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Non-equilibrium structure in attractive colloidal dispersions: The case of intermediate and high volume fractions.

Experiment number:
SC2200

Beamline: ID02A	Date of experiment: from: 27-04-2007 to: 30-04-2007	Date of report: <i>Received at ESRF:</i>
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Names and affiliations of applicants (* indicates experimentalists):

Mr. Basavaraja Madivala*, Dept. of Chemical Engineering, KULeuven, Belgium

Prof. Jan Vermant*, Dept. of Chemical Engineering, KULeuven, Belgium

Dr.T. Narayanan*, ESRF

Dr. George Petekidis*, FORTH, Institute of Electronic Structure & Laser, Heraklion, Crete, Greece

Prof. Dimitris Vlassopoulos, FORTH, Institute of Electronic Structure & Laser, Heraklion, Crete, Greece

Mr. Frank Snijkers*, Dept. of Chemical Engineering, KULeuven, Belgium

Report:

The goal of the experiments was to investigate how the quiescent and shear induced structure and rheological properties of a model aggregating suspension made of sticky spheres. We especially wanted to explore the entire range of volume fractions, as one gradually goes from the fractal gels to the concentrated glass-like systems. Special emphasis was on elucidating the non-equilibrium structure and the anisotropy thereof.

The expected results as listed in the proposal were :

1. To obtain a full description of the microstructural hierarchy in weakly aggregated suspensions at intermediate and high volume fractions.
2. To elucidate the role of the mesoscale structure for intermediate volume fraction
3. To provide guidance to further theoretical developments for the description of attractive colloids

Materials

We have investigated the quiescent and flow-induced microstructure of model system of sticky sphere suspensions over wide range of volume fractions. Aqueous charge stabilized silica particle suspension (LUDOX TM-50) obtained from Grace Division was used as starting material for the synthesis of sticky sphere suspensions. These were coated with a layer of 1-Octadecanol following a procedure developed by van Helden et al [1]. Thus synthesized particles had an average particle diameter of 27.6 nm and a polydispersity of 10%, obtained by form factor fit to SAXS data assuming Schultz type size distribution [2-3]. Sticky sphere suspensions were formulated by dispersing a known weight of dried silica particles in n-Tetra-decane, which gives rise to a thermally reversible hard-sphere to sticky sphere transition at a well defined temperature. Static microstructures were measured with USAXS (at volume fraction of 0.10, 0.25, 0.35, 0.50 and 0.55) and SAXS (at volume fraction of 0.25 and 0.40) in flat walled 0.5mm thick glass capillaries. low-SAXS measurements were done in a polycarbonate Couette flow cell installed in the beam flight path at ID02 which provided insights into microstructure in velocity gradient plane.

1) Quiescent Structure:

Investigation of static structure and rheology of thermal and depletion gels has received considerable attention in recent years [4-18]. Recently, some controversy arose, as depletion gels were shown to possess a heterogeneous structure; which was suggested to be absent in thermal gels. The latter has important consequences for the suitability of e.g. Mode coupling theory in predicting the mechanical properties [8]. Thanks to the recent improvements in ID02, combined with an adequate choice of particle size, we could extend the measurement range to lower qR (with q the scattering vector and R the particle radius), so that for thermal gels a regime could be investigated which so far had eluded experimental determination. Figure 1a) shows the evolution of $I(q)$ for a suspension of 0.25 volume fraction. Shape of the scattering curve at high temperature (50°C) corresponds to that of a stable (or repulsive hard sphere) suspension. As the attraction is turned on by decreasing temperature, transition to sticky sphere occurs at about 45°C due to increased attraction. At temperatures well below 45°C , significant increase in $I(q)$ is observed which is attributed to the presence of large clusters [9]. Similar behaviour was observed at other low and intermediate volume fractions. At highest concentration studied ($\phi = 0.55$) changes in static structure observed was very subtle in agreement with earlier studies [9]. Evolution of $S(q)$ (not shown here) at $\Phi = 0.25$ and $\Phi = 0.40$ shows a low q -upturn attributed to the presence of structural heterogeneities [19]. This result directly contradicts the data reported by Ramakrishnan et al [17]. We believe that using suitable particle size and the increased SAXS resolution due to recent improvements on ID02, enable us to capture the low q upturn of $S(q)$, which could not be accessed by the other groups using larger particles and a less performant beamline compared to ID02. Structural heterogeneities thus observed here suggest that these systems are structurally no different from depletion systems [5,11]. Figure 1 b) depicts the length scale of structural heterogeneity (or cluster size) extracted from $I(q)$ curves at $\Phi = 0.10, 0.25$ and 0.40 as a function of temperature. Even at $\Phi=0.40$ heterogeneities were detected. At volume fraction studies cluster size varies by almost 2 orders of magnitude and equilibrium cluster size appears to increase with decreasing volume fraction.

