Dynamics of alkyl chains in monolayer protected metal clusters and their superlattices

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Abstract. Alkyl chains dynamics in monolayer protected metal cluster (MPC) systems of gold and silver have been studied by the quasielastic neutron scattering (QENS) technique. Isolated MPCs investigated are 6, 12 and 18 carbon n-alkyl chain thiolate protected 4 nm diameter gold clusters while the superlattices are their silver analogues. Evolution of dynamics with temperature is found to be very different in the isolated clusters and their superlattices. While continuous evolution of the dynamics of the monolayer was observed in isolated MPCs, it is abrupt in superlattice systems and occurs at a temperature consistent with the superlattice melting detected in calorimetry measurements. A model where the chain undergoes uniaxial rotational diffusion with additional body axis fluctuation was found to describe the data consistently. For the superlattice systems, the chains are found to be held by strong inter-chain interactions below the superlattice melting. The data from the planar silver thiolate systems show similar behavior like the superlattice systems, consistent with the calorimetric data.

1. Introduction

Monolayer protected clusters (MPCs) are nanoparticles capped with monolayers, typically having a hydrocarbon chain [1]. Each MPC has a compact, crystalline metal core of 1-4 nanometer diameter. Monolayers of thiols on noble metal surfaces (planar or 2D SAMs) have been the simplest of systems on which many of the fundamental properties such as friction, lubrication, etc. could be investigated. These monolayers are alternately referred to as three-dimensional self-assembled monolayers (3D SAMs), to distinguish themselves from their planar counterparts (2D SAMs). Due to interactions of monolayers, the isolated clusters may crystallize to yield particle crystals, called superlattices as they possess double periodicity, one due to the metal core and another due to the organized particle assembly. The temperature dependent phase behavior of such systems has been a topic of intense investigations in our group as well as in others. Orientational freedom of the alkyl chain assembly is one of the critical issues concerning the structure of the monolayers. Applications of monolayer systems in several areas, utilizing distance specific organization of molecules, depend on the structural and conformational rigidity of the monolayer chain. Quasielastic neutron scattering (QENS) technique was suitably exploited to elucidate interesting results in recent studies [2,3]. Here we report the dynamics of alkyl chains in both isolated (gold clusters) and superlattice (silver clusters) systems with varying chain lengths, using QENS. We specifically investigate the evolution of dynamics in these systems as a function of temperature across the phase transition.

2. Experiment

Preparation and characterization of these nanosystems have been discussed previously [4]. The nanoparticle cores are 4 nm in diameter. From temperature programmed desorption, it is seen that the silver systems have larger monolayer density. Experiments were carried out using a time-of-flight spectrometer IN5 at ILL, Grenoble, France using an incident wavelength of 5 Å and a Q-range of 0.2-2.2 Å^{-1} with an energy resolution 50 μeV. Measurements were carried out with MPCs protected with several thiol (R-SH) molecules of varying chain length, viz., hexanethiol (HT, C_6H_{13}-SH), dodecanethiol (DDT, $C_{12}H_{25}$-SH) and octadecanethiol (ODT, $C_{18}H_{37}$-SH) stabilized gold (isolated) and silver (superlattice) clusters. The experiments were conducted over a temperature range of 200-400 K. Measurements have been done also for the 2D variety, namely layered silver thiolates (HT, DDT and ODT). In the superlattices used here perfect crystals made of MPCs were not seen [5], but short range periodicity is seen in the form of 2D ordering of particles on the TEM grid. Three dimensional order is seen in X-ray diffraction. However, perfect 3D superlattices have been seen in water soluble MPCs [6].

3. Results and Discussion

Quasielastic spectra for the Au-cluster systems (HT, DDT and ODT stabilized) show the presence of broadening over the whole range of temperature studied (270-400 K). The quasielastic component was found to evolve continuously with increase of temperature almost the same way in all the systems.

