained. Conversely, the samples prepared at fixed initial particle volume fraction ϕ_0 and different amount of surfactant c_s (and therefore different strength of attractive interactions, full squares in the figure) are not in perfect index-matching conditions, which prevents from obtaining quantitative volume fraction profiles. Nevertheless, in sect. 3.2 we show that valuable information can be obtained even in this case.

2.2. Analytical centrifugation. – We measured the sedimentation profiles using an analytical centrifuge (LUMiSizer, LUM GmbH), which allows to monitor the settling process of up to 12 samples by measuring their optical extinction profile with a linear

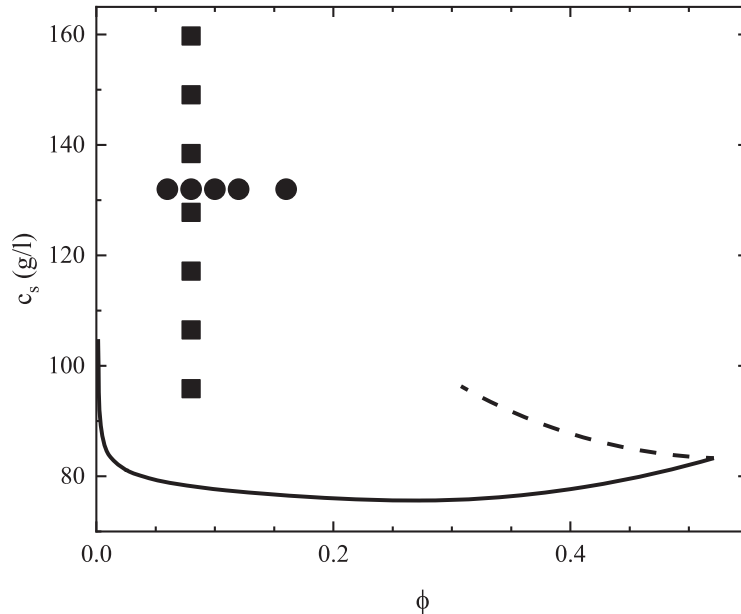


Fig. 1. – Composition of the investigated samples. The full dots correspond to the series of samples prepared at constant surfactant concentration $c_s \simeq 132$ g/l, for which the index-matching condition is met. The full squares indicate the samples investigated by varying the surfactant concentration at constant initial particle volume fraction $\phi_0 = 8\%$. The representative curves of the experimental coexistence line (solid line) and of the dependence of the lower gel phase concentration on c_s (dashed line) reported in ref. [11] are also displayed.

detector array, with an accurate temperature control in the range $4^\circ\text{C} \leq T \leq 40^\circ\text{C}$. For a concentrated dispersion, this usually yields just a semiquantitative concentration profile, because the sample transmittance depends both on concentration and on the suspension structure factor. For MFA particles in index-matching conditions, however, the natural extinction profile measured is strictly proportional to the suspension volume fraction profile ϕ . In what follows, we quantify the (local) strength of the artificial gravity using the so-called relative centrifugal force $\text{RCF} = \omega^2 r/g$, where ω is the rotor angular velocity, r is the distance from the center of rotation, and g is the gravity acceleration. For the sake of convenience, the values given in the text are calculated for $r = \mathcal{R}$, where $\mathcal{R} \simeq 130$ mm is the distance of the cell bottom from the rotor center.

After preparation, the samples were poured in optical cuvettes suitable for centrifugation and let sediment for 30 days to reach mechanical equilibrium in natural gravity. Then, the cuvettes were gently inserted in the centrifuge and spun at the lowest RCF. The initial sedimentation profiles are taken as the natural gravity profiles. The samples are then spun at different values of RCF from 6 to 2300 in pre-selected progressive steps. The sedimentation profiles are monitored in time until they reach a stationary condition where no further changes can be detected (which can require several days for the lower RCF values), and a detailed measurement of the profile is taken.

