

Report Run SC3278 (brigitte.pansu@u-psud.fr)
Insertion of gold nanoparticles in lyotropic lamellar systems:
tailoring interactions

Hydrophobically-coated gold nanoparticles can be successfully inserted in the hydrophobic regions of oil swollen lamellar phases. We have recently shown that confinement in the hydrophobic regions promotes a new repulsive interaction whose range varies as the lamellar period d^1 . The physical origin of this repulsion is still under debate, but it could be linked to the fluctuations of the water membrane. The proposal was mainly focus on the effect of the water membrane (in blue in Fig. 1) flexibility on this new interaction range.

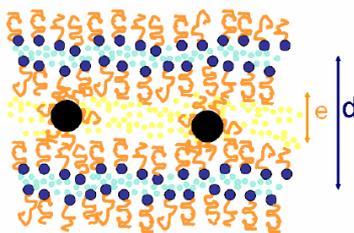


Figure 1 : Schematic drawing of the mixed system

The main results of the previous run on D2AM are summarized in Fig. 2.

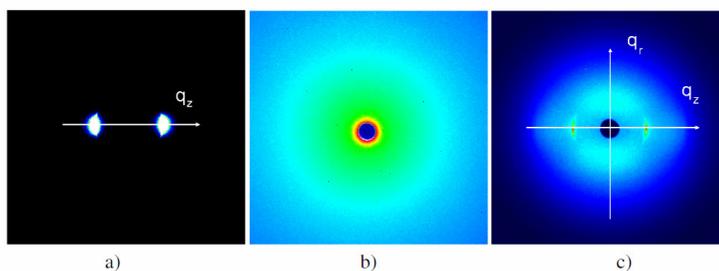


Figure 4: Diffraction patterns performed on a) the pure swollen (C) well oriented lamellar phase with q_z along the lamellar director b) the pure 20% w/w Au-C6 dispersion c) a well oriented doped lamellar phase (20% w/w Au-C6 , swelling C) where q_z is still along the lamellar director and q_r is in the lamellar plane.

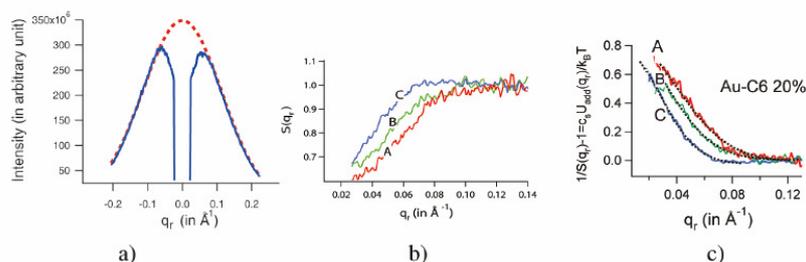


Figure 5. (a) Line scan of the intensity $I(q_r)$ in the q_r direction (20% w/w Au-C6, swelling C). The dotted line corresponds to the nanoparticle form factor. (b) Structure factor in the layer plane for the 20% w/w dispersion of hexane-thiol capped gold nanoparticles in lamellar phases at three different swelling ratios, from lower swelling ratio A to higher swelling ratio C. (c) Corresponding pair interaction potential $\bar{U}_{ada}(q)$ deduced from eq 3 and comparison with Gaussian models.

Figure 2: Main results of the previous run (D2AM 2010)

¹ [1] Pansu, B; Lecchi, A; Constantin, D; Imp rator-Clerc, M; Veber, M; Dozov, I. Insertion of Gold Nanoparticles in Fluid Mesophases: Size Filtering and Control of Interactions; *J. Phys. Chem. C*, 2011, 115 (36), pp 17682–17687 DOI: 10.1021/jp2046189

Main objectives of the run:

- The first objective was to try to understand how the flexibility of the water membrane affects the interaction between the gold nanoparticles inserted in the oil-swollen hydrophobic layers.
- The second objective was to increase the concentration of gold nanoparticles inside the hydrophobic layer.
- As we also plan to use other oil than dodecane we have also quickly tested the bulk interaction of gold nanoparticles in toluene often used as a swelling agent.