As a typical representative, the extracted Elastic Incoherent Structure Factor (EISF) for Au-DDT, at different temperatures are shown in figure 1. It is clear from the behavior of the EISF that it is strongly temperature depended and as the temperature is increased the quasielastic component increases systematically. Two things can happen with the increase of temperature, 1) higher proportion of the chains can take part in the dynamics and 2) the chains can become more and more flexible. Keeping in mind of both the possibilities, the generalized scattering law can be written as,

$$S(Q,\omega) = (1-p_x)\delta(\omega) + p_x\left[A_0\delta(\omega) + (1-A_0)L(\omega,\Gamma)\right] \tag{1}$$

where A_0 is the model EISF and P_x, represents the proportion of mobile or dynamic alkyl chains. The total elastic fraction can be written as,

$$EISF_{Tot} = \left[p_xA_0 + (1-p_x)\right] \tag{2}$$

It may be noted that A_0 is a function of the radius of gyration R. It is found that with increase of temperature, P_x increases indicating that increasing proportion of the chains contribute to the dynamics.

From the geometry of the MPCs, 1) the simplest model one can envisage is the rotation of the chain about its own axis, namely uniaxial rotational diffusion (URD), M1, 2) the other possibility could be rotation of the chain axis in a cone, M2 or 3) chain rotates about its axis coupled with fluctuations about the body axis, M3.

For URD the average EISF for a powder sample can be written as [7],

$$A_0 = \overline{A_0(Q)} = \frac{1}{N\pi}\sum_{i=1}^{N}\int_{0}^{\pi} j_o(2Qa_i\sin x)dx \tag{3}$$

where N is the total number of hydrogen atoms in the molecule and a_i is the radius of rotation of ith hydrogen. The alkyl chains are assumed to be in an all trans conformation.

The EISF for a model where chain precessing on a cone, it is assumed that the long axis of the chain is aligned along Y-axis. The EISF for such a model can be written as [6],

$$\overline{A_0(Q)} = \frac{1}{N\pi}\sum_{i=1}^{N}\int_{0}^{\pi} j_o(2Qr_i\sin x)dx \tag{4}$$

Here, r_i is a function of cone-angle θ.

The EISF for the chain hydrogens, due to rotation about chain axis and a fluctuation around its equilibrium position, can be expressed after averaging over the various distances of the hydrogens from the equilibrium point and the distances of the hydrogens from the molecular axis [8],

$$\overline{A_0(Q)} = \frac{1}{N}\sum_{i=1}^{N}\sum_{l=0}^{\infty}(2l+1)j_l^2(Qp_i)S_l^2(\delta)P_l^2(\cos\beta_i) \qquad (5)$$

and $\sin\beta_i = \dfrac{p_i}{q_i}$ Here q_i are the distances of hydrogen atoms in alkyl chain from the point of fluctuation and p_i are the distances of the same hydrogen atoms from the molecular axis. Therefore, knowing the positions of all the hydrogens in the alkyl chain with respect to chain axis, one can fit the experimentally obtained EISF with δ (as defined in equation (5)) as parameters. Average amplitudes of fluctuation ($\Delta\alpha$) are then obtained from the fact that, $\Delta\alpha=\cos^{-1}(S_l)$. Here, S_l is the orientational order parameter and can be expressed in terms of δ so that $S_l=<\cos\alpha>= \coth\delta$-$1/\delta$.

The model EISF calculated as per the different models described above is shown in the figure 1. It is found that with increase of temperature, P_x increases indicating increasing proportion of the chains
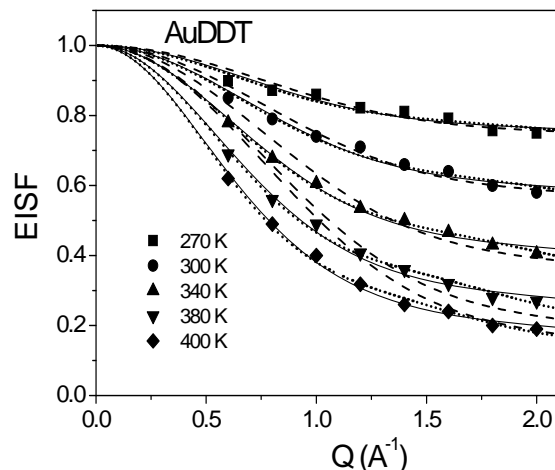