To exclude possible history-depending effects, we also prepared several samples and separately centrifuged them directly at each of the selected RCF values, *i.e.*, not in progressive steps. The stationary profiles, however, did not show any appreciable difference from those obtained with the discussed method.

2.3. Yield stress measurement by compressive rheology. – All soft materials are known to weakly resist to shear stress, while they are basically incompressible for what concerns volume changes. The dispersed phase, however, *can* be squeezed to smaller volumes by expelling part of the solvent. This can be done simply by subjecting the dispersed phase and the solvent to different forces, which happens in sedimentation (natural or forced as in a centrifuge) when the two phases have a different density. Therefore, natural or forced sedimentation can be exploited to perform *compressive rheology*, a relatively recent term used to generically indicate these squeezing techniques for the investigation of the behavior of a particle network when compressed (for a review, see ref. [14]).

The theoretical analysis of the plastic squeezing of colloidal disordered solids was developed by Buscall and White [15]. Using this approach, the stationary profile of the gel can be evaluated from the compressive yield stress $\Pi(\phi)$, which quantifies the mechanical strength of the network. More precisely, the compressive yield stress $\Pi(\phi)$ is the maximum stress a portion of gel at local volume fraction ϕ can sustain without undergoing any deformation. When the stress exceeds this value, the structure collapses and consolidates with an increase in the local volume fraction until, all over the sample, the local volume fraction reaches a value that is large enough, so that $\Pi(\phi)$ is barely sufficient to sustain the compressive stress due to the weight of the material lying above. Therefore, $\Pi(\phi)$ can be measured from the sediment profile after centrifugation by pairing the volume fraction profile to the compressive stress profile,

$$(1) \quad \Pi(z) = \Delta\rho\omega^2 \int_{\mathcal{R}-z}^{\mathcal{R}-h} x\phi(x) dx,$$

where $\Delta\rho$ is the density difference between the particles and the solvent, z is the distance from the cell bottom towards the rotor center, and h is the equilibrium height of the gel. Therefore, finding the full dependence of the yield stress on ϕ only requires a numerical integration of the volume fraction profile, provided of course that the latter can be quantitatively measured, which is the case of the index-matched suspensions we investigated.

3. – Results

3.1. Compressive yield stress of depletion gels at fixed attraction strength. – We discuss first the results obtained for the gels in index-matching conditions ($c_s = 132$ g/l, hence for fixed strength of the interactions) and different initial particle volume fraction ϕ_0 . In the inset of fig. 2 we show two representative equilibrium profiles for the gels at $\phi_0 = 10\%$, compressed at two different values of RCF. At low centrifugal force (RCF = 6) the volume fraction profile smoothly grows from $\phi = 0$ to $\phi \simeq 0.56$. For $\phi \simeq 0.29$, however, a change of slope can be noticed. Since it is difficult to state unambiguously whether the region with $\phi \lesssim 0.29$ still belongs to an arrested gel or, rather, to a non-equilibrated sediment of non-compacted settled clusters, we conservatively decided to evaluate the compressive yield stress using eq. (1) only for the part of the profile with $\phi \gtrsim 0.29$ (full dots). The profile obtained at RCF = 2300, on the other hand, is an almost step function, which grows rapidly from $\phi = 0$ to $\phi \simeq 0.60$. Similarly to the results obtained in ref. [6] for the same system in natural gravity, we found that, for a fixed value of RCF, the shape of the equilibrium profiles does not depend on the initial particle volume fraction ϕ_0 . This is shown in the body of fig. 2, where the profiles obtained with RCF = 6 superimpose when shifted along the z -axis. This suggests that gels with the same strength of interactions

