

## Yielding and flow of sheared colloidal glasses

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S3955

(<http://iopscience.iop.org/0953-8984/16/38/013>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 17:44

Please note that [terms and conditions apply](#).

## Yielding and flow of sheared colloidal glasses

G Petekidis<sup>1</sup>, D Vlassopoulos<sup>1</sup> and P N Pusey<sup>2</sup>

<sup>1</sup> Institute of Electronic Structure and Laser-FORTH, PO Box 1527, Heraklion 71110, Crete, Greece

<sup>2</sup> School of Physics, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, UK

Received 5 May 2004, in final form 9 August 2004

Published 10 September 2004

Online at [stacks.iop.org/JPhysCM/16/S3955](http://stacks.iop.org/JPhysCM/16/S3955)

doi:10.1088/0953-8984/16/38/013

### Abstract

We have studied some of the rheological properties of suspensions of hard-sphere colloids with particular reference to behaviour near the concentration of the glass transition. First we monitored the strain on the samples during and after a transient step stress. We find that, at all values of applied step stress, colloidal glasses show a rapid, apparently elastic, recovery of strain after the stress is removed. This recovery is found even in samples which have flowed significantly during stressing. We attribute this behaviour to ‘cage elasticity’, the recovery of the stress-induced distorted environment of any particle to a more isotropic state when the stress is removed. Second, we monitored the stress as the strain rate  $\dot{\gamma}$  of flowing samples was slowly decreased. Suspensions which are glassy at rest show a stress which becomes independent of  $\dot{\gamma}$  as  $\dot{\gamma} \rightarrow 0$ . This limiting stress can be interpreted as the yield stress of the glass and agrees well both with the yield stress deduced from the step stress and recovery measurements and that predicted by a recent mode coupling theory of sheared suspensions. Thus, the behaviours under steady shearing and transient step stress both support the idea that colloidal glasses have a finite yield stress. We note however that the samples do exhibit a slow accumulation of strain due to creep at stresses below the yield stress.

### 1. Introduction

As its concentration is increased, a suspension of nearly equal-sized colloidal hard spheres undergoes a freezing transition from a colloidal fluid to a colloidal crystal [1]. The fluid is thermodynamically stable for colloid volume fractions  $\phi$  less than 0.494, and the crystal is stable for  $\phi > 0.545$  [2]; for  $0.494 \leq \phi \leq 0.545$ , coexistence of the two phases is observed. Experimentally it is found that a sample prepared and mixed at a volume fraction greater than about 0.58 does not exhibit the quite rapid (minutes to hours) homogeneously nucleated crystallization observed at lower concentrations, but rather remains in an amorphous state for hours to days (after which heterogeneously nucleated crystallization

is sometimes observed) [1]. Dynamic light scattering (DLS) experiments [3, 4] performed on the metastable fluid states before crystallization takes place reveal a dramatic slowing down of particle diffusion as  $\phi$  approaches 0.58. At  $\phi \approx 0.58$ , a non-decaying (non-ergodic) component appears in the measured intermediate scattering function at long times, reflecting structural arrest, the suppression of long distance diffusion of the particles and the partial freezing in of the density fluctuations. These two observations, structural arrest and the suppression of homogeneous nucleation of crystallization, lead to the identification of a colloidal glass transition at  $\phi_G \approx 0.58$  [1, 3, 4]. The underlying physical mechanism is the cage effect. In the fluid state, any particle is temporarily caged by its neighbours but, in time, can escape from the cage; repeated cagings and escapes allow long distance diffusion and fluidity. As the sample's concentration is increased, the cages tighten, first slowing diffusion and then leading to permanent entrapment of the particles in the glass state. Even within the glass, except at the highest concentration of random close packing, the particles still have freedom for local motions within their cages. The caging mechanism is described by mode coupling theories (MCT) of the glass transition [5]; colloidal systems have proved to be a good testing ground for MCT [4, 6].

One would expect a structurally arrested material to be a solid and to show solid properties such as reversible elastic deformation and resistance to flow at small applied stresses, before yielding and deforming irreversibly at larger stresses. However, colloidal glasses are very weak mechanically—they are classic examples of 'soft solids'. Just tilting the sample cell slightly induces flow. Thus there have been few detailed measurements of their mechanical properties at very small stresses (however, see [7, 8]).