Figure 1 Experimental EISF, as obtained from QENS data for Au-DDT (isolated MPC) system, fitted with fitted with the different models, M1: dashed line, M2: dotted line and M3: solid line
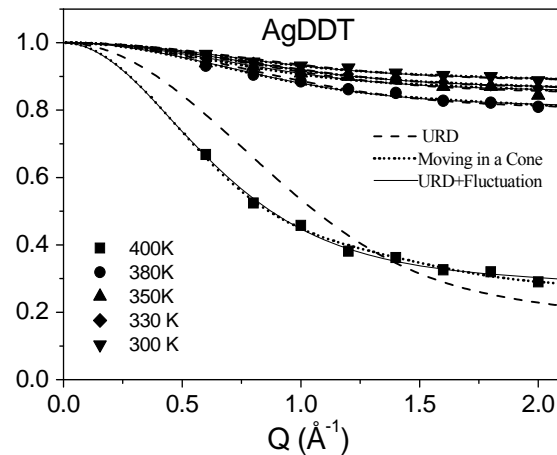
Figure 2 Experimental EISF, as obtained from QENS data for Ag-DDT (superlattice) system, fitted with fitted with the different models, M1: dashed line, M2: dotted line and M3: solid line.

contribute to the dynamics. Simple URD model M1 could not account the observed data, and description by the model where the chain move by an uniaxial rotational diffusion plus fluctuation, M3 is definitely better suited than the one where the chain moves on a cone, M2, as shown in the figure. The obtained values of P_x increases 27 to 86% and $\Delta\alpha$ goes 5 to 10 degrees in the case of model where the chains undergo uniaxial rotational diffusion and 30 to 100 % and θ goes from 3 to 7 degrees when the chain precess on a cone as temperature was increased from 270 to 400 K. P_x as obtained from the fit showed monotonic behavior with increase in temperature [3].

The QENS data in the superlattice MPC (silver clusters) systems show interesting behavior and show very different features compared to the isolated ones. Here the dynamics evolve rather abruptly at 400 K, which is just above the superlattice melting transition temperature. At temperatures below T_c, observed weak quasielastic broadening indicates the existence of dynamical features not like the case of isolated cluster system. Although the quasielastic broadening is observed to evolve slowly as the temperature is increased from 220 to 380 K, but at 400 K it is clearly a jump ahead. As can be seen

in the extracted EISF, as shown in figure 2, it is flat at temperatures up to 380 K and then suddenly falls off. The observed dynamics at and below 380 K should mainly be related to the chains not involved in the cross-linking of the two neighboring clusters. It may be noted in the superlattice structure the chains of the neighboring MPCs are interdigitated. The alkyl chains are connected to the metal clusters via the sulphur atoms and they diverge out as they go away from the metal surface. The silver cluster geometry is of a truncated icosahedron and from geometry considerations for a simple cubic lattice, only those chains along the unit cell axes would be involve in the cross-linking and so held by strong interactions. However, at 400 K, above the superlattice melting transition, those chains earlier held by strong interactions are also expected to be dynamic and the observed quasielastic broadening should correspond to all the chains.