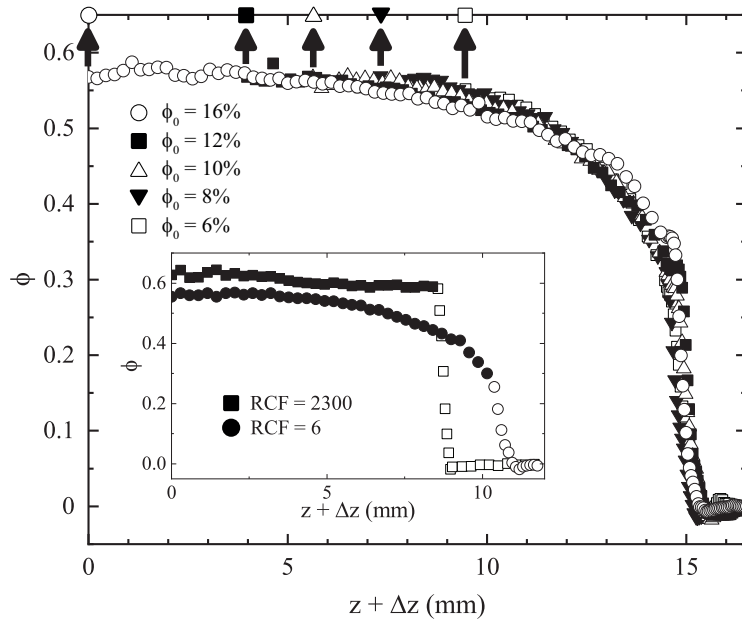


Fig. 2. – Inset: Stationary profiles for MFA gels at fixed initial particle volume fraction $\phi_0 = 10\%$ and depletant concentration $c_s = 132$ g/l, obtained at RCF = 6 (circles) and RCF = 2300 (squares). The gel yield stress is evaluated using the data shown in full symbols. Body: The volume fraction profiles obtained at RCF = 6 are scaled on the profile for the sample at $\phi_0 = 16\%$ by translating the data along the z -axis by an amount Δz . For each curve, Δz can be obtained from the position of the cell bottom, indicated by the arrows at the top of the plot.

but prepared at different ϕ_0 have the same compressive yield stress. A similar rescaling works for all the other investigated values of RCF.

In fig. 3 we show in a log-log plot the dependence of the compressive yield stress Π on the local volume fraction ϕ , obtained from the equilibrium profiles using eq. (1). The data for different values of ϕ_0 , obtained by joining without any adjustment the results for the profiles obtained for several values of RCF, collapse onto a single master curve. For $\phi \lesssim 0.5$ the yield stress grows as a power law $\Pi(\phi) = A_0\phi^\alpha$, a behavior often reported for colloidal gels, with an exponent $\alpha = 4.2$ that agrees with the value found in ref. [6] for the same system for $\phi \lesssim 0.45$. Using a centrifuge it is possible to reach higher values of the sediment volume fraction, possibly approaching the random close packing value ϕ_{rcp} . The behavior of the compressive yield stress, however, definitely deviates from the power-law behavior, taking on a much more rapidly increasing trend, which apparently diverges for a volume fraction of the order of ϕ_{rcp} . This behavior should be expected, since the compressibility of a random close packing of hard spheres *must* vanish. This deviation occurs for values of ϕ pretty close to the cluster volume fraction ϕ_c reported in refs. [4, 8] (indicated by the shaded area in fig. 3).

3.2. Compressive yield stress with varying the strength of interactions. – When the index-matching condition is not fulfilled, as happens for $c_s \neq 132$ g/l, the measured natural extinction profile is no more strictly proportional to the local volume fraction. In the past, several methods have been developed to estimate $\Pi(\phi)$ without the need to precisely

