

A LETTERS JOURNAL EXPLORING THE FRONTIERS OF PHYSICS



You may also like

- Quark-hadron phase transition in DGP including BD brane Tayeb Golanbari, Terife Haddad, Abolhassan Mohammadi et al.
- Effects of cavity resonance and antenna resonance on mode transitions in helicon plasma Tianliang Zhang, Ying Cui, Zhangyu Xia et al.
- Investigation of Aging Effects in Layered Lithium Transition Metal Oxides Using X-Ray and Plasma-Based Techniques Marco Evertz, Martin Winter and Sascha Nowak

Re-entrant glass transition and logarithmic decay in a jammed micellar system. Rheology and dynamics investigation

To cite this article: J. Grandjean and A. Mourchid 2004 EPL 65 712

View the article online for updates and enhancements.

EUROPHYSICS LETTERS

Europhys. Lett., **65** (5), pp. 712–718 (2004) DOI: 10.1209/ep1/i2003-10172-5

Re-entrant glass transition and logarithmic decay in a jammed micellar system. Rheology and dynamics investigation

J. GRANDJEAN and A. MOURCHID

Complex Fluids Laboratory, Unité Mixte de Recherche 166 du CNRS-Rhodia 259 Prospect Plains Rd, Cranbury, NJ 08512, USA

(received 5 June 2003; accepted in final form 18 December 2003)

PACS. 82.70.Dd - Colloids.

PACS. 61.25.Hq – Macromolecular and polymer solutions; polymer melts; swelling. PACS. 64.70.Pf – Glass transitions.

Abstract. – Rheology and dynamics of micellar solutions of polystyrene-poly(acrylic acid) block copolymers are investigated in the jammed regime. With increasing attraction between soft spheres, both techniques capture the re-entrant liquid-to-glass transition. The dynamics was also investigated at an attraction strength above the re-entrant transition branch. With increasing concentration of sticky soft spheres in this region, the particle dynamics shows a remarkable extended logarithmic decay. All the theoretical predictions of mode coupling theory can be found in our system.

In recent years, the study of structural arrest of hard-sphere colloids has been the subject of intense investigation both theoretically [1, 2] and experimentally [3–8]. Of significance is the study of the liquid-glass transition driven by jamming. The subject has gained more importance since the predictions of the mode coupling theory (MCT) [9]. The idea that that dynamics of the particles can depict the physics of glassy systems has proven to be powerful. The basics of MCT are the couplings between pairs of density fluctuations. Increasing the coupling between particles induces the structural arrest and a sharp ergodic–to–non-ergodic transition occurs. Under these conditions, a particle trapped in the cage formed by its neighbors can no longer move. Two non-exponential relaxation processes, α (final) and β (initial), emerge in the dynamic structure factor, f(q, t), close to the transition threshold. When the fluid structure is arrested, the α process vanishes and $f(q, t \to \infty) > 0$.

More recently, emphasis on the behavior of colloids with hard-core and short-range attractive interactions has attracted much more attention [10–23]. Two key parameters, the volume fraction (ϕ) and the strength of attraction, |U/kT|, control the phase diagram of such systems. MCT [10–14] and molecular dynamics [15–18] have been successful in drawing the phase diagram with two intersecting transition lines separating the fluid, the attractive and the repulsive glass phases. Experimental studies have already reported a re-entrant transition induced by attraction [24]. However, it was only recently that studies of the structure and dynamics confirmed this behavior [18–20]. It has been shown that switching on attraction between the spheres shifts the liquid-repulsive glass transition threshold to higher volume fraction values. Increasing attraction further induces an attractive glass phase. The liquidattractive glass transition branch intersects the re-entrant liquid-repulsive glass branch and ends in the glass region by a cusplike bifurcation point (A_3 , 3rd-order singularity in the MCT equation). In the vicinity of A_3 singularity, the dynamics is influenced by both repulsive caging and attractive bonding effects and expressed by a logarithmic decay.

