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# Solvent-driven interactions between hydrophobically-coated nanoparticles

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March 22, 2015

## Abstract

Interaction between hydrophobically-coated gold nanoparticles suspended in oil is usually described combining strong attractive van der Waals attraction between the gold cores and interaction between the ligands. This last interaction is expected to be purely repulsive if the suspending medium is a good solvent for the ligands or partially attractive for a bad solvent. By measuring the structure factor of interacting gold nanoparticles in various solvents, we show that the chemical affinity of the ligand with the solvent is not the only parameter that controls the interaction between the ligands and that the solvent conformation (small rigid or long flexible molecules) also plays a crucial role. Gold nanoparticles covered with hexanethiol or dodecanethiol thus undergo a larger attraction in n-dodecane or n-hexadecane compared to toluene or cyclohexane. As a consequence, self-assembly of these nanoparticles into superlattices appears at a much lower volume fraction than predicted in n-hexadecane or n-dodecane. Analogy with the behavior of polymer grafted colloids in a polymer melt is proposed to explain these unexpected results.

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## 1 Introduction

Colloidal nanoparticles (NPs) can spontaneously self-assemble into ordered structures. They have thus gained much attention in materials science, since these superlattices are expected to exhibit original physical properties.<sup>1</sup> The possibility to control the NP size, shape and composition allows the tuning of their electronic, optical and magnetic properties. The interactions between the individual colloidal NPs are crucial for building these superlattices<sup>2</sup> but are not yet sufficiently understood. The synthesis of metallic NPs is now quite well controlled and much research effort has been made for functionalizing these nanoparticles using ligand exchange reaction in order to tune the interactions between the NPs. Playing with the nature of the ligands has thus provided many different coatings able to modulate the apparent size and the behavior of the NPs. However recent experiments have shown that the solvent also plays an important role in the self-assembly mechanism.<sup>3</sup> The interaction between hydrophobically-coated spherical nanoparticles in different organic medium is commonly described using standard models derived from polymer science but no direct measurement of this interaction has yet been done. The structure factor of concentrated NP suspensions is much sensitive to the interaction between NPs and useful information can be extracted from it. Metallic NPs give a strong signal in X-ray scattering and thus Small Angle X-ray Scattering (SAXS) is a pertinent tool<sup>4</sup> to measure their structure factor  $S(q)$  where  $q$  is the scattering vector. The main goal of this paper is the measurement by SAXS and the analysis of the structure factor  $S(q)$  of small gold spherical NPs covered with alkanethiols and dispersed in various solvents: n-heptane, n-dodecane, n-hexadecane, cyclohexane and toluene. The role of the solvent on the interaction between the NPs will then be discussed. Interaction between hydrophobically coated gold nanoparticles in organic medium is the combination of van der Waals forces and ligand interaction. It is usually described, as a function of the center–center distance  $r$ , by the sum of three contributions: the van der Waals attraction, the free energy of mixing of the ligands, and the elastic compression of the ligands.

The van der Waals interaction is dominated by the attraction between the metallic

cores with diameter  $D$  and is given by:

$$u_{vdW}(r) = -\frac{A}{12} \left[ \frac{D^2}{r^2 - D^2} + \frac{D^2}{r^2} + 2Ln\left(1 - \frac{D^2}{r^2}\right) \right] \quad (1)$$

Due to the gold high polarizability, the effective Hamaker constant  $A$  can be considered as solvent independent for the inorganic solvents used here and, as in many studies, will be taken as 75 kT.<sup>5</sup>

The mixing energy is described in the literature using the Alexander-de Gennes model and the Flory theory of mixing.<sup>6</sup> There are two regimes as a function of the separation distance  $r$  between the nanoparticles ( $D+L < r < D+2L$  and  $D < r < D+L$ ) where  $L$  is the contour length of the ligand chain. The interaction in both regimes depends on the affinity between the ligands and the organic medium through the Flory-Huggins parameter  $\chi$ . When  $\chi$  is smaller than 1/2, that is in the case of a good solvent, this mixing energy is repulsive but becomes attractive when  $\chi$  is larger than 1/2 (bad solvent). Considering  $V_s$  as the volume of the solvent molecule and  $\Phi_{av}$  as the average volume fraction of the ligand segments in the ligand shell, this interaction is described as following:

$$u_{mix,1}(r) = kT \frac{\pi D}{2V_s} \Phi_{av}^2 (1/2 - \chi) [(D+2L) - r]^2, \text{ for } D+L < r < D+2L \quad (2)$$

$$u_{mix,2}(r) = kT \frac{\pi D}{V_s} \Phi_{av}^2 (1/2 - \chi) L^2 \left[ 3Ln\left(\frac{L}{r-D}\right) + 2\frac{r-D}{L} - 3/2 \right], \text{ for } D < r < D+L \quad (3)$$