Preparation of the samples

Samples are usually prepared by adding a suspension of nanoparticles in oil to a pure lamellar phase.

In the first experiment¹ (D2AM 2010), the composition of the pure lamellar phase that had been used was :

SDS 30.6 w%, pentanol 22w%, water, 47.4% (labelled as P)

The flexibility of the water layer can be decreased by changing the composition. In this second run, the composition of the pure lamellar phase that have been used was:

SDS 43.9 w%, pentanol 21.8w%, water, 34.3% (labelled as Q)

During his Phd, E. Freyssingeas has shown that the Q phase was 10 times less flexible than the P phase ($\kappa_Q=10 \kappa_P$). In such a lamellar system, the fluctuation correlation length corresponding to the fluctuation maximum wavelength is expected to be equal to:

$\xi = d \sqrt{\frac{32}{3\pi}} \sqrt{\frac{\kappa}{kT}}$. Depending on the values of κ , one thus expect for $d=50\text{\AA}$: $\xi=45 \text{\AA}$ ($q=0.14 \text{\AA}^{-1}$) for the swollen P phase and $\xi=142\text{\AA}$ ($q=0.04 \text{\AA}^{-1}$) for the swollen Q phase. Therefore this length is expected to be three times larger in the Q type phases than in the P type phases for the same value of the lamellar period d.

Three different swellings of the P phase had been used:

A: $d=5.3 \text{ nm}$ B: $d=6.4 \text{ nm}$ C : $d=78.5 \text{ nm}$

We have used three different swellings of the Q phase with the same ranges of lamellar period and the same labels (A, B and C).

The gold nanoparticles that have been inserted have a gold core of about 2.3 nm and are coated with hexane-thiol (with layer thickness about 0.68 nm). Different volume fractions have been used: 10 w%, 20 w% in the swelling oil (dodecane+pentanol), as in the run performed in 2010, but also 30 w% since we wanted to test the effect of increasing volume fraction. Table 1 gives an example of composition for the the largest swelling

	QC		QC-10		QC-20		QC-30	
	Q+solution		Q+ disp.10%		Q+disp.20%		Q+disp.30	
Q	53.09		39.94		48.99		43.40	
solution	47.95		42.39		55.83		56.21	
SDS	23.32	23%	17.55	21%	21.52	24%	19.07	19.14%
pentanol	15.50	15%	11.83	14%	14.34	16%	12.69	12.74%
Water	18.20	18%	13.69	17%	3.22	4%	14.88	14.94%
dodecane	44.02	44%	35.02	43%	41.02	45%	36.21	36.35%
AU 102	0.00	0%	4.24	5%	11.14	12%	16.77	16.83%
	101.04		82.33		91.24		99.61	

Table 1 : Example of compositions for the highly swollen Q phase (QC)

All the samples have been sucked in flat glass capillaries (2mmx0.1 mm or 1mmx0.1mm). An oscillatory flow was applied to some of them in order to promote homeotropic alignment, that is when the membranes are parallel to the glass surfaces. All the capillaries were sealed to prevent water and pentanol evaporation.