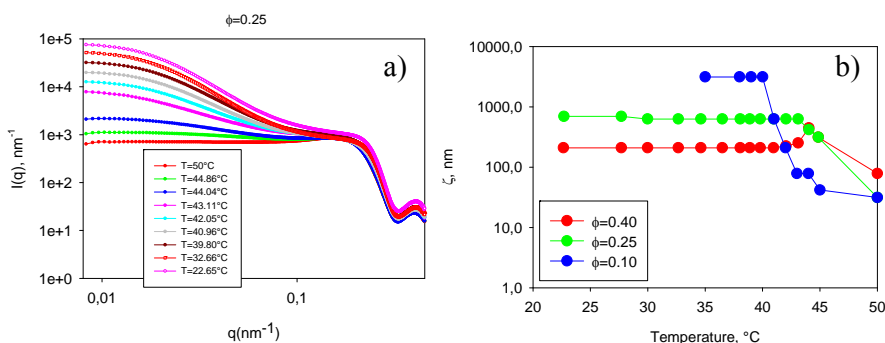


Figure 1. a) SAXS curves showing the evolution of $I(q)$ at $\Phi = 0.25$. b) Cluster size at $\Phi = 0.10, 0.25$ and 0.40 as a function of temperature.

2) Flow-induced Microstructure:

Taking advantage of the time and spatial resolution of ID02 we investigated the steady state and transient structure evolution under flow. The flow induced microstructure of dispersions at $\Phi = 0.10, 0.25, 0.40$ and 0.54 were investigated. Low amplitude oscillatory measurements were done on suspension of $\Phi = 0.40$. Most of the measurements were done at 35°C , well below temperature of aggregation ($\sim 45^\circ\text{C}$). In all measurements the thermo-reversibility was exploited to erase any shear and loading history and to obtain reproducible initial structure with clean and reproducible results. All samples were left to equilibrate at measurement temperature for 15 minutes before each measurement. Flow-induced microstructures in sticky sphere suspensions have been studied earlier at lower volume fraction [16,18]. Flow-induced structures observed in $\phi=0.10$ suspension fell outside SAXS window, hence no anisotropy was observed, whereas at 0.54 anisotropy observed was due to macroscopically visible fracture of the sample.