Here we report two kinds of measurements. First we monitor the samples' strain on the application and release of a step shear stress (some of this work has been described previously in [9]). At low stresses we do indeed find reversible elastic deformation of the colloidal glasses and we are able to identify yielding at higher stresses. However, significant irreversible creep of the samples is observed at stresses below yielding. Second, we monitor the shear stress on a flowing sample as the rate of strain  $\dot{\gamma}$  is decreased. In the glassy state we find that the stress reaches a limiting value, which can be identified as the yield stress, as  $\dot{\gamma} \rightarrow 0$ . For several samples the values of yield stress determined by the two methods agree rather well. Furthermore, they also agree well with the predictions of a recent mode coupling theory of a sheared suspension [10].

We speculate that the observed elastic behaviour of colloidal glasses can be associated with distortion and recovery of the local cage structure. Interestingly, samples which have flowed quite extensively under a high applied stress recover a significant strain, associated, we think, with cage relaxation, when the stress is removed.

## 2. Experimental details

### 2.1. Samples

The particles comprised poly(methyl methacrylate) cores, stabilized sterically by thin layers of a slightly flexible polymer, poly-12-hydroxystearic acid. They were suspended in dodecane. Extensive previous work has shown that these particles are good 'model' hard spheres [11, 12]. The particles had an average radius of 183 nm and a size polydispersity of about 12%. This degree of polydispersity is large enough to suppress crystallization [13], so the samples at concentrations below  $\phi_G$  remained in fluid states and crystallization did not complicate the measurements. Lacking crystallization as a 'thermodynamic marker', concentrations were determined relative to random close packing. Thus the samples were prepared by diluting a

sample centrifuged to a dense, close-packed, amorphous sediment. For these particles, we assumed that the volume fraction at random close packing was 0.67 [14].

## 2.2. Rheology

Experiments were conducted in a controlled stress rheometer (Rheometric Scientific, DSR-200). A cone–plate geometry (diameter 25 mm and cone angle 0.1 or 0.04 rad) was used to ensure a constant strain throughout the sample. A strict experimental protocol was followed for all samples to ensure reproducibility and comparability of different measurements and to eliminate the effects of sample loading and shear history. In a step stress (creep) and recovery measurement a constant stress was applied for a certain period of time (typically 100 s) while the resulting strain was measured. The stress was then removed and the recovered strain was measured for certain period of time (typically 500 s). The measurement was repeated for a second time immediately after the end of the recovery time to ensure reproducibility of the result. Before each measurement a steady pre-shear for a period of 50 s was performed at a stress above the yield stress, followed by delay time of typically 300 s.

For the measurement of the flow curves care was taken to ensure that the sheared sample had reached a steady state. To achieve this the measurement time for each data point (each shear rate) was increased as the rate of strain,  $\dot{\gamma}$ , was lowered; furthermore, pre-shear was applied for period comparable to the measurement time. Hence, a typical experiment involved:

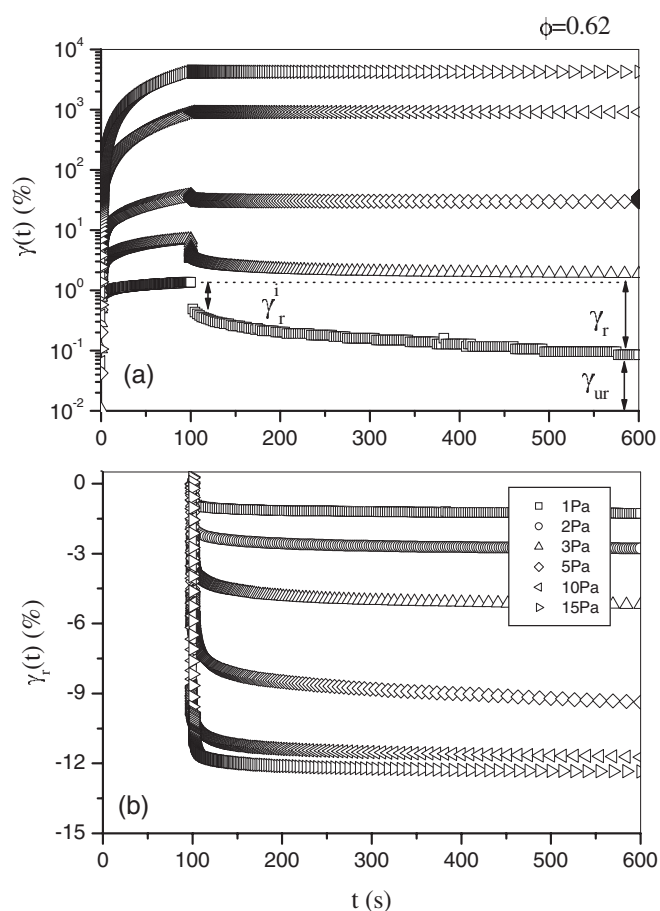
- (a) pre-shear of 10 s, followed by a measurement averaging over 10 s for  $\dot{\gamma}$  in the range between 50 and 1 s<sup>-1</sup>,
- (b) pre-shear of 100 s, followed by a measurement of 100 s for  $\dot{\gamma}$  in the range between 1 and 10<sup>-2</sup> s<sup>-1</sup> and
- (c) pre-shear of 1000 s, and a measurement of 1000 s for all  $\dot{\gamma} < 10^{-2}$  s<sup>-1</sup>.

For long time measurements (more than 6 h) the elimination of evaporation was achieved by sealing the colloidal suspension with a layer of ethylene glycol around the cone and plate of the rheometer. For shorter measurements a solvent bath saturating the atmosphere around the sample in a closed environment was used. The temperature of the sample was stabilized at  $T = 20^\circ\text{C}$  using a circulating fluid bath.

## 3. Results

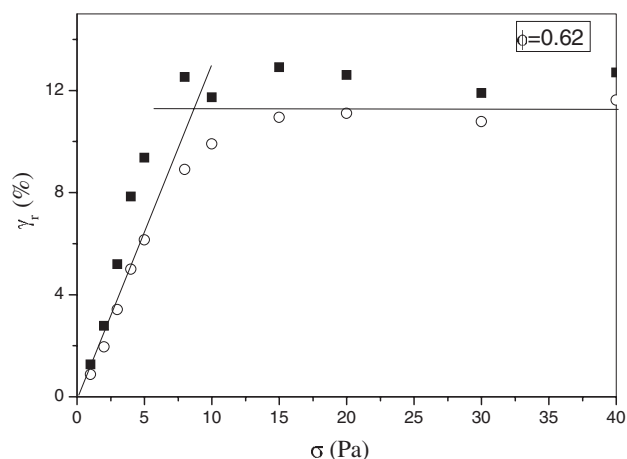
### 3.1. Step stress and recovery

Samples ranging in concentration from  $\phi \approx 0.57$  to  $\phi \approx 0.65$  were studied. The stress  $\sigma$  was applied at time  $t = 0$  and removed at  $t = 100$  s. Figure 1 shows the resulting strain  $\gamma(t)$  as a function of time for various values of applied stress  $\sigma$  for a sample at concentration  $\phi = 0.62$ . The following features of the results were noted at all values of  $\sigma$ . On application of the stress the sample attained an ‘instantaneous’ strain; here ‘instantaneous’ means within 1 s. Then, over the 100 s of the applied stress, the sample accumulated further strain: creep at low stresses, and flow at higher stresses (see below for further discussion). On removal of the stress, whatever its value, the sample recovered some strain  $\gamma_r^i$  instantaneously (within 1 s) and a further amount, to a total of  $\gamma_r$ , over the next few hundred seconds (see figure 1(a), where the logarithmic strain axis rather obscures the strain recovery at higher stresses). When strain recovery is essentially complete, there remains some unrecovered strain  $\gamma_{ur}$ , resulting from creep or flow (figure 1(a)). To within the uncertainty of the measurements we found that, at stresses below yielding, the instantaneous strain attained on application of the stress was equal to the instantaneous strain  $\gamma_r^i$  recovered when the stress was removed.