According to the regular solution theory, the Flory-Huggins interaction parameter can be expressed, as in polymer science, as a function of the solubility parameters of both solvent and ligand.<sup>7,8</sup> In the literature, two main approaches are used to determine these parameters: the Hansen method involving dispersive, polar and hydrogen bonding interaction and the Hildebrand method (SI1). In the case of the ligands (hexanethiol or dodecanethiol) used in this study, the best chemical affinity is expected for linear alkanes for both approaches. Cyclohexane is also expected to be a good solvent but

toluene should behave like a poor or even a bad solvent. The mixing interaction is expected to be repulsive for linear alkanes and cyclohexane but could be attractive for toluene at least in the case of hexanethiol as ligand.

The third term is the elastic energy due to the compression of the chains between two nanocrystal cores, it depends on the number of ligands per unit area at the gold surface ( $\sigma$ ) and is purely repulsive.

$$u_{el}(r) = kT\pi\sigma D \left[ (r-D) \left( Ln \frac{L}{r-D} - 1 \right) + L \right], \text{ for } D < r < D+L \quad (4)$$

Thus one expects the existence of some repulsive core, that is the sum of the metallic hard core (diameter  $D$ ) and the compression range ( $d_c$ ). In the most simple approach, it can be considered as a hard core repulsion with diameter  $D_{HSe}$  where  $D_{HSe} = D + d_c$  where  $d_c$  depends on the ligand length and grafting density. This classical description involving the three contributions (van der Waals, mixing and elastic) has been already used to understand the formation of superlattices of these nanoparticles when they self-assemble.<sup>3</sup> This classical analytical description seems to be also in good agreement with molecular simulations.<sup>9</sup> Nevertheless there is not yet any experiment that confirms the validity of this model. The main goal of this paper is to focus on the effect of the solvent on the interaction between the ligand parts revealed by the structure factor between the NPs. Therefore, to limit the van der Waals attraction, quite small gold nanoparticles with diameter close to 2 nm have been used.

## 2 Experimental methods

The NPs have been synthesized using the Brust's procedure<sup>10</sup> and are capped with either hexanethiol or dodecanethiol. Organic solvents and the other chemicals were purchased from Sigma-Aldrich Co. and were used as received. The size and polydispersity of NPs have been determined by performing SAXS on dilute suspension (SI2). Data analysis has been done using a Schulz-Hardy distribution and the NIST tools.<sup>11</sup> The Brust synthesis is very reproducible and the typical gold diameters ob-

tained by this method are  $D_6 = 2.4$  nm (with 16% polydispersity) with hexanethiol ligands and  $D_{12} = 2.2$  nm (with 12% polydispersity) for dodecanethiol ligands. In the following the NPs will be respectively labelled as 2C6 and 2C12. The grafting density, 5.4 ligands/nm<sup>2</sup> (resp. 6.3) for 2C6 (resp. 2C12) has been estimated using Thermo Gravimetry Analysis (TGA) and is fully compatible with standard values.<sup>12</sup> Suspensions of NPs with various concentrations have been prepared at the same molar concentration in different solvents: toluene and cyclohexane as small rigid molecules and linear alkanes with different length (n-heptane, n-dodecane, n-hexadecane). The reference in terms of molar concentration is the NP weight fraction in n-dodecane: 10w%, 20w%, 30w%... The suspensions were contained in sealed optical flat or cylindrical X-ray glass capillaries and studied at three different temperatures (25°C, 45°C, 65°C).

The interaction between the particles is revealed at high concentration through the structure factor  $S(q)$  defined as  $I(q) = nS(q)F(q)$ , where  $I(q)$  is the scattered intensity,  $n$  is the scattering objects density and  $F(q)$  is their form factor. Without any interaction between the NPs,  $S(q)$  is equal to 1. This is the case at low concentration (1 w% typically) where the intensity scattered by the NPs depends only on the form factor  $F(q)$ , so their shape, size and polydispersity can thus be determined (SI2). At high concentration, the structure factor  $S(q)$  can be measured using  $S(q) = \alpha \frac{I(q)}{F(q)}$ . When  $q$  is large enough,  $S(q)$  remains close to 1, thus fixing the value of  $\alpha$ . Experiments have been performed on the Swing beamline of the Soleil synchrotron laboratory (Gif/Yvette, France). Complementary tests have been done on the D2AM beamline of the ESRF synchrotron laboratory (Grenoble, France). During the  $S(q)$  extraction, a special care must be taken to correctly subtract the background (SI3). The structure factor is related to the Fourier transform of the total pair correlation function  $g(r)$  through the following relationship (eq. 5):