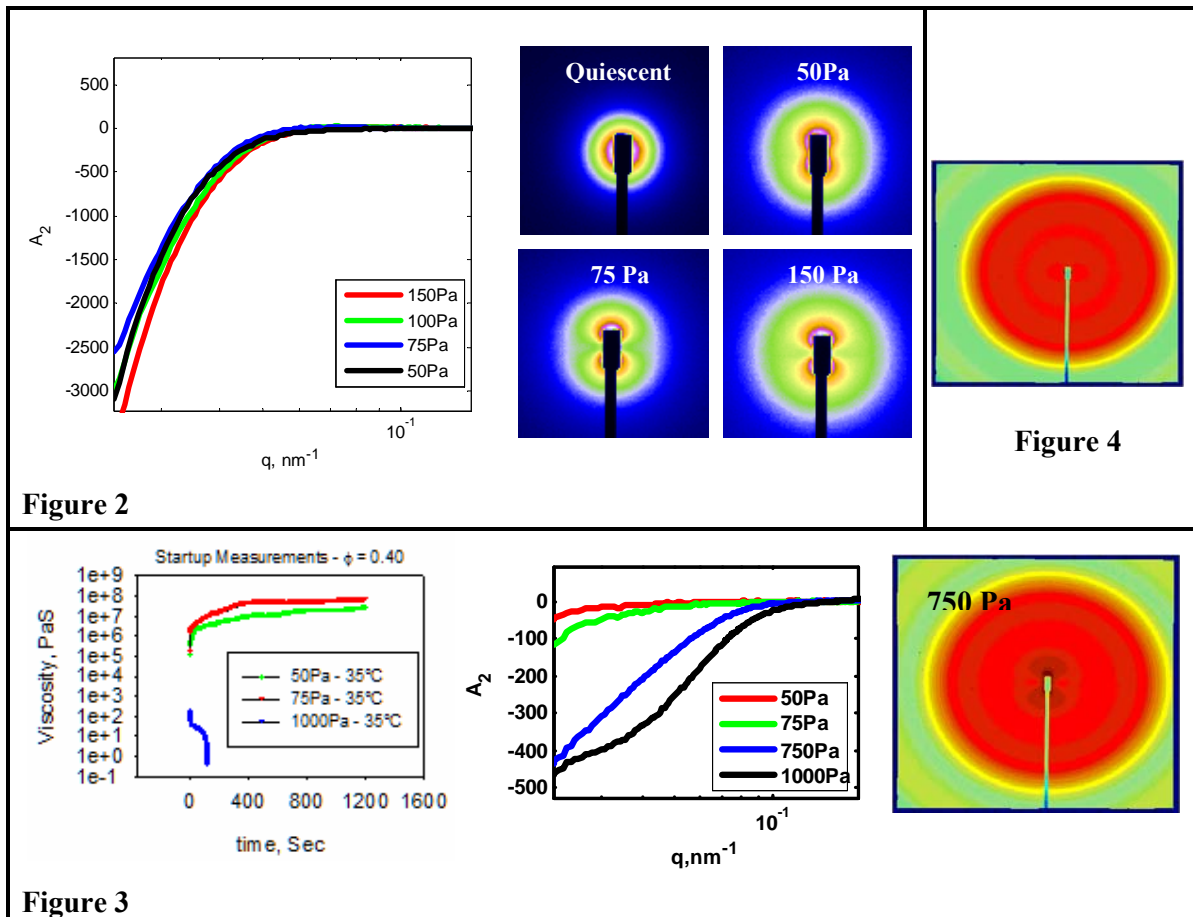


Figure 2. $\Phi = 0.25$ - Quiescent and steady state anisotropic pattern at 50Pa, 75Pa and 150 Pa and corresponding Anisotropy (2-fold symmetry). **Figure 3.** $\Phi = 0.40$ - Viscosity vs time at different stresses, corresponding Anisotropy with 2-fold symmetry and representative steady state anisotropic pattern at 750 Pa. **Figure 4.** Relaxation of butterfly pattern as in Figure 3 (750 Pa) 40 minutes after cessation of flow.

Two-lobe butterfly patterns were observed in suspensions of $\Phi = 0.25$ and at $\Phi = 0.40$ during start up measurements upon application of shear stresses above its yield stress [Yield stress $\sim 50\text{Pa}$ for $\Phi = 0.20$ and $\sim 750\text{Pa}$ for $\Phi = 0.40$ suspension]. These patterns were observed to be oriented in flow direction, implying a structure oriented predominantly along the vorticity direction. Due to the selected particle size and the excellent performance of ID02 the entire anisotropic microstructural organization could be brought into the experimental SAXS window for the first time. Earlier results required combinations of SAXS and SALS, whereas now detailed quantitative analysis of the entire structure factor is possible, within one experiment. Anisotropy seen was quantified by integrating 2D SAXS pattern over azimuthal angle weighted by harmonics of cosine [18,20-21]. Anisotropy factor A_2 , is zero for iso-tropic scattering patterns. As depicted both in Figure 2 and 3, anisotropy factor A_2 , differs significantly from zero above yield stress. Anisotropy shifts to higher q or smaller length scales with increasing stress levels for both suspensions of $\Phi = 0.25$ and that of $\Phi = 0.40$. Flow-induced structures in 40 volume% suspension relaxed significantly 40 minutes after cessation of flow as shown in Figure 4 (at 750 Pa). Whereas in 25 volume% suspension, relaxation observed was subtle. Two-lobe butterfly patterns were also observed during oscillatory measurements.