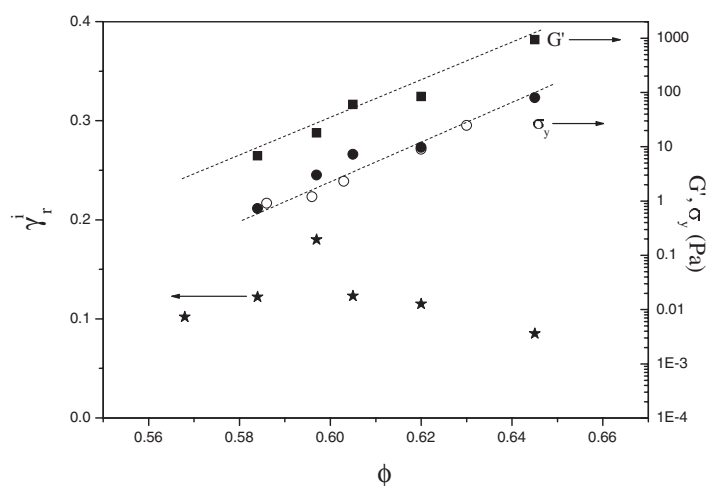


**Figure 1.** (a) The time dependence of the strain,  $\gamma(t)$  (%), achieved during a step stress (creep) and recovery experiment at  $\phi = 0.62$ , for several stresses as indicated. The instantaneous and total recovered strain,  $\gamma_r^i$  and  $\gamma_r$  respectively, and the final unrecovered strain,  $\gamma_{ur}$ , are indicated by vertical arrows. (b) The recovered strain after the cessation of flow,  $\gamma_r(t)$ , corresponding to the data of figure 1(a).

Figure 1(b) shows the recovered strain  $\gamma_r(t)$  (taken from figure 1(a) and now on a linear scale) for various stresses. We observe that the magnitude of the recovered strain initially increases with applied stress, but saturates at higher stresses where the sample has flowed (see below). Figure 2 shows the values of the instantaneous recovered strain and the total recovered strain, as functions of the applied step stress for the same sample at  $\phi = 0.62$ . For small values of the stress  $\sigma$ , the recovered strain increases roughly linearly with  $\sigma$ . Thus we can estimate an elastic shear modulus,  $G' \approx 84$  Pa, for this sample, from the slope of the line in figure 2. At larger stresses, at which flow of the sample is observed, the recovered strain saturates, as indicated by the horizontal line in figure 2. The stress at which the two lines in figure 2 intersect is a marker of the transition from elastic deformation at small  $\sigma$  to Newtonian flow at large  $\sigma$ ; it can thus be taken as a measure of the sample's yield stress  $\sigma_y$ . However, at the intermediate regime between the solid-like and fluid-like limits the sample behaves as a viscoelastic fluid. In this region the sample exhibits a nonlinear elasticity since the recovered strain increases nonlinearly with stress, while after sufficient time it flows attaining a constant viscosity.



**Figure 2.** The stress dependence of the instantaneous,  $\gamma_r^i$  (○), and the total,  $\gamma_r$  (■), recovered strain determined during a creep and recovery experiment for  $\phi = 0.62$ . The lines indicate the linear increase of the recovered strain at low stresses and the stress independent region at high stresses.