$$S(q) = 1 + 4\pi n \int (g(r) - 1) \frac{\sin(qr)}{qr} r^2 dr \quad (5)$$

The link between the pair potential  $V(r)$  and the structure factor is simple only for dilute suspensions and interactions weaker than  $kT$ :  $g(r) \approx \exp[-V(r)/kT]$ . In such

conditions,  $S(q) \approx 1 - nV(q)/kT$ , where  $V(q)$  is the Fourier transform of  $V(r)$ . This is no longer true at high concentration or for strong interaction<sup>13, 14</sup>. In the general case, the structure factor can be expressed using the direct pair correlation function  $c(r)$  through the Ornstein-Zernicke expression  $S(q) = 1/(1 - nc(q))$  where  $c(q)$  is the Fourier transform of the direct correlation function  $c(r)$ . To express  $S(q)$ , a closure relation involving  $c(r)$ ,  $g(r)$  and  $V(r)$  is required. Different closure relations relating these three functions have been proposed. We have used the Percus-Yevick approximation that leads to an analytical solution for hard spheres and sticky hard spheres and the hypernetted chain approximation (HNC) largely used for electrostatic systems. The structure factor using the Percus-Yevick approximation has been computed using the NIST packages.<sup>11</sup> For the computation based on the HNC approximation, we have used a Fortran program kindly provided by Luc Belloni (IRAMIS, CEA Saclay, France).

### 3 Results and discussion

Dodecanethiol or hexanethiol coated Au NPs with gold diameter close to 2 nm are employed in the present investigation. Each synthesis produces 100mg of a NPs powder. A small amount of this powder is dispersed in different solvents at various concentrations. The scattered X-ray intensity is recorded on a 2D detector and then radially integrated. Experiments performed on different batches are perfectly reproducible. A typical curve  $I(q)$  is presented in Fig. 1 for 2C12 NPs dispersed in n-dodecane at 20w% concentration. The dotted line corresponds to the NP form factor. At lower  $q$ , the intensity is clearly different from what is expected from independent particles, revealing interactions between the NPs. The structure factor that can be extracted is shown on Fig. 2 for three different concentrations.

The same procedure has been applied to suspensions in other solvents with the same molar concentration in NPs. Results are shown on Fig. 3 for 2C12 (2.1 mM) and Fig. 4 for 2C6 (1.9 mM). The main sources of errors are due to the subtraction of the solvent contribution and the nanoparticle form factor. Typical error on  $S(q)$  can be estimated to

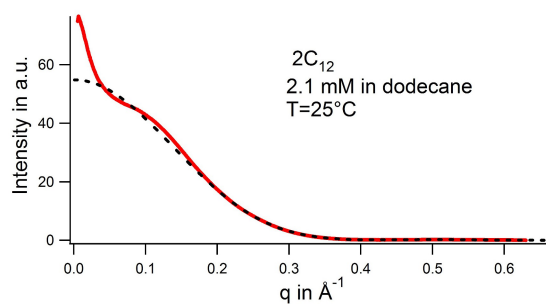


Figure 1: Recorded scattered intensity  $I$  as a function of  $q$  for a suspension of 2C12 NPs in n-dodecane (20w% or 2.1mM). The dotted line corresponds to the form factor of polydisperse spheres with diameter  $D_{12}=2.14\text{nm}$  and 12% polydispersity.

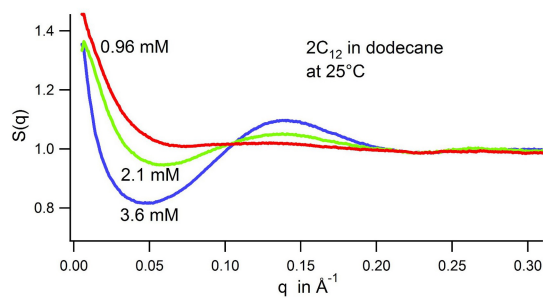


Figure 2: Structure factor of 2C12 gold NPs in n-dodecane, at room temperature and for three concentrations: 0.96 mM (10w%), 2.1 mM (20w%), 3.6 mM (30w%).



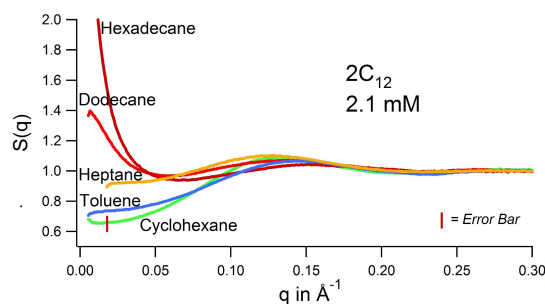


Figure 3: Structure factor of 2C12 gold NPs suspended in various solvents at room temperature. Their concentration is 2.1 mM (20w% in n-dodecane).