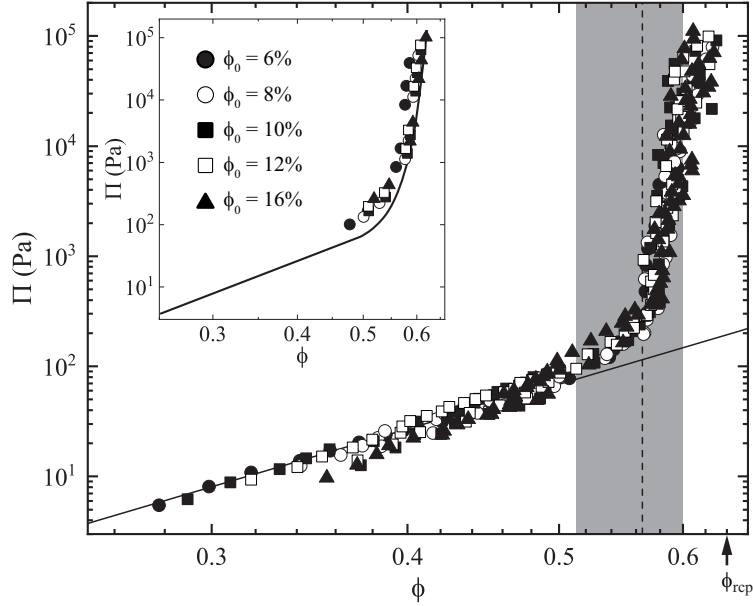


Fig. 3. – Body: compressive yield stress as a function of ϕ for gels at fixed depletant concentration $c_s = 132$ g/l (index-matching condition) and different initial particle volume fraction, obtained using eq. (1) on the profiles obtained at 7 different values of RCF (from 6 to 2300, data from ref. [11]). The solid line is a power-law fit $\Pi = A_0\phi^\alpha$ of the data in the range $\phi < 0.5$, giving $\alpha = 4.2$ and $A_0 = 1265$ Pa. The shaded area indicates the range of the values for the liquid branch obtained in refs. [4, 8] ($0.52 \lesssim \phi \lesssim 0.60$), and the dashed line is the average value $\phi \simeq 0.56$ of the same data. $\phi_{\text{rcp}} \simeq 0.64$ is the random close packing value for hard spheres. Inset: compressive yield stress obtained from the same profiles using eq. (2). The solid line is obtained as the average of the results shown in the body of this figure.

measure the concentration profile. These methods only require the sediment height h to be measured at mechanical equilibrium and are found to be in good agreement with the results obtained by standard macroscopic rheological measurements [15]. However they turn out to be very time consuming, since they actually require the derivative of h to be evaluated with respect to the centrifugal force and, therefore, investigation of a large number of profiles obtained at different values of RCF. For our purposes it is sufficient to use an approximate but easier approach, which is expected to yield reasonably good data for the dependence of Π on ϕ for profiles with an almost step-like shape (see inset of fig. 1). From the profile we can estimate the height h and the average volume fraction $\bar{\phi} = \phi_0(h_0/h)$ of the gel, where h_0 is the initial height of the suspension. Since the profiles we studied never extend by more than 15 mm, we can consider $\mathcal{R} \gg h$, and assuming a nearly uniform volume fraction profile, we can estimate the average compressive yield stress as [16].

$$(2) \quad \Pi = \Delta\rho\omega^2 \left(\mathcal{R} - \frac{h}{2} \right) \frac{h_0\phi_0}{2}.$$

There are two main issues in using this method. The first one is that it is difficult to precisely assess the position of the interface when the sediment and the solvent differ