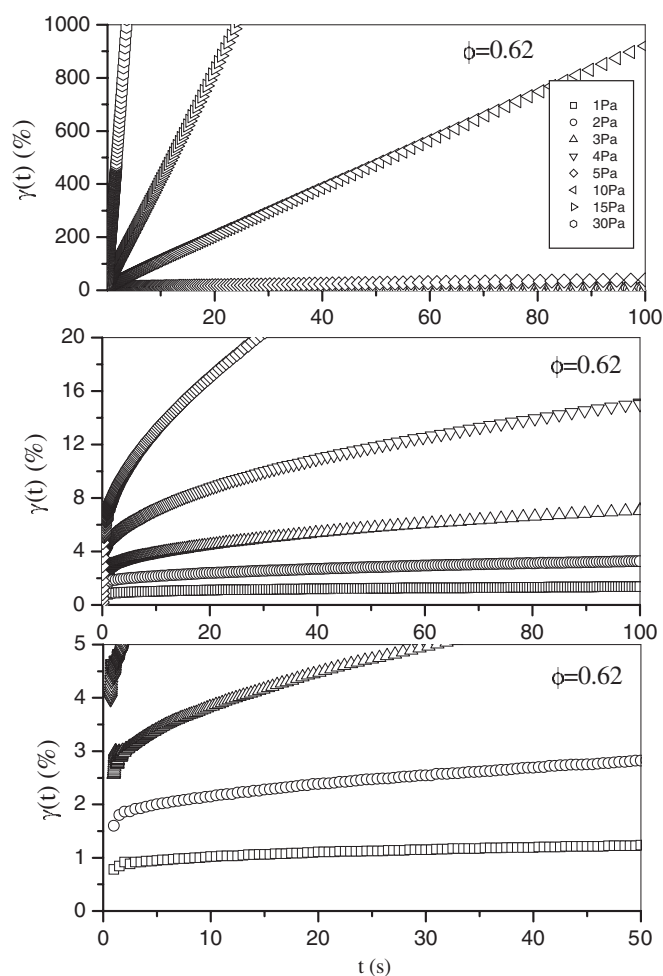


**Figure 3.** The volume fraction dependence of the instantaneously recovered strain,  $\gamma_r^i$  (★), with their values indicated on the left axis, and of the elastic modulus,  $G'$  (■), and yield stress,  $\sigma_y$  (● and ○), with the corresponding values indicated on the right axes. The quantities depicted by solid symbols were determined from creep experiments while the open circles represent  $\sigma_y$  determined from the flow curves (see figure 5). The lines are to guide the eye.

Figure 3 collects the results of this kind of analysis for several samples over a range of concentration; the dashed lines are simply to guide the eye. We see that the shear modulus increases from about 10 Pa at  $\phi \approx 0.58$  to about 1000 Pa at  $\phi \approx 0.645$ . The yield stresses (solid circles) are roughly 1/10 of the shear moduli, consistent with a ‘saturated’ yield strain of around 0.1 (stars in figure 3).

### 3.2. Creep and flow

Figure 4 shows the same data as figure 1(a), but now limited to times  $0 < t < 100$  s during which stress was applied to the sample. The use of linear strain axes clearly reveals the changing

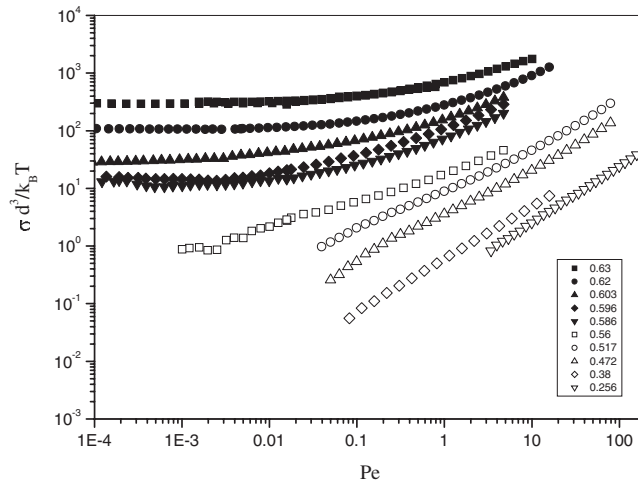


**Figure 4.** Linear plots of the time dependence of the strain,  $\gamma(t)$  (%), achieved during the step stress (creep) period at  $\phi = 0.62$ . From the bottom to the top, different measurements are shown with increasing stress as indicated in the label: low stress experiments (bottom and middle) reveal a creeping behaviour whereas the data at high stresses (top) show a clear flow of the sample.

nature of the strain accumulated during stressing. At low stresses, the instantaneously achieved strain is followed by a slow creep of the sample. For example, at  $\sigma = 3$  Pa the instantaneous strain is about 2.5% and after 100 s the sample has suffered a total strain of about 6.5%. At  $\sigma = 5$  Pa the creep becomes larger. At and above  $\sigma = 10$  Pa, the strain increases linearly with time from the moment that the stress is applied, corresponding to fully developed flow. Qualitatively similar observations were made for samples at other concentrations.