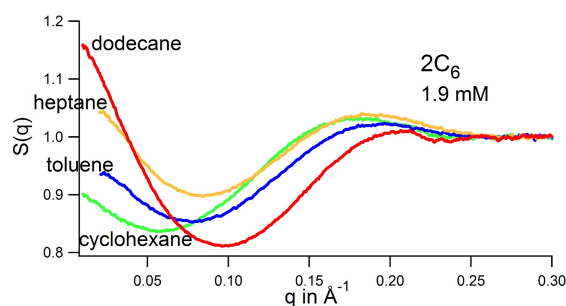


Figure 4: Structure factor of 2C6 gold NPs suspended in various solvents at room temperature. Their concentration is 1.9 mM (20w% in n-dodecane).

5%. For 2C12 as for 2C6 NPs, the structure factor in cyclohexane and toluene are close from each other whereas the structure factors in n-dodecane and n-hexadecane are very different from those in toluene or cyclohexane. The structure factor in cyclohexane, toluene or heptane does not change upon temperature at least from 25°C to 65°C. This is no longer the case for the 2C12 NPs suspended in n-dodecane and n-hexadecane as shown in Fig. 5. The structure factor in n-dodecane as in n-hexadecane strongly varies upon temperature and for large enough temperature it becomes close to the structure factor in heptane.

Since the grafted layer is dense, the expected range of the apparent hard sphere diameter ( $De$ ) associated with repulsive interaction can be estimated adding the core diameter  $D$  and the extended ligand chain length  $\ell$ :  $\ell_6 = 0.8$  nm for hexanethiol and  $\ell_{12} = 1.6$  nm for dodecanethiol. This leads to  $De_6 = D_6 + \ell_6 = 3.2$  nm and  $De_{12} = D_{12} + \ell_{12} = 3.8$  nm. The van der Waals interaction diverges when the gold cores are

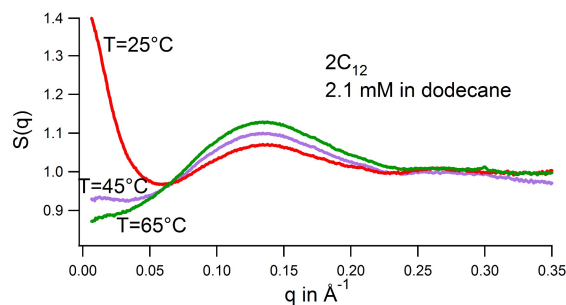


Figure 5: Structure factor of 2C12 gold NPs suspended in n-dodecane (20w% or 2.1 mM) at three different temperatures: 25°C, 45°C and 65°C.

w% in n-dodecane	$n$ mM 2C6	$\Phi_e$ 2C6	$\Phi_m$ 2C6	$n$ mM 2C12	$\Phi_e$ 2C12	$\Phi_m$ 2C12
10	0.86	0.9%	1.7%	0.96	1.7%	4.8%
20	1.9	2%	3.8%	2.1	3.6%	10.5%
30	3.17	3.3%	6.4%	3.6	6.3%	17.2%

Table 1: Nanoparticle concentration and different volume fractions that can be deduced depending on the external apparent diameter that is considered:  $\Phi_e$  when the ligand chains are elongated and totally interpenetrated ( $De = D + \ell$ ) or  $\Phi_m$  when the ligand chains are elongated but with no interpenetration ( $D_m = D + 2\ell$ ).  $\Phi_m$  is thus the highest volume fraction occupied by the NPs that can be considered.

close and is thus very sensitive to the ligand shell thickness. The estimated van der Waals interaction energy between the gold cores at the distance  $De$  is thus -1.2 kT for 2C6 and -0.14 kT for 2C12. This interaction is much lower than kT for the 2C12 NPs and thus one can expect to reveal more easily the contribution of the ligand interactions in that case. The volume fraction occupied by the particles is largely dependent on the ligand shell conformation and different volume fractions can thus be estimated (Table 1). They are always smaller than the volume fraction for which hard spheres are expected to crystallize (49.4%).