To model the observed EISF, as before, different models were tried, simple uniaxial rotational diffusion model could not account the observed data. However, model M2 and M3 are able to describe the observed EISF very well both below and above 400 K, but model M3 is better suited at 400 K, that is, above T_c where the chains supposed to have melted. The obtained values of Px and θ within model M2 are 18 % and 3 degrees at 350 K and 24 % and 2.5 degrees at 380 K, but it jumps to 90 % and 8 degrees at 400 K. In model M3 the obtained parameters (P_x and $\Delta\alpha$) are 16 % and 5 degrees and 21 % and 5 degrees at 350 and 380 K, respectively which jump to 75 % and 11 degrees at 400 K. The variation of P_x with temperature is shown in figure 3. The abrupt jump in P_x at 400 K indicates the
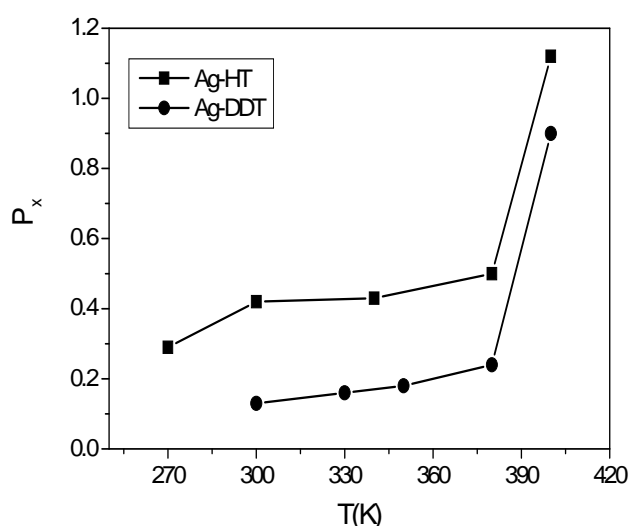

Figure 3. P_x as obtained for the different chain length with model M3.
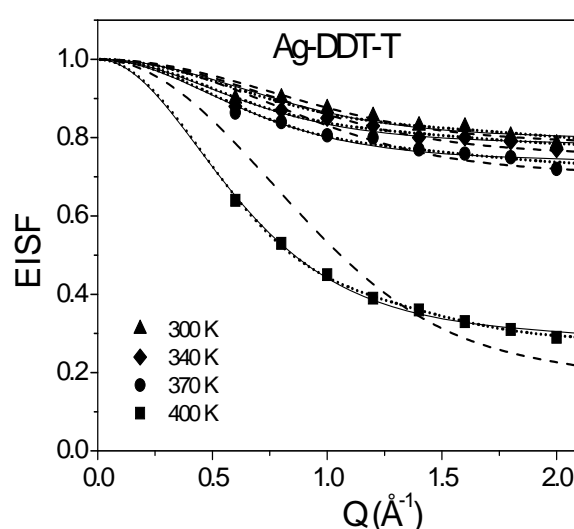

Figure 4. Experimental EISF, as obtained from QENS data for Ag-DDT thiolate system, fitted with the different models.

transition consistent with the calorimetric data. This clearly demonstrates that the sharp peak in enthalpy as observed in DSC is related to the chain melting.

Results obtained from superlattice and isolated cluster MPCs (3D SAMs) were compared with corresponding planar planer two-dimensional monolayer. Extracted EISF for Ag-DDT-thiolate system is shown in figure 4 along with the fitted ones assuming model M1, M2 and M3. Again M1 could not describe the data. The P_x and θ corresponding to model M2 lie in the range 25-33 % and 4-7 deg in the temperature window of 330-380 K while the P_x and $\Delta\alpha$ for model M3 is 22-27 % and 6-10 deg, respectively. However, at 400 K the P_x jumps to 88 % and 74 % in model M2 and M3, respectively, showing discontinuous transition as indicated in DSC [5].

4. Conclusion

Dynamical behaviour of the alkyl chains in monolayer protected metal cluster systems has been studied by quasielastic neutron scattering technique. The studies have definitively established that the evolution of dynamics is very different in superlattice and isolated clusters. While continuous evolution of the chain dynamics was observed in isolated MPCs, it is abrupt in the superlattice system at a temperature where the superlattice melting occurs. This is a clear demonstration of the QENS technique providing a direct evidence of the phase transition connected to the evolution of the dynamical motion. A model where the chain undergoes uniaxial rotational diffusion with additional chain axis fluctuation is found to describe the data for all the systems consistently.

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