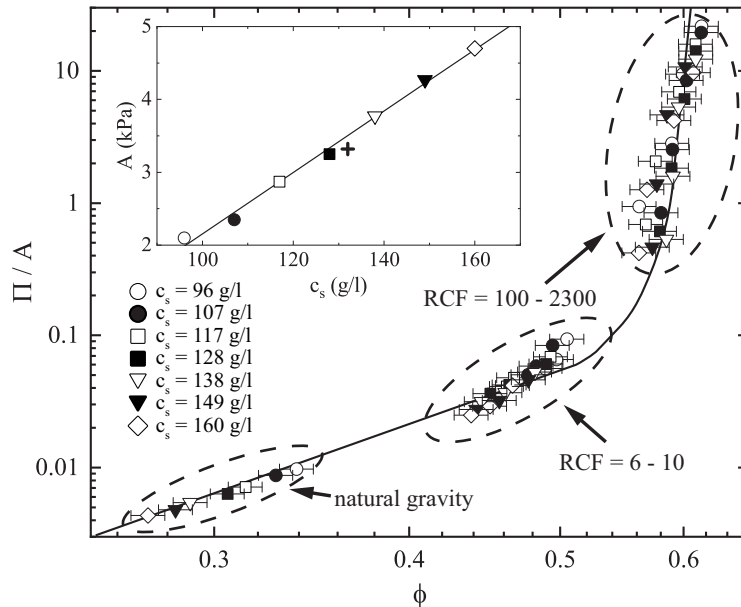


Fig. 4. – Body: compressive yield stress for different values of c_s and fixed initial particle volume fraction $\phi_0 = 8\%$ rescaled to the amplitude values A . The solid line, as in fig. 3, is obtained as the average of the results obtained in index-matching and scaled to the amplitude $A = A_0 = 1265$ Pa. The error bars in ϕ are obtained from the minimum and maximum values of the gel height h . Inset: dependence of the amplitude A on the depletant concentration c_s (same symbols as figure body). The solid line is a linear fit of the data. As a reference, the plus sign indicates the value obtained from the results for the profiles in index-matching shown in the inset of fig. 3.

by refractive index. This gives, in practice, an uncertainty of about 5% in the estimate of h and, consequently, of $\bar{\phi}$. A more serious source of inaccuracy, however, is that the profile *cannot* be constant, especially at low values of RCF. This would imply, in fact, a fully incompressible structure, which is possible only for $\phi \simeq \phi_{\text{rcp}}$. For example, eq. (2) overestimates the compressive yield stress by about 25% for the profile of the inset of fig. 2 obtained at $\text{RCF} = 2300$ and by a factor of about 2.6 for the profile obtained at $\text{RCF} = 6$. However, this mostly affects the absolute values of Π and much less the dependence of Π on ϕ . For the gels investigated in natural gravity in ref. [6], it was found that in the low- ϕ region the compressive yield stress has a power-law dependence with an exponent that does not depend on the amount of surfactant c_s . Therefore, even if the values of Π are affected by a marked error, it is worth looking at the results of $\Pi(\phi)$ obtained at different strength of interactions by varying the amount of depletant c_s .

Therefore, we investigated samples at fixed initial particle volume fraction $\phi_0 = 8\%$ and for 7 different values of c_s ($96 \text{ g/l} \leq c_s \leq 160 \text{ g/l}$), in natural and forced gravity, from moderate ($\text{RCF} = 6, 7, 10$) to large values ($\text{RCF} = 100, 300, 1000, 2300$) of the centrifugal acceleration. In fig. 4 these two regimes are associated to the power-law and diverging behavior of $\Pi(\phi)$, respectively. When the results are fitted to the low- ϕ dependence of the profiles in index-matching ($\Pi(\phi) = A\phi^{4.2}$), all the curves can be rescaled with good approximation on the same master curve by dividing the yield stress

by the amplitude value A . Noticeably, the scaling is valid also for the diverging region ($\phi > 0.5$), suggesting that the value for which the deviation starts barely depends on the depletant concentration c_s . In addition, the values of the amplitude A grow linearly with c_s , in agreement with results reported in the literature [17].

4. – Conclusions

A simple picture of the properties of depletion gels can be drawn, based on our measurements. Initially, clusters at volume fraction ϕ_c , which barely depends on the strength of the attractive interactions, form upon spinodal decomposition. These clusters start to settle and compact under their own weight (real or effective when the samples are centrifuged), showing a compressive yield stress $\Pi(\phi)$ that grows as a power law of the gel volume fraction ϕ , up to an average volume fraction approximately equal to ϕ_c , where the clusters are likely to be closely packed. For $\phi \gtrsim \phi_c$, the compressive yield stress dramatically rises, showing that it is much harder to compress gels with an average volume fraction larger than ϕ_c . The gel compressibility, however, still appears to be finite until the volume fraction reaches values comparable to the random close packing for hard spheres. We are tempted, then, to associate ϕ_c with the volume fraction of the liquid branch of the coexistence line. Therefore, the abrupt change of the compressive yield stress would provide an estimate of ϕ_c , obtained by macroscopic rheological measurements. Our results seem to support the suggestion made in ref. [4], that ϕ_c essentially coincides with the liquid branch of the coexistence curve.

