



Evolution of dynamical motions in monolayer protected metal-clusters

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Abstract

Here we report orientational dynamics in monolayer protected metal-cluster (MPC) systems as studied by quasi-elastic neutron scattering (QENS) technique. Experiments carried out using two different instruments having very different energy windows, thus covering a time scale of 10^{-9} – 10^{-12} s. Clear evidence of absence of ‘rotator phase’ has been found in isolated MPCs (Au-SC₁₈H₃₇, Au-SC₁₂H₂₅, Au-SC₈H₁₇ and Au-SC₆H₁₃), a superlattice MPC (Ag-SC₁₈H₃₇) as well as planar thiolates (Ag-SC₆H₁₃, Ag-SC₁₂H₂₅, Ag-SC₁₈H₃₇) at room temperature. However, dynamics were found to evolve on increase of temperature and its behaviour is found to be different in the superlattice and isolated cluster systems. Detailed dynamical informations for MPCs are obtained for the first time in these systems.

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1. Introduction

The behaviour of self-assembled monolayers (SAMs), being model systems, has been a central point of investigation right from the early period of research in this area. SAMs are ordered molecular assemblies, classified in terms of their dimensionality. 2D SAMs are formed on planar solid substrate and are generally formed on the Au(111) face. 3D SAMs are monolayer of surfactants

formed on nanosized metal-cluster core. In general metallic particles tend to coagulate, the coating of the clusters by suitable surfactants prevent coagulation process. That is why the 3D SAMs are called as monolayer protected clusters (MPCs). Schematic of a MPC is shown in Fig. 1. MPCs can exist as an isolated entity (Fig. 1(a)) as well as extended superlattice structure (Fig. 1(b)), the latter is facilitated by virtue of the strong interaction between the chains of the neighbouring clusters. The number of atoms in a metal-cluster can have a distribution from 900 to 1500 with a core radius typically of the order of 30 Å and the chain length typically of the order of 9 Å. Results of molecular dynamics simulations [1,2] as well as many experimental studies

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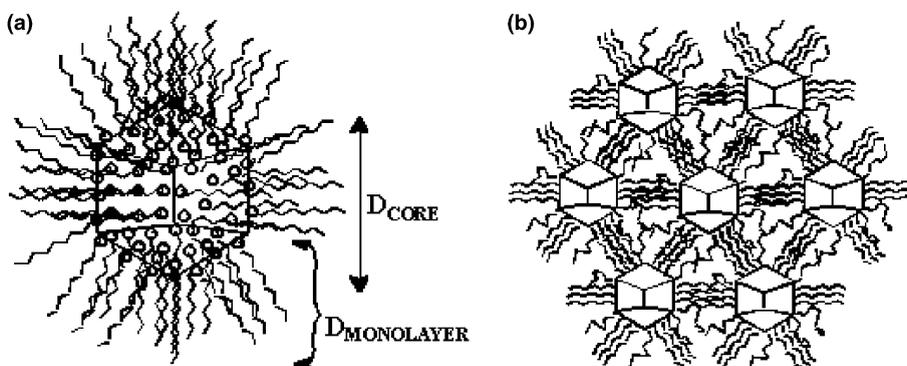


Fig. 1. (a) Schematic of a monolayer protected cluster (MPC). Specific lattice planes are seen on the surface of the metal nano-cluster on which the thiols are adsorbed. Alkyl chains are seen diverging as they move away from the core. (b) Schematic of the superlattice assembly of MPCs. Interdigitation among individual clusters is seen in the case of ordered chains where the dynamics are frozen.

[3–6] indicate presence of organized alkyl chain bundles on cluster surfaces in the monolayer assembly on a metal-cluster. Information regarding structural and conformational rigidity of the monolayer chain is of importance for its application point of view. Applications of monolayer systems in several areas utilize distance specific organization of molecules. Orientational freedom of the alkyl chain assembly is one of the critical issues concerning the structure of monolayers. The packing densities of molecular chains on the cluster surface are higher, but chain-disordering temperature is lower than the corresponding planar monolayers. Whether alkyl chains possess orientational freedom is an unsolved question. In the first ever report [7] of dynamics of alkyl chains in MPCs using quasielastic neutron scattering (QENS), we presented an investigation on two kinds of cluster systems, namely octadecanethiolate protected gold clusters (Au-ODT), in which the cluster along with its monolayers exist as an isolated molecular entity in the solid state, and octanethiolate protected silver clusters (Ag-OT), which form an extended superlattice in the solid state due to interdigitation of the alkyl chains of adjacent clusters. We compared the results of the cluster systems with a layered silver thiolate, which represents a planar alkyl chain assembly. Our results clearly showed that dynamical motion in planar thiolate is not active below 400 K. This is in contradiction to the general belief as inferred from the many experimental [8–10] as well as molecular

dynamics simulation studies [11–16] that the 2D SAMs exist in rotator phase.