All these observations raise interesting questions on the phase behavior of glassy systems, on their dynamics and how it is related to rheology. For this purpose, we have carried out measurements of the linear rheological behavior and the dynamics of dispersions of adhesive soft spheres. We achieved this physically through the use of micellar solutions of block polyelectrolytes with a polystyrene frozen core [25, 26]. The polyelectrolyte arms carry hydrophobic groups providing the stickiness between micelles. The detailed predictions of the models discussed above are the following: 1) without attractive forces the system evolves towards a repulsive glass in the crowded regime showing generic classical behavior. 2) Switching on attraction between the micelles softens the system and accelerates the microscopic dynamics [16–19]. The rheology is then expected to follow this speeding-up. In other words, the loosening-up of the glass triggered by the re-entrant transition induces a decrease of the elasticity [14]. 3) Increasing attraction further, we anticipate a much more pronounced stretching of the relaxation when the system gets close to the intersection of the liquid-repulsive glass branch and the liquid-attractive glass branch [11–13, 15, 16].

We will show that rheology captures the re-entrant transition line. Explicitly, the limiting value of the elastic modulus at low frequency is found to follow the decrease of the non-ergodic plateau value at long time triggered by attraction. When attraction becomes strong enough, a logarithmic decay of f(q, t) takes place in the liquid phase and continues in the glass phase expanding over several time decades and as long as the system is near the attractive branch.

The diblock polymers were synthesized as polystyrene-poly(ethyl-acrylate) with molecular weights of 5300–8100 and 2000–19500 g/mol. A post-polymerization hydrolysis reaction was performed on 10% polymer solutions by addition of NaOH. The amount of NaOH was varied between 50% and 200% of the molar concentration of ethyl acrylate units. The reaction mixture was held at 90 °C and stirred for 24 h. After hydrolysis, the copolymers were dialyzed against de-ionized water for one week and against water at pH = 10 for another week. The final product at 100% degree of hydrolysis is polystyrene-poly(acrylic acid), PS-PAA, with molecular weights of 5300–5800 (symmetric) and 2000–14000 g/mol (asymmetric). A degree of hydrolysis < 100% means that hydrophobic ethyl acrylate units (stickers) remain in the PAA block. The fraction of these stickers was determined using 400 MHz ¹H NMR. The samples were prepared either by osmotic stress method using dextran 110000 solutions [27] or by dissolving freeze-dried polymer in water at pH = 10 at the desired concentration and stirring for several days at 80 °C. Samples were allowed to rest for at least one week prior to any measurement.

Small-angle neutron scattering (SANS) experiments were performed on the PAXY beamline at Laboratoire Léon Brillouin (CEA-CNRS) in Saclay, France. Samples for SANS were prepared by dissolving freeze-dried copolymer in D₂O (Cambridge Isotope Lab.). Quartz cells of 1 mm path length were used and all the experiments were performed at room temperature. The spectra, collected for scattering vectors, q, in the range between 0.003 and 0.2 Å⁻¹, were corrected for background, empty cell and incoherent scattering and were obtained in absolute scale.

Dynamic light scattering (DLS) measurements were carried out at scattering angles of 90, 120 and 150° by using an argon laser emitting at 514 or 488 nm equipped with a goniometer (Brookhaven) and correlator (BI9000 AT). Diluted and concentrated samples were filtered

through 0.45 and 0.8 μ m Millipore filters, respectively. We used optical cells of 0.5 and 1.0 cm diameter in a refractive index matched and thermostated bath. Special care was taken by averaging each measurement over many different sample positions, following the experimental procedure described by van Megen and Underwood [6]. The typical duration of a single experiment was 1000 s for all samples, and the typical number of measurements ranged from 10 for fluid solutions to 100 for solid samples. The ensemble-averaged intensity autocorrelation function was then converted to the dynamic sturture factor, f(q, t), via the Siegert relation.