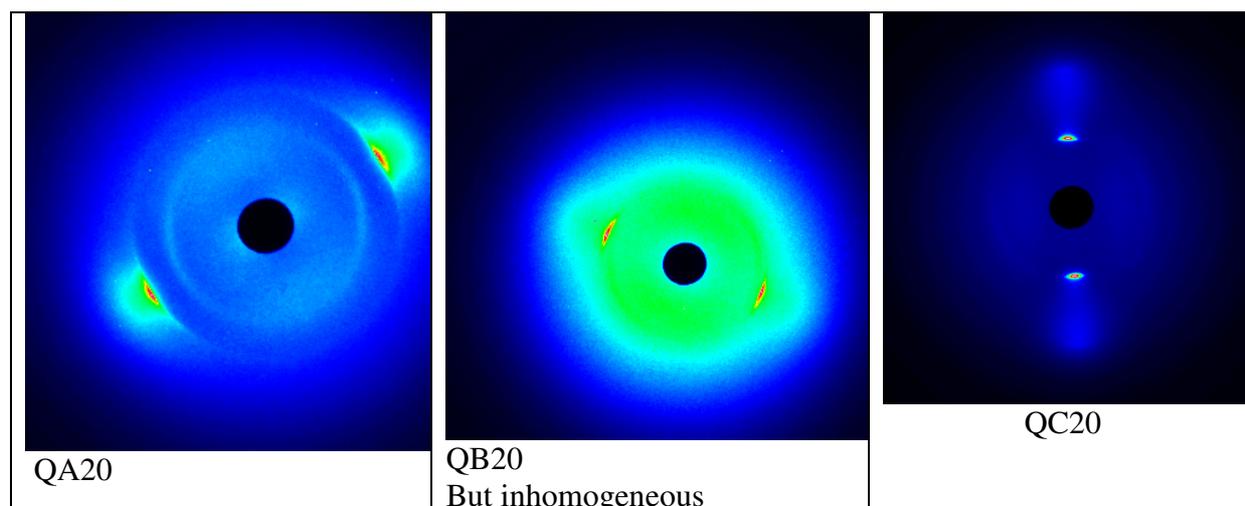
Experiments

All the capillaries were scanned vertically and horizontally in order to find good orientation (planar or homeotropic). The period was measured for all the patterns in order to check inhomogeneities that could be induced by a bad sealing.

	P	PA	PB	PC	Q	QA	QB	QC
expected d in Å	38				32			
water thickness (W) en Å	18				11			
SDS thickness in Å	20				21			
flexibility : κ/kT *	0.24				2.4			
swelling amount: added solvent/lamellar phase		30	50	70		40	65	90
d (2010 measurements)	37.4	52.6	63.9	78.4	32.2			
d (2011 measurements)		52	63	73.3		48	60	73
additional oil thickness in Å		14	25	35		16	28	41

Table 2 : Characterization of the lamellar phases
(* Eric Freyssingeas PhD Bordeaux , 1994)

Samples that have been prepared with the Q lamellar phase where the water membrane is expected to be less flexible than in the P phase has revealed **more difficult to align**.