The structure factor has been numerically computed using the HNC approximation (Fig. 6) for hard sphere with diameter  $D_{HSe}$ , interacting through a van der Waals interaction between cores with a diameter  $D$  and a Hamaker constant  $A = 75kT$ , with different concentrations  $n$ . As expected, 2C12 NPs are not very sensitive to van der Waals attraction and the structure factor is close to that of pure hard spheres. The main difference between 2C6 and 2C12 is observed at low  $q$  where the van der Waals

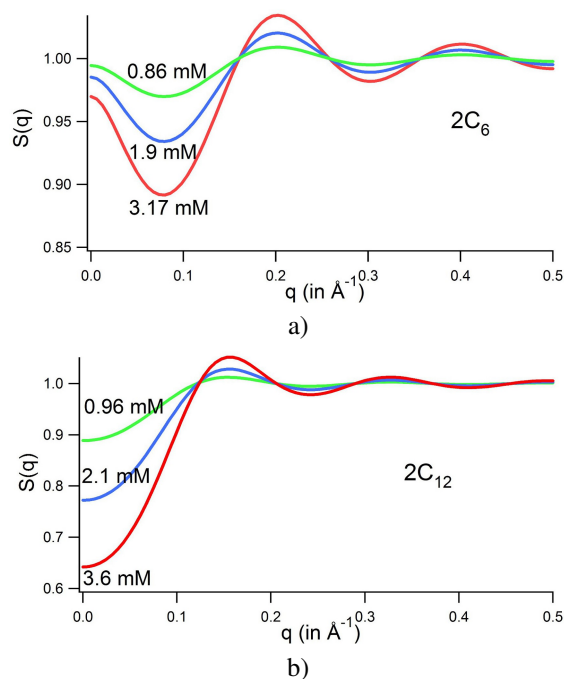


Figure 6: Structure factor computed by HNC approach of hard sphere with diameter  $D_6 + \ell_6 = 3.2\text{nm}$  (a) or  $D_{12} + \ell_{12} = 3.8\text{nm}$  (b) interacting via van der Waals interaction between the gold core with diameter  $D_6 = 2.4\text{ nm}$  (a),  $D_{12} = 2.2\text{ nm}$  (b), the Hamaker constant used is equal to  $75\text{ kT}$ .

attraction makes  $S(q)$  rising for  $2C_6$  NPs.

When comparing the experimental structure factors and the computed one, the model combining hard sphere repulsion and van der Waals attraction is appropriate when the NPs are suspended in cyclohexane and in toluene but clearly fails to describe interaction in n-dodecane or n-hexadecane. Indeed the structure factor of the  $2C_{12}$  NPs suspended in cyclohexane or toluene is well described by a hard sphere structure factor with no further interaction (Fig. 7). The apparent hard sphere diameter  $D_{HSa}$  has been determined using the Percus-Yevick approximation. It depends on the solvent:  $D_{HSa2} = D_{12} + 2.3\text{ nm}$  in cyclohexane and  $D_{HSa1} = D_{12} + 1.9\text{ nm}$  in toluene. As expected, the ligand shell is more swollen in cyclohexane that is a better solvent for the ligand chain than toluene and due to swelling, the apparent diameter  $D_{HSa}$  is larger than the diameter  $D_{HSe}$  predicted by considering full interpenetration of extended chains ( $D_{HSa} > D_{12} + \ell_{12}$ ). The mixing energy (Eq.2) for a distance between the NPs equal

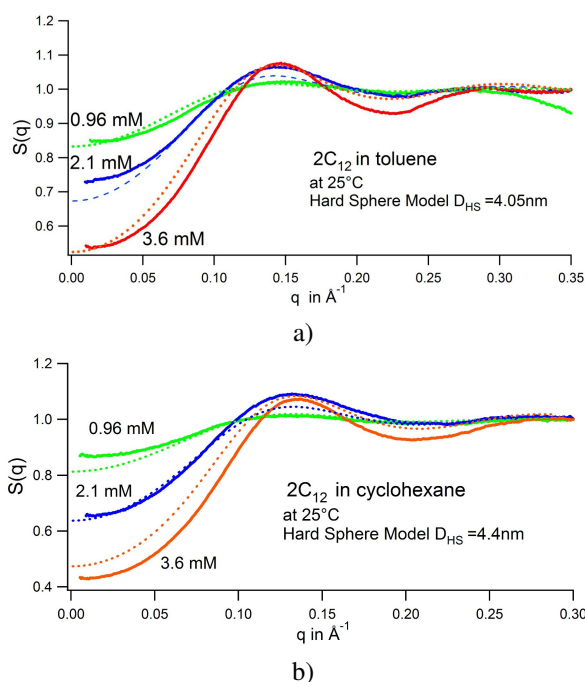


Figure 7: Experimental structure factor  $S(q)$  for 2C<sub>12</sub> NPs suspended either in toluene (a) or in cyclohexane (b) at different concentrations and at room temperature. The dotted lines represent the theoretical structure factor of hard spheres with an apparent diameter  $D_{HSa}$ :  $D_{HSa1} = 4.05$  nm for toluene,  $D_{HSa2} = 4.4$  nm for cyclohexane.

to the apparent diameter can easily be computed from Eq. 2 using the Flory-Huggins parameter deduced from the Hansen solubility parameters (SI4). The total energy including van der Waals attraction and mixing energy is about 1.6 kT for both solvents, so close to kT, confirming the validity of the model.