In this paper, we report the absence of the rotator phase in the alkyl chain assembly in MPCs at room temperature and the evolution of dynamics in them as a function of temperature. Our study include both the isolated (Au-clusters) as well as superlattice MPCs (Ag-clusters). It may be noted that Au-clusters do not form superlattice structure [17].

2. Experimental details

Preparation and characterization of these nanosystems have been discussed previously [17]. The experiments were carried out using two instruments. The first instrument is a medium resolution quasielastic spectrometer at Dhruva reactor in Trombay [18]. The spectrometer is having an energy resolution of 200 μeV with incident neutron energy of 5.1 meV. The quasielastic spectra were recorded in the wavevector transfer (Q) range of 0.8–1.8 \AA^{-1} . The second instrument is a high-resolution LAM-80ET spectrometer [19] at KENS, KEK, Japan. In LAM-80ET the (006) reflection of a mica analyser provides an energy resolution, ΔE of 17 μeV at a fixed final energy of 1.92 meV with a Q range of 0.25–1.65 \AA^{-1} and the (004) reflection provides a ΔE of 6.5 μeV , at a fixed final energy of 0.85 meV with a Q range of 0.17–1.1 \AA^{-1} .

Measurements were carried out at different temperatures in the range of 300–400 K. The systems studied are octadecanethiolate ($C_{18}H_{37}S^-$) stabilized gold clusters (Au-ODT) of 3 nm core diameter and two other clusters of shorter chain lengths, namely $C_8H_{17}S^-$ (Au-OT) and $C_6H_{13}S^-$ (Au-HT). Results of the measurements with a superlattice MPCs of similar core dimension, namely Ag-ODT, where the monolayers are strongly interacting are also reported.

3. Results and discussion

The spectra from Au-ODT at room temperature using QENS spectrometer at Dhruva ($\Delta E \sim 200 \mu\text{eV}$) do not show any quasielastic broadening over the resolution function of the instrument indicating absence of dynamical motion of the alkyl chain. Measurements were also carried out on the smaller chain length Au-OT and Au-HT systems. No observable quasielastic broadening was found in these systems also, suggesting non-existence of rotator phase at room temperature in thiolate protected Au-clusters at least within the realm of QENS spectrometer (time scale $\sim 10^{-11}$ – 10^{-12} s). To observe possible slower dynamics, further measurements were carried out using high-resolution spectrometer LAM80-ET ($\Delta E \sim 6.5$ and $17 \mu\text{eV}$), and no QE broadening was found at 297 K. Combining the results of these two instruments, it can be said that no dynamical motion is present in these systems over a time scale range of 10^{-9} – 10^{-12} s at 300 K. QENS

spectra from Ag-ODT, as obtained using the QENS spectrometer at Dhruva and high-resolution spectrometer at KEK, suggest the absence of any QE broadening indicating absence of dynamical motion of the alkyl chain in the superlattice MPC system also. Here we depict the data from superlattice system only. Fig. 2 presents the typical QENS spectra recorded using both the spectrometer along with the instrumental resolution function for Ag-ODT at 300 K. However, upon increase of temperature to 340 K, significant QE broadening was observed. It may be noted that calorimetry studies [20] showed a transition at 335 K on heating which was attributed to chain melting and so the QENS observation is consistent with that. QENS measurements were also carried out at 360 and 380 K. Data at 340, 360 and 380 K are shown in Fig. 3. The QE broadening over the instrumental resolution is evident. To understand the observed dynamics we have separated the elastic and quasielastic components in the total spectrum. The incoherent scattering law can be written as [21]

$$S_{\text{inc}}(Q, \omega) \propto A(Q)\delta(\omega) + [1 - A(Q)]L(\Gamma, \omega), \quad (1)$$

where the first term is the elastic part and the other, quasielastic. $L(\Gamma, \omega)$ is the Lorentzian function of which Γ , is the half width at half maximum (HWHM) related to inverse of the residence time τ . Model scattering law is to be convoluted with the instrumental resolution function, while compared with the measured experimental data. Elastic incoherent structure factor (EISF), which provides information about the geometry of the motion,