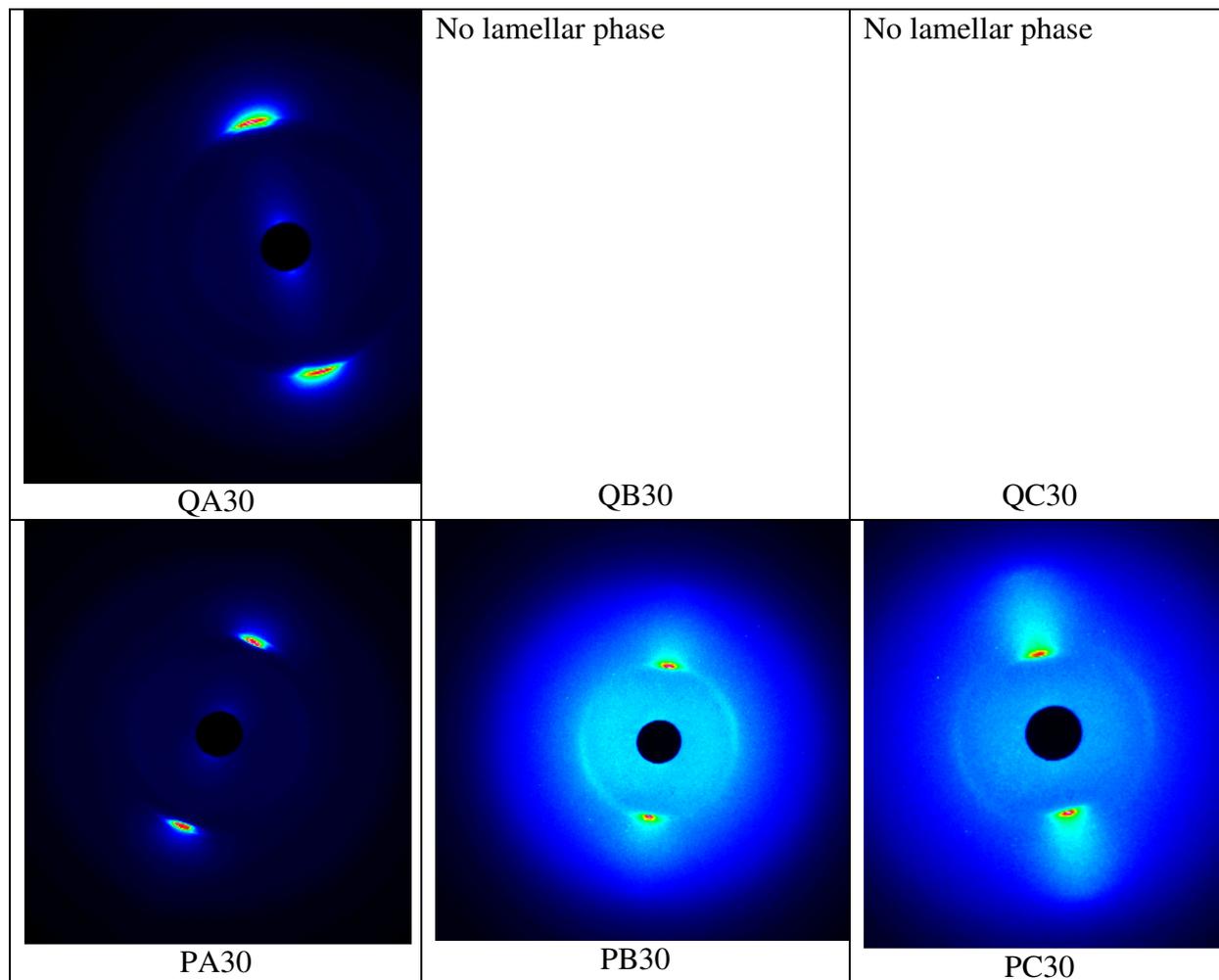


Figure 3: Scattering patterns on planar oriented samples

A detailed analysis of the profiles along the smectic period is required to check that the flexibility is really different for the Q phase.

The diffuse scattering perpendicular to the smectic order is lower for the Q phases compared to the P phase.

No clear homotropic orientation has been observed.

Nevertheless structure factors could be extracted: in red QA, in green QB, in blue QC.

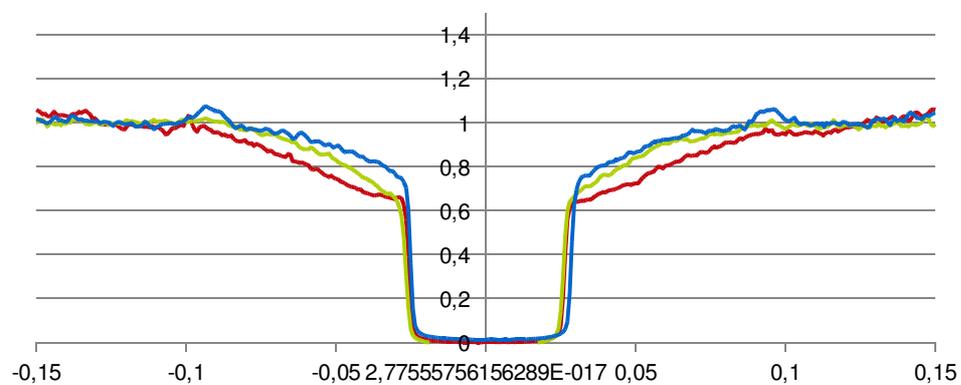


Figure 4: In-plane structure factor in swollen Q lamellar phase doped with gold nanoparticles (20w%). in red QA20, in green QB20, in blue QC20.