For 2C<sub>6</sub> NPs, the van der Waals attraction cannot be neglected. HNC computation has thus been done combining simply hard sphere repulsion and van der Waals attraction between the gold cores with a Hamaker constant equal to 75kT. But as shown in Fig. 8 for 2C<sub>6</sub> NPs suspended in cyclohexane, such approach cannot reproduce well the experimental structure factor. In that case, the van der Waals attraction is important but the Hamaker constant is not precisely known and is suspected to depend on the NP size.<sup>15</sup> The polydispersity is not taken into account in the HNC computation and, as shown by Brust,<sup>10</sup> the nanoparticles are not perfectly spherical. Moreover the ligand interaction cannot probably be simply described by a hard sphere repulsion and

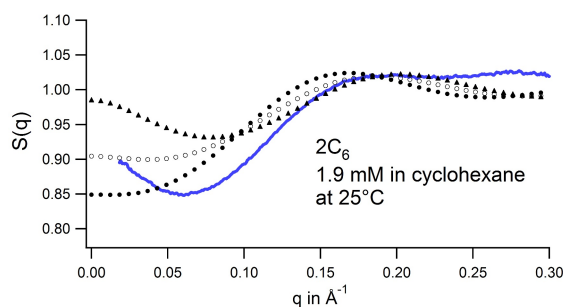


Figure 8: Experimental structure factor  $S(q)$  for 2C6 NPs, 1.9 mM (full line) and structure factors computed with the HNC approximation including hard sphere repulsion and van der Waals attraction (75 kT) between gold cores ( $D=2.4$  nm). The only adjustable parameter is the hard sphere diameter: 3.6 nm (full circles), 3.3 nm (empty circles), 3.2 nm (triangles).

a more subtle potential has certainly to be considered. Moreover the ligand grafting arrangement has also recently been shown as being non spherical when the NPs are in contact.<sup>16</sup> The simple model combining hard sphere repulsion and van der Waals attraction clearly fails to describe properly the structure factor for the shorter ligands but it captures the global behavior of  $S(q)$ . The classical approach combining van der Waals attraction between the gold cores, mixing energy and elastic energy between the ligands is really appropriate to describe the interaction between NPs suspended in cyclohexane or toluene.

This is no longer the case when the NPs are suspended in n-dodecane or n-hexadecane. Combining van der Waals attraction and hard sphere repulsion is totally incompatible with the structure factors that have been measured in n-dodecane and in n-hexadecane and even when taking into account other parameters as particle shape or polydispersity could not help. In these solvents, and by comparison with cyclohexane or toluene, we observe a strong increase of the structure factor at low  $q$ . This increase at low  $q$  reveals a large attraction between the particles that cannot be attributed to the van der Waals attraction. This attraction is larger for n-hexadecane than for n-dodecane but vanishes when temperature is increased (Fig. 5). It is interpreted as due to large NP concentration fluctuations induced by an unexpected attraction mediated by the solvent that is not at all predicted by the standard models since following the Alexander-de Gennes model,<sup>6</sup> the interaction between the ligands is expected to be purely repulsive.

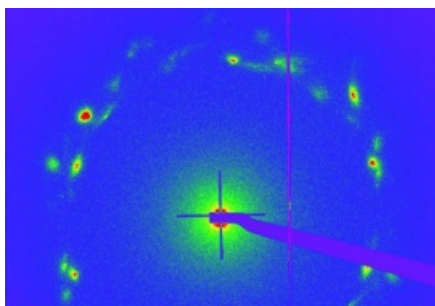


Figure 9: Superlattice observed by X-ray scattering in a suspension of 2C6 NPs in n-dodecane at 50w%, that is much less than 15% in volume fraction.

This is not due to small aggregates or phase separation as shown using PSGE-NMR. Various potentials have been considered to model this attractive interaction: a sticky hard sphere potential, an exponentially decreasing potential.... But none of these models could describe properly the behavior of the structure factor of NPs suspended in alkanes using the HNC approximation. More theoretical studies are thus required to understand the role of the solvent. Another evidence of this unexpected attraction is that 2C6 NPs suspended in n-dodecane and n-hexadecane self-assemble in superlattices at very low concentration as revealed by the presence of intense Bragg spots (Fig. 9). Crystallization occurs for very low concentration, typically 40w% in n-dodecane and less than 20w% in n-hexadecane. Self assembly of the same NPs in superlattices is observed at much higher concentration in cyclohexane or in toluene.