On the other hand, our findings do not seem to agree with the results obtained in ref. [10], where ϕ_c substantially decreases as the strength of the attractive interactions is increased. The interpretation of the results, however, was based on the fact that the dense phase turns out to be basically incompressible, contrarily to what we found. There is, nonetheless, a possible explanation for the very different compressive behavior of the depletion gels we studied with respect to the one displayed by the protein gels investigated in ref. [10]. From fig. 4, we notice that the minimum value of the relative centrifugal force RCF_{\min} required to access the diverging behavior of the compressive yield stress is about 100. For a wide class of colloidal gels, it is also known that the yield stress scales as the inverse of the square of the particle size [17]. We could then make a rough estimation of the corresponding RCF'_{\min} value for lysozime, assuming this scaling to be valid in general and that the strength of the attractive interactions that hold together depletion and protein gels are comparable. We can then write

$$\text{RCF}'_{\min} = \frac{\Delta\rho}{\Delta\rho'} \left(\frac{a}{a'}\right)^2 \text{RCF}_{\min},$$

where $a = 90$ nm and $a' = 2.5$ nm are the particle radii of MFA and lysozime, respectively, and $\Delta\rho = 1.14$ g/cm³ and $\Delta\rho' = 0.35$ g/cm³ their density difference with the solvent. This gives $\text{RCF}'_{\min} \simeq 4 \times 10^5$, which is by more than one order of magnitude larger than the maximal centrifugal force used in the experiments reported in ref. [10]. This suggests that the final compression regime is extremely hard to be accessed for protein gels, because of their much larger compressive yield stress.

* * *

I acknowledge R. Piazza and S. Buzzaccaro, with whom I share the results discussed here.

REFERENCES

- [1] MILLER M. A. and FRENKEL D., *J. Chem. Phys.*, **121** (2004) 535.
- [2] ZACCARELLI E., *J. Phys.: Condens. Matter*, **19** (2007) 323101.
- [3] MANLEY S. *et al.*, *Phys. Rev. Lett.*, **95** (2005) 238302.
- [4] LU P. *et al.*, *Nature*, **453** (2008) 499.
- [5] BRAMBILLA G. *et al.*, *Phys. Rev. Lett.*, **106** (2011) 118302.
- [6] BUZZACCARO S. *et al.*, *J. Phys.: Condens. Matter*, **24** (2012) 284103.
- [7] SECCHI E., BUZZACCARO S. and PIAZZA R., *Soft Matter*, **10** (2014) 5296.
- [8] BARTLETT P., TEECE L. J. and FAERS M. A., *Phys. Rev. E*, **85** (2012) 021404.
- [9] ZIA R. N., BENJAMIN J. and RUSSEL W. B., *J. Rheol.*, **58** (2014) 021404.
- [10] CARDINAUX F. *et al.*, *Phys. Rev. Lett.*, **99** (2007) 118301.
- [11] LATTUADA E., BUZZACCARO S. and PIAZZA R., *J. Phys.: Condens. Matter*, **30** (2018) 044005.
- [12] DEGIORGIO V. *et al.*, *Adv. Colloid Interface Sci.*, **48** (1994) 61.
- [13] BUZZACCARO S., RUSCONI R. and PIAZZA R., *Phys. Rev. Lett.*, **99** (2007) 098301.
- [14] DE KRETZER R. G., BOGER D. V. and SCALES P. J., in *Rheology Reviews* (British Society of Rheology) 2003, p. 125.
- [15] BUSCALL R. and WHITE L. R., *J. Chem. Soc., Faraday Trans. 1*, **83** (1987) 873.
- [16] BUSCALL R., *Colloids Surf.*, **5** (1982) 269.
- [17] KIM C. *et al.*, *Phys. Rev. Lett.*, **99** (2007) 028303.