Conclusions:

- 1) Using suitable particle size and increased SAXS resolution, we have captured the low q upturn of $S(q)$ indicating the presence of heterogeneities in thermal gels.
- 2) Cluster size appears to depend on volume fraction.
- 3) Flow enhances the heterogeneity in dense colloidal gels in manners which are identical to what has been described for fractal gels.

- 4) Flow induced anisotropy is observed at least up to volume fractions of 0.4. This is important for the limits of the use approaches such as mode coupling theory
- 5) Microstructure still relaxes significantly after shear flow in a suspension at this volume fraction of 0.4.

Given the unexpected outcome of the results concerning the maximum volume fraction at which flow induced heterogeneity we will ask for a continuation of the proposal to finish experiments on 2 more volume fractions. We would also like to get more quantitative on how cluster size depends on volume fraction, as this is an important feature in the fundamental understanding of the heterogeneity which is still lacking. As this proposal was block-allocated with SC-2201, we lacked some time to finish our experimental program. Two manuscripts will be prepared, one dealing with the structure and steady state rheology, one dealing with the transient rheology.

References:

- [1]. van Helden, A. K.; Jansen, J. W.; Vrij, A. *J. Colloid Interface Sci.* 1981, *81*, 354-368.
- [2]. Aragon, S.R. and Pecora, R. (1976), *J. Chem. Phys.*, **64**, 2395.
- [3]. Kotlarchyk, M. and Chen, S.-H. (1983) *J. Chem. Phys.*, **79**, 2461.
- [4]. Rueb CJ, Zukoski CF, Viscoelastic properties of colloidal gels, *J. Rheol.*, 41 (2): 197-218 (1997)
- [5]. Dibble CJ, Kogan M, Solomon MJ. *Phys. Rev. E* 74 (4) 041403 (2006)
- [6]. Zaccarelli E, Foffi G, Dawson KA, Sciortino F, Tartaglia P, *Phys. Rev. E* 63,031501 (2001)
- [7]. Dawson, K, Foffi, G.; Fuchs, M.; Götze, W. , Sciortino, F. Sperl, M. and Tartaglia, P. and Voigtmann, Th. and Zaccarelli, E. *Phys. Rev. E.* 63, 011401 (2001).
- [8]. Ramakrishnan, S; Chen, YL; Schweizer, KS; Zukoski, CF, *Phys. Rev. E*, 70 (4): Art. No. 040401 (2005)
- [9]. Sztucki M, Narayanan T, Belina G Moussaid, A. Pignon, F Hoekstra, H. *Phys. Rev. E* 74, 051504 (2006)
- [10]. Sedgwick, H; Egelhaaf, SU; Poon, WCK. *J. Phys.: Condens Matter*, 16 (42): S4913-S4922. (2004)
- [11]. Gopalakrishnan V, Zukoski CF. *Phys. Rev. E* 75 (2),021406 (2007)
- [12]. Varadan P, Solomon MJ. *Langmuir* 19 (3): 509-512 (2003)
- [13]. Shah, SA; Chen, YL; Ramakrishnan, S; Schweizer, KS; Zukoski, CF. *J. Phys.: Condens Matter*, 15, 4751-4778 (2003)
- [14]. Verduin H, Dhont JKG. *J. Colloid Interface Sci.* 172 (2): 425-437 (1995)
- [15]. Verduin H, de Gans, Dhont JKG. *Langmuir.* 12, 2947-2955 (1996)
- [16]. Varadan, P; Solomon, MJ, *Langmuir*, 17 (10): 2918-2929 (2001).
- [17]. S. Ramakrishnan, Zukoski CF *Langmuir*, 22, 7833-7842 (2006)
- [18]. Hoekstra, H; Mewis, J; Narayanan, T; Vermant, J. *Langmuir*, 21,11017-11025(2005)
- [19]. H. Weber, W. Paul, W. Kob, and K. Binder, *Phys. Rev. Lett.* 78, 2136 (1997).
- [20] Wagner, N. J.; Ackerson, B. J. *J. Chem. Phys.* **1992**, *97* (2), 1473-1483
- [21] Maranzano, B. J.; Wagner, N. J. *J. Chem. Phys.* **2002**, *117* (22),10291-10302.