The phase diagram of hydrophobically coated gold nanoparticles in organic medium is thus very sensitive to the nature of the medium. A similar effect has been observed in layered organosilicate hybrid suspended in oil.<sup>17</sup> In this system, the solvent quality for the grafted chains at a given temperature controls the balance between attractions and repulsions, and hence the phase diagram of the nanoparticles and their tendency to gel. Assuming the presence of this unexpected attraction observed with n-alkanes, one can suspect an original phase diagram, analogous to that predicted for adhesive hard spheres<sup>18</sup> or observed for colloids interacting via depletion forces.<sup>19</sup> For large enough attraction, the phase diagram exhibits a critical point and strong fluctuations of density are expected in its vicinity. The near-critical structure factor has been orig-

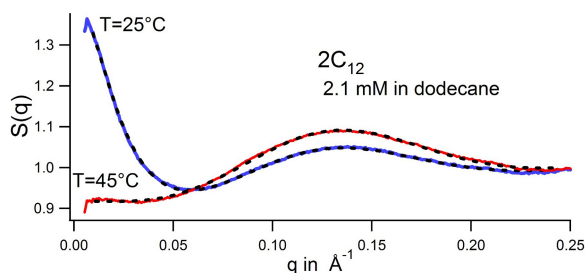


Figure 10: Structure factor of 2C12 NP dispersed in n-dodecane (20w%). Best fit with a structure factor (dotted line) combining the near-critical structure factor and a structure factor of hard sphere with diameter  $D_{HS}$ :  $\xi=3.9$  nm at 25°C (1.1 nm at 45°C),  $c_2=1.4$  (3.7 at 45°C),  $D_{HS}=4.1$ nm,  $\Phi_{HS}=3.9\%$  at 25°C corresponding to 1.9 mM of "free" NPs.

inally proposed by Ornstein and Zernike around 1917. In the small- $q$  approximation, it can be expressed as  $S_c(q) \approx \frac{1}{c_2} \frac{1}{1+q^2\xi^2}$  where  $\xi$  is the correlation length and  $c_2$  is the second term of the Taylor series expansion of the Fourier transform of the direct pair correlation function  $c(r)$ .<sup>14</sup> The experimental structure factors in n-dodecane and n-hexadecane have been fitted (Fig. 10) by a combination of this near-critical structure factor and a structure factor of hard sphere with diameter  $D_{HS}$  and volume fraction  $\Phi_{HS}$ :

$$S(q) = \frac{1}{c_2} \frac{1}{1+q^2\xi^2} + S_{HS}(q, D_{HS}, \Phi_{HS}) \quad (6)$$

The correlation length  $\xi$  can be interpreted through the formation of transient large concentration fluctuations<sup>18</sup> that requires the presence of an attractive interaction. The correlation length  $\xi$  as well as the intensity of these fluctuations  $1/c_2$  and the NP fraction involved in these fluctuations decrease with increasing temperature. This attractive interaction is clearly not predicted by the models commonly used. In these models, the interaction between ligands is derived from polymer theory even if the ligands cannot often be treated really as polymers. Dodecane as well as hexadecane are chemically close from the thiol-alkane ligands and thus only repulsion is expected between the ligand chains. Weak attraction could thus be expected for toluene but not for n-dodecane.

A possible explanation for the source of this attractive interaction also comes from polymer science. Indeed a great attention has been paid to the stability of polymer

grafted colloids in a polymer melt both from an experimental and a theoretical point of view. It has been shown<sup>20</sup> that, for large grafting density ( $\sigma$ ) and when the matrix polymer length ( $P$ ) is larger than the ligand length ( $N$ ), dewetting was expected. These studies lead to phase diagrams for NP miscibility with respect to  $\sigma$ ,  $P$ , and  $N$  and determination of the allophobic and autophobic transitions that correspond to the wetting or the drying of the graft polymer brush which control NP stability in polymer matrices. In our system,  $N$  is equal to 12 for 2C12 NPs and 6 for 2C6 NPs and the grafted density is large. One could expect the same effect at least for solvent chain length as long as  $P=12$  or 16. The final behavior could thus be the same as in polymer science but at the oligomeric scale as sketched in Fig. 11. In heptane ( $P=7$ ), the effect is much smaller but still exists. Indeed, considering the Flory-Huggins parameters, one would have expected a structure factor in heptane close to that in cyclohexane but it appears experimentally to be closer to that observed in toluene, the less good solvent of the series. The repulsion between the ligands in heptane is therefore smaller than expected and the flexibility of the heptane molecules has thus to be also taken into account.