### 3.3. Yielding as the limit of decreasing flow

So far we have viewed yielding as the onset of flow as the applied stress is increased. Now we consider the behaviour of a flowing sample as the flow rate is decreased. Thus we slowly decrease the rate of strain  $\dot{\gamma}$  and monitor the stress on the sample. The results are shown in figure 5 where dimensionless units are used for the stress and rate of strain. The stress is



**Figure 5.** Flow curves for several volume fractions inside the glass regime and at concentrated liquid suspensions, as indicated in the label. The normalized stress,  $\sigma d^3/k_B T$ , is depicted as a function of the Peclet number (normalized shear rate).

scaled by  $k_B T/d^3 = 0.0825$  Pa, where  $k_B T$  is the thermal energy and  $d$  the particle diameter ( $T = 293$  K,  $d = 366$  nm). The bare Peclet number is  $Pe = \dot{\gamma} d^2/D_0 = 0.158\dot{\gamma}$ , where  $D_0$  is the free particle diffusion constant.

Depending on the concentrations of the samples, these data fall into two groups. For  $\phi < 0.58$ , the stresses continue to decrease as the flow rate is decreased. For the samples at  $\phi \leq 0.4$ , the stress is linearly proportional to  $\dot{\gamma}$ , corresponding to a Newtonian fluid with constant viscosity. By contrast, for  $\phi > 0.58 \approx \phi_G$ , the stresses on the samples tend towards defined non-zero values as  $\dot{\gamma} \rightarrow 0$ . These are the stresses necessary to keep the colloidal glasses flowing and can be interpreted as different estimates of the yield stresses from those described above. These yield stresses, taken from figure 5, are plotted as open circles in figure 3. We see that, to within the experimental uncertainty, the yield stresses determined by increasing the stress on the samples (solid circles) are the same as those determined by reducing the flow rate (open circles).

## 4. Discussion

### 4.1. Cage elasticity

In order to explain some of these observations we invoke the concept of ‘cage elasticity’ [9]. In an unstressed colloidal glass, the cage of particles surrounding any given particle is, on average, isotropic. On the application of a small shear stress, the cage distorts as the particles above the central particle move in one direction and the particles below move in the opposite direction. The applied stress is then balanced by an internal osmotic stress, essentially an anisotropic osmotic pressure. On removal of the applied stress, the cages relax back to their isotropic quiescent states, causing recovery of the macroscopic strain.

Application of a large enough stress causes the glass to flow. Now, rather than keeping the same neighbours in a distorted environment as at low stresses, a particle changes neighbours many times as the flow proceeds. Our results show, however, that when the stress is removed and the flow ceases the sample recovers a strain whose magnitude appears to be independent



of the flow rate. An interpretation of this observation is that, when the flow stops, the sample instantaneously finds itself with ‘maximally distorted’ cages. These then relax back to isotropy.

At first sight, this maximum distortion, a strain of 10–15%, seems surprisingly large for samples at such high concentrations. We have argued elsewhere [9], however, that cage distortion must involve strongly cooperative motions of the particles. This notion is supported by the results of dynamic light scattering experiments [15] that show that individual particles in a quiescent colloidal glass can attain maximum root mean square Brownian displacements of at least 10% of their radius.

The cage picture can also be invoked to provide a possible explanation of the slow component ( $t > 1$  s) of the recovery of the strain observed in figure 1(b). Dynamic light scattering measurements on quiescent colloidal glasses made near the peaks of their static structure factors measure the spontaneous Brownian fluctuations of the particle cages ( $\beta$ -relaxation); see figure 5 of [4]. These spontaneous fluctuations decay over a wide range of time. While most of the decay occurs within 1 s—instantaneously on the timescale of our measurements—a significant fraction, 10–20%, of the decay is much slower, taking 100 s or more. Thus it is possible that the slow recovery of a strained sample is simply caused by the slow  $\beta$ -relaxation of the distorted cages.

#### 4.2. Comparison with theory

Recent theoretical work [10] has treated sheared suspensions, specifically an ‘isotropically sheared hard-sphere model’, in the framework of mode coupling theory. Figure 6 of [10] can be compared with our figure 5. Qualitatively similar behaviour is observed. In particular, in the colloidal glasses the stress is predicted to ‘plateau’ at a non-zero value as the rate of strain is decreased. For several reasons—simplifications in the theory, experimental uncertainties etc—quantitative agreement is not expected. Nevertheless, for one quantity, the yield stress near the concentration of the glass transition, we can make a quantitative comparison. The theory predicts  $\sigma_y d^3/k_B T = 6.04$  at  $\phi = \phi_G$ , rising to about 16 at  $\phi = 1.01 \phi_G$ . Our results, figure 5, give  $\sigma_y d^3/k_B T \approx 10$ –15 for the lowest concentration glass studied. Given an experimental uncertainty in concentration of about 1%, there is excellent agreement between experiment and theory. Further analysis will be necessary to determine whether this quantitative agreement is meaningful or fortuitous.

#### 4.3. Creep

Above we showed that, even at stresses well below the yield stress, all the glassy samples exhibit significant creep, the accumulation of strain which is not recovered when the stress is removed. Creep is a commonly observed phenomenon in ‘solid’ colloidal systems, a fact which has led to vigorous and prolonged debate about the meaning, indeed the reality, of a yield stress [16]. Here we simply note that all stressed solid materials creep if observed over a long enough time. In crystalline molecular materials, creep is often associated with defects such as grain boundaries and dislocations. An interesting possibility is that creep in colloidal glasses might involve concentration of the stress at the ‘dynamic heterogeneities’, transient regions of lower density and higher mobility than average, that are increasingly thought to play an important role in the properties of glasses; see e.g. [17].

### 5. Conclusions

Here we presented rheological experiments on colloidal suspensions near and above the concentration of the glass transition. Creep and recovery measurements have shown a relatively

high elastic recovery of colloidal glasses even in samples which have flowed significantly under external stress, a behaviour attributed to 'cage elasticity'. Furthermore, flow curves from colloidal glasses revealed a finite yield stress which agrees well both with the yield stress deduced from creep experiments as well as with recent mode coupling predictions. Finally, the complicated viscoelastic nature of colloidal glasses is manifested by the slow accumulation of strain (creep) below the yield stress, which could possibly represent the rheological consequences of dynamic heterogeneities.

### Acknowledgments

We thank M Fuchs and M E Cates for valuable discussions and suggestions and A B Schofield for providing the PMMA particles.

### References

- [1] Pusey P N and van Megen W 1986 *Nature* **320** 340
- [2] Hoover W G and Ree F H 1968 *J. Chem. Phys.* **49** 3609
- [3] Pusey P N and van Megen W 1987 *Phys. Rev. Lett.* **59** 2083
- [4] van Megen W and Underwood S M 1994 *Phys. Rev. E* **49** 4206
- [5] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
- [6] Götze W 1999 *J. Phys.: Condens. Matter* **11** A1
- [7] Paulin S E, Ackerson B J and Wolfe M S 1997 *Phys. Rev. E* **55** 5812
- [8] Senff H and Richtering W 2000 *Colloid Polym. Sci.* **278** 830
- [9] Petekidis G, Vlassopoulos D and Pusey P N 2003 *Faraday Discuss.* **123** 287
- [10] Fuchs M and Cates M E 2003 *Faraday Discuss.* **123** 267
- [11] Underwood S M, Taylor J R and van Megen W 1994 *Langmuir* **10** 3550
- [12] Phan S E, Russel W B, Cheng Z D, Zhu J X, Chaikin P M, Dunsmuir J H and Ottewill R H 1996 *Phys. Rev. E* **54** 6633
- [13] Pusey P N 1987 *J. Physique* **48** 709
- [14] Schaertl W and Sillescu H 1994 *J. Stat. Phys.* **77** 1007
- [15] van Megen W, Mortensen T C, Williams S R and Müller J 1998 *Phys. Rev. E* **58** 6073
- [16] Barnes H A 1999 *J. Non-Newton. Fluid* **81** 133
- [17] Vollmayr-Lee K, Kob W, Binder K and Zippelius A 2002 *J. Chem. Phys.* **116** 5158