Viscosimetry was performed using Couette geometry on a sensitive low shear rheometer (Contraves) measuring low viscosities for polymer concentration C < 0.04 wt. %. The frequency stress response of the concentrated samples (C > 0.5%) was measured with a strain controlled rheometer (ARES, Rheometrics). Samples were held at fixed temperature using a cone and plate geometry fitted with a solvent trap to prevent evaporation. The amplitude of the applied strain was chosen in the linear viscoelastic domain. The data were recorded after a standing period of at least 3 hours. The variation of shear moduli, G' and G'', with frequency was obtained for different polymer concentrations and fractions of stickers on the micelles.

Previously, we showed that the symmetric diblock polymer forms polydisperse spherical micelles of 101 Å PS core radius, a polydipersity of 19% and a hydrodynamic radius, $R_{\rm h}$, of 500 Å. The asymmetric copolymers lead to micelles of the same core size and polydipersity and a $R_{\rm h} = 1000$ Å. In solutions, both copolymer aqueous solutions exhibit a sharp transition from a liquid phase to a viscoelastic glasslike phase [26]. The glass phase is identified by a plateau modulus in G' at low frequencies and one correlation peak in the scattered intensity. The transition appears over a small range of concentrations, corresponding to effective volume fractions between 0.60 and 0.74. We continue our study of the rheology behavior in the elastic solid phase by varying the fraction of stickers. Figure 1 shows the evolution of the zero-frequency limiting value of G' as a function of the fraction of stickers on the micelles at a polymer concentration of 2.1 wt. % for both the symmetric and the asymmetric copolymers. We note that when the fraction of stickers increases from zero, the elastic modulus first decreases, reaches a minimum value and then increases. A final decrease of G' is observed for samples with large number of stickers. We believe that this last effect is due to the collapse of the corona. Increasing the number of stickers further results in flocculation of the copolymer solutions.

The behavior shown in fig. 1 agrees with the phase diagram of attractive hard spheres [14, 18]. The re-entrant glass transition line and the second transition line in the phase diagram could explain the evolution of G' with the percentage of stickers in the corona. To examine this assumption, we measured the dynamic structure factor f(q, t) given by the correlations in the intensity of scattered light at $q \times R_{\rm h} = 1.21$ for the samples investigated by rheology. The results are presented in fig. 2 for the symmetric copolymer at a concentration of 2.1 wt. %(sample 1 without stickers, sample 2 with a fraction of stickers of 0.22). The inset represents typical time-averaged intensity correlation functions, $g_{\rm T}^{(2)}(q,t)$, corresponding to different volumes probed for sample 1. We observe that $g^{(2)}$ does not decay to 1 due to the emergence of the non-ergodic plateau. We also note that the value of the intercept depends on the sample volume probed. This result is expected for a colloidal glass. The dynamic structure factors in fig. 2 show a tremendous acceleration of the particle dynamics when stickers are added to the micelles. Attraction promotes bonding of neighboring particles. Simultaneously, additional free volume is available to other particles that can escape from their cage [18,19]. We note from the results in fig. 2 that the system remains non-ergodic when we put stickers on the micelles, as f(q,t) does not decay to zero during the time delay investigated. However, the reduction of the plateau value of $f(q, t \to \infty)$ from 0.5 to 0.15 when the percentage of stickers goes from 0 (sample 1) to 22% (sample 2) indicates that attraction has loosened up the glass, in agreement



Fig. 1 – Evolution of the elastic modulus for the symmetric (circles, C = 2.1 wt. %) and the asymmetric (crosses, C = 2.1 wt. %) copolymers with the fraction of stickers on the micelles. The dashed curve is a guide to the eye. Results of DLS drawn in fig. 2 are those of samples 1 and 2 (symmetric copolymer).