The interaction is still repulsive but its range is not so different from the P phase. It has been modeled as previously by $U(r) = U_0 \exp\left(-\frac{1}{2}\left(\frac{r}{\xi}\right)^2\right)$.

	d in Å	Swelling rate	Number of particles per Å ² for each lamella	Mean Distance between particles in nm	Surface fraction	width Gauss	ξ en Å	U0
QC10	73	90	2.15303E-05	22	0.0093	0.03625	39	1.71
								1.68
QC20	73	90	4.75359E-05	15	0.0204	0.044	32	1.64
QB10	60	65	1.49841E-05	26	0.0064	0.05236	27	4.73
								3.88
QB20	60	65	3.30828E-05	17	0.0142	0.0457	31	3.03
QA10	48	40	8.9136E-06	33	0.0038	0.064185	22	17.91
								11.49
QA20	48	40	0.00001968	23	0.0085	0.0457	31	5.07
PC10	79	70	1.82165E-05	23	0.0078	0.03625	39	2.02
								3.15
PC20	79	70	1.82165E-05	23	0.0078	0.044	32	4.28
PB10	64	50	1.19467E-05	29	0.0051	0.05236	27	5.93
								7.16
PB20	64	50	1.19467E-05	29	0.0051	0.0457	31	8.39
PA10	53	30	6.84923E-06	38	0.0029	0.064185	22	23.31
								18.97
PA20	53	30	6.84923E-06	38	0.0029	0.0457	31	14.64

Table 3 : Analysis of the repulsive interaction in different lamellar phases.

Main Results

Conclusion 1 : Unfortunately the role of the flexibility of the membranes could not be clearly established. Theoretical models are at present developed by J.B. Fournier (MSC, Paris-Diderot) to understand whether fluctuations can induce repulsive interaction and what would be the range of this interaction.

Conclusion 2: Increasing the particle concentration destabilizes the lamellar phase but the Q phase is more easily destabilized than the P phase. It is well known that insertion is favored by flexibility.

Before destabilization, a strong anisotropic scattering is observed at low angle and could be due to anisotropic aggregates. A detailed analysis of the scattering profile at low angle must be done to check this assumption. At large enough concentration, the lateral interaction would thus become attractive.

Conclusion 3: In the experiments performed on D2AM in 2010, the structure factor at small q could not be explained by van der Waals interaction and steric repulsion between the ligand shells. Since we plan to swell surfactant phases by other oils like cyclohexane or toluene, we wanted to check the interaction between gold nanoparticles and surprisingly, the behavior of $S(q)$ at small q reveals very different for particles suspended either in dodecane or in toluene.

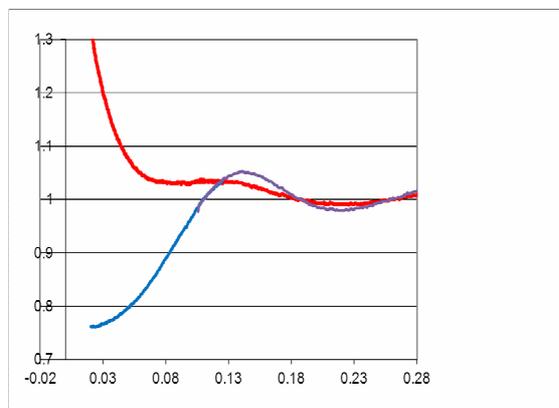


Figure 4: Structure factor measured as a function of q in \AA^{-1} for dispersion of gold nanoparticles with C12-thiol ligands either in dodecane in red or in toluene in blue (10 w%)

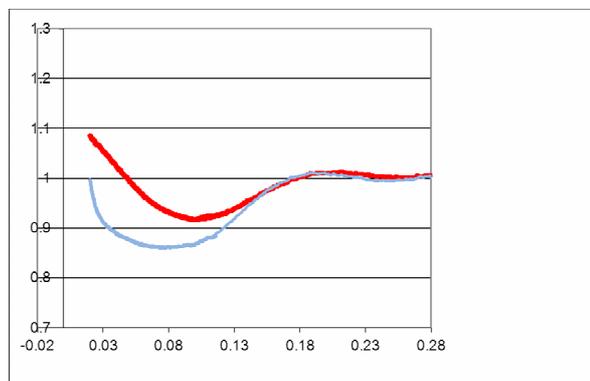


Figure 5: Structure factor $S(q)$ as a function of q in \AA^{-1} for dispersion of gold nanoparticles with C6-thiol ligands either in dodecane in red or in toluene in blue (10 w%)

Further studies with various concentrations, temperatures and solvents are required to describe properly the effect of the solvent on the ligand shell and thus on the interaction between particles.