The classical model combining van der Waals attraction between the gold cores, mixing and elastic energy between the ligands totally fails to describe interaction between hydrophobically-coated NPs dispersed in n-hexadecane, n-dodecane and more generally linear alkanes contrary to cyclohexane or toluene. A large attraction mediated by the solvent must be added for linear alkanes. Volatile solvents as hexane or toluene are commonly used to build superlattices but the solvent effect that is observed is clearly not only driven by the Flory-Huggins parameter. However a proper understanding of the interaction between the NPs is essential to analyse the formation of NP superlattices in terms of structure, global shape or kinetics.<sup>3</sup> Our results also show that non volatile solvents can be efficiently used to grow NP superlattices.

## 4 Conclusion

This study has revealed the presence of a new interaction between hydrophobically coated nanoparticles when alkanes are used as suspending solvent. The measurement



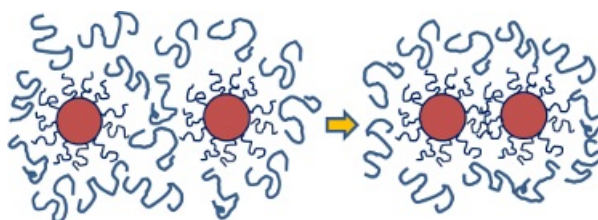


Figure 11: Schematic drawing of the attraction between gold nanoparticles covered with alkanethiols dispersed in an alkane with long enough chains.

by SAXS of the structure factor  $S(q)$  of gold NPs covered with alkanethiols and suspended in various solvents (n-heptane, n-dodecane, n-hexadecane, cyclohexane and toluene) has revealed large transient concentration fluctuations when the solvent is a flexible molecule as n-alkanes. This is the signature of an unexpected attraction that is larger for longer n-alkanes but whose origin needs further investigations to be fully understood. This interaction certainly plays a role in the formation of superlattices. Indeed the formation of superlattices in n-alkanes longer than the ligand chain occurs at quite low volume fraction and phase diagrams analog to that of attracting colloids are expected. The experimental study of these phase diagrams is at present in progress. The classical model describing the interaction between hydrophobically coated nanoparticles dispersed in oil are in good agreement with the measured structure factor in solvent like cyclohexane and toluene. But it must be revisited when the solvent molecules are flexible and with typical size close to the ligand length. In that case, further experimental and theoretical work is needed in order to carefully determine the role of the solvent in the ligand conformation and on the interaction between the NPs.

## Acknowledgements

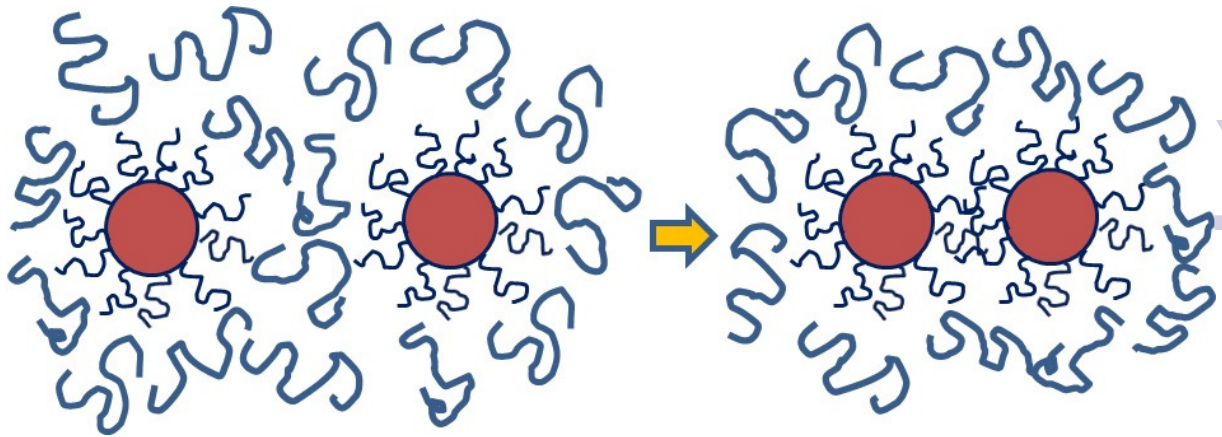
We acknowledge the support of the National Institute of Standards and Technology, U.S. Department of Commerce, in providing the analysis procedures used in this work. We express our deep gratitude to Luc Belloni for fruitful discussions and providing a program for computing the structure factors. We thank Florian Meneau (Soleil,

Gif/Yvette, France) and C. Rochas (ESRF, Grenoble, France) for their efficient and kind assistance. TGA measurements have been performed at ICMMO (Orsay, France) with the help of Giulia Fornasieri. We thank Mehdi Zeghal (LPS, Orsay, France) for the PSGE-NMR experiments.

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**Observation of a large attraction between gold nano-particles covered with hexanethiol or dodecanethiol suspended in flexible linear alkanes.**