Fig. 2 – Comparison of the dynamic structure factors of samples 1 and 2 in fig. 1 (symmetric copolymer, C = 2.1 wt. %) at a fraction of stickers 0 and 0.22. Inset: typical time-averaged measurements for sample 1.

with the reduction of the plateau elastic modulus value, $G'(\omega \to 0)$, from 60 to 6 Pa. The increase of the elastic modulus when the number of stickers increases further indicates that at this strength of attraction level, the bonding effect promotes the attractive glass phase [18–20].

However, we cannot rule out the possibility of micellar volume or aggregation number changes with addition of stickers in the corona. The variation of one or the other of these quantities can lead to a dramatic change of the volume fraction. To examine this hypothesis, we measured the hydrodynamic radius of the micelles using DLS for the symmetric copolymers, with different amounts of stickers at very low concentration. We did not observe any noticeable variation of the hydrodynamic radius within experimental errors. The study of the form factor of the micelles by SANS confirmed this result. Figure 3 represents the scattered intensity and the model fit, for 0.5 wt. % polymer solutions and variable amounts of stickers, normalized to unity at low q. Remarkably, all the data collapse onto a single curve indicating that the micelles are not perturbed by addition of stickers in the corona. It is worth noting that the difference between the scattering length density of the corona and D₂O is small, especially for acrylic acid. The similarities between the scattering curves at varying amounts of stickers strongly suggest that the shape and the size of the micelles are not altered and that the softening of the glass is only driven by stickiness.

In order to set a rigorous comparison with glass transition in suspensions of hard spheres, we performed DLS measurements on our copolymer solutions as a function of the scattering angle. It is expected that near the glass transition the intermediate scattering functions collapse onto a single master curve when normalized by the first cumulant for all q values near the correlation peak [28,29]. Thus, presentation of $\ln(f(q,t))/D_sq^2$ vs. time leads to a single curve for all q, where D_s is the short-time q-dependent diffusion coefficient. The results shown in fig. 4 were obtained on the symmetric copolymer at C = 1.9 wt. % and fraction of stickers of 0.22 with scattering angles ranging from 90 to 150°. Indeed, the data can be scaled together as for a hard-sphere glass and strongly suggests that the measured intermediate scattering function is related to the structural arrest [28,29].



Fig. 3 – Intensity vs. scattering vector for dilute symmetric copolymer samples (C = 0.5 wt. %) at percentage of stickers of 3 (squares), 15 (diamonds), 22 (triangles) and 34% (circles). The solid line is the static form factor for polydisperse spheres with a mean core radius of 10.1 nm and a polydispersity of 19%.

Fig. 4 – The scaling form for a glass at C = 1.9 wt. % and fraction of stickers of 0.22. The data were collected at scattering angles of 90 (circles), 120 (diamonds) and 150° (squares).

We now come to the region of the phase diagram where the liquid-repulsive glass and the liquid-attractive glass transition lines merge [11–14, 16]. As discussed above, the structural relaxation is predicted to show a logarithmic decay in this case [12, 15, 16]. We explored the region of the phase diagram above the re-entrant transition in order to get closer to the cusplike singularity, *i.e.*, at a sticker amount ≥ 0.15 . The data shown in fig. 5 were obtained on the asymmetric copolymer at scattering angle of 90° corresponding to $q \times R_{\rm h} = 2.43$. The results are drawn for a polymer concentration of 1.4 wt. % with a fraction of stickers of 0.15 and are compared with data collected for a fraction of stickers of 0.34 at the same polymer concentration. At a fraction of stickers of 0.15, the rheology measurements show that the onset of elasticity ($G' \sim G''$) is located at C = 1.4 wt. %. When the fraction of stickers is



Fig. 5 – Evolution of the dynamic structure factor at fraction of stickers f = 0.15 (1) and 0.34 (2) with copolymer concentration of 1.4 wt. %. The solid line is the fit to the logarithmic decay and the dashed lines display the initial and final times of the logarithmic regime for curve 2.

0.34, the onset of elasticity shifts to 1.1 wt. %. Thus, these two samples are located on the transition line, and in the glass phase, respectively.

When the fraction of stickers is 0.15, the sample shows a fluidlike behavior in the intermediate scattering function in agreement with the rheology behavior of the sample. Addition of more stickers on the micelles leads to a stringent different behavior. At a fraction of stickers of 0.34, we note that the dynamics is influenced by the cusplike singularity as the data show a logarithmic decay [12]. Beautifully, f(q, t) shows a logarithmic behavior extending over 4 orders of magnitude in time at a polymer concentration of 1.4 wt. % and a fraction of stickers of 0.34.

We also observed that for the fraction of stickers of 0.34, the increase of concentration in the glass phase ($C \ge 1.4$ wt. %) induces the appearance of the non-ergodic plateau in the intermediate scattering function and the expansion of the time interval where the logarithmic decay occurs. These measurements agree with most recent predictions of MCT [12]. We also observed that at high polymer concentration the logarithmic decay of the correlation function vanishes and f(q,t) shows a non-ergodic plateau around 0.9. This high value of $f(q,t \to \infty)$ is expected for attractive glasses [13,18,19], and is in good agreement with MCT. Indeed, the theory predicts that both initial time and final time limiting the logarithmic decay increase continuously with volume fraction, and diverge on the A_3 singularity [12]. This behavior is correctly verified in our system.

We used the adhesive hard-sphere potential of Baxter in order to quantitatively measure the attraction between the micelles, *i.e.*, the stickiness parameter $1/\tau$ [30,31]. The viscosity and diffusion coefficient in the dilute limit are related to $1/\tau$ in a simple way. Our results show that for the asymmetric copolymer $1/\tau$ ranges from 0 for the purely repulsive micelles to 5 for a percentage of stickers of 34%, where we observe the logarithmic behavior. The value of $1/\tau = 5$ is consistent with molecular-dynamics simulation showing a maximum of the dynamics for $|U/kT| = 2 (1/\tau \sim 4)$ [18]. Even though MCT predicts that A_3 singularity is located at a lower $1/\tau$ value (~ 1) [11], experimental mapping of the phase boundaries has shown that MCT underestimates the onset of attraction [18].

In summary, we have shown the first experimental evidence of the relationship between rheology and dynamics showing a re-entrant glass transition. The two techniques reveal that inducing a weak attraction between the micelles causes the softening of the glass. Increasing attraction further we were able to get near the higher-order cusplike bifurcation point in the phase diagram of adhesive spheres. In the vicinity of this singularity, the logarithmic decay of the dynamic structure factor is observed over 4 decades. This work provides also a remarkable extension of the adhesive hard-sphere picture to polydisperse soft spheres of polyelectrolyte copolymer solutions.

* * *

The authors thank G. LIZZARAGA of the Rhodia Synthesis and Development Laboratory for providing the PS-PEA copolymers and A. LAPP of the Laboratoire Léon Brillouin (CNRS-CEA) for assistance with the SANS measurements.

REFERENCES

- [1] GÖTZE W. and SJÖGREN L., Rep. Prog. Phys., 55 (1992) 241.
- [2] ANGELL C. A., in *Complex Behavior of Glassy Systems*, edited by RUBI M. and PEREZ-VINCENTE C. (Springer, Berlin) 1997.
- [3] PUSEY P. N. and VAN MEGEN W., Phys. Rev. Lett., 59 (1987) 2083.
- [4] VAN MEGEN W. and PUSEY P. N., Phys. Rev. A, 43 (1991) 5429.
- [5] BARTSCH E., ANTONIETTI M., SCHUPP W. and SILLESCU H., J. Chem. Phys., 97 (1992) 3950.

- [6] VAN MEGEN W. and UNDERWOOD S. M., Phys. Rev. E, 49 (1994) 4206.
- [7] VAN MEGEN W., MORTENSEN T. C. and WILLIAMS S. R., Phys. Rev. E, 58 (1998) 6073.
- [8] ROMER S., SCHEFFOLD F. and SCHURTENBERGER P., Phys. Rev. Lett., 85 (2000) 4980.
- [9] BENGTZELIUS U., GÖTZE W. and SJÖLANDER A., J. Phys. C, 17 (1984) 5915.
- [10] CIPELLETTI L. and RAMOS L., Curr. Opin. Colloid Interface Sci., 7 (2002) 228.
- [11] FABBIAN L., GÖTZE W., SCIORTINO F., TARTAGLIA P. and THIERRY F., Phys. Rev. E, 59 (1999) R1347.
- [12] GÖTZE W. and SPERL M., Phys. Rev. E, 66 (2002) 011405.
- [13] DAWSON K. A., FOFFI G., FUCHS M., GÖTZE W., SCIORTINO F., SPERL M., TARTAGLIA P., VOIGTMANN TH. and ZACCARELLI E., Phys. Rev. E, 63 (2000) 011401.
- [14] ZACCARELLI E., FOFFI G., DAWSON K. A., SCIORTINO F. and TARTAGLIA P., *Phys. Rev. E*, 63 (2001) 031501.
- [15] PUERTAS A. M., FUCHS M. and CATES M. E., Phys. Rev. Lett., 88 (2002) 098301-1.
- [16] ZACCARELLI E., FOFFI G., DAWSON K. A., BULDYREV S. V., SCIORTINO F. and TARTAGLIA P., Phys. Rev. E, 66 (2002) 041402.
- [17] FOFFI G., DAWSON K. A., BULDYREV S. V., SCIORTINO F., ZACCARELLI E. and TARTAGLIA P., Phys. Rev. E, 65 (2002) 050802.
- [18] PHAM K. N., PUERTAS A. M., BERGENHOLTZ J., EGELHAAF S. U., MOUSSAÏD A., PUSEY P. N., SCHOFIELD A. B., CATES M. E., FUCHS M. and POON W. C. K., *Science*, **296** (2002) 104.
- [19] ECKERT T. and BARTSCH E., Phys. Rev. Lett., 89 (2002) 125701.
- [20] CHEN W. R., CHEN S. H. and MALLAMACE F., Phys. Rev. E, 66 (2002) 021403.
- [21] MALLAMACE F., GAMBADAURO P., MICALI N., TARTAGLIA P., LIAO C. and CHEN S. H., Phys. Rev. Lett., 84 (2000) 5431.
- [22] STIAKAKIS E., VLASSOPOULOS D., LIKOS C. N., ROOVERS J. and MEIER, Phys. Rev. Lett., 89 (2002) 208302.
- [23] PONTONI D., NARAYANAN T., PETIT J. M., GRUBEL G. and BEYSENS D., Phys. Rev. Lett., 90 (2003) 188301.
- [24] POON W. C. K., SELFE J. S., ROBERTSON M. B., ILETT S. M., PIRIE A. D. and PUSEY P. N., J. Phys. II, 3 (1993) 1075.
- [25] BHATIA S. R., MOURCHID A. and JOANICOT M., Curr. Opin. Colloid Interface Sci., 6 (2001) 471.
- [26] BHATIA S. R. and MOURCHID A., Langmuir, 18 (2002) 6469; BHATIA S. R., CRICHTON M., MOURCHID A., PRUD'HOMME R. K. and LAL J., J. Polym. Prepr., 42 (2001) 326.
- [27] MOURCHID A., DELVILLE A., LAMBARD J., LECOLIER E. and LEVITZ P., Langmuir, 11 (1995) 1942.
- [28] SEGRE P. N. and PUSEY P. N., Phys. Rev. Lett., 77 (1996) 771.
- [29] SEGRE P. N., PRASAD V., SCHOFIELD A. B. and WEITZ D. A., Phys. Rev. Lett., 86 (2001) 6042.
- [30] BAXTER R. J., J. Chem. Phys., 49 (1968) 2770.
- [31] PHAM Q. T., RUSSEL W. B., THIBEAULT J. C. and LAU W., Macromolecules, **32** (1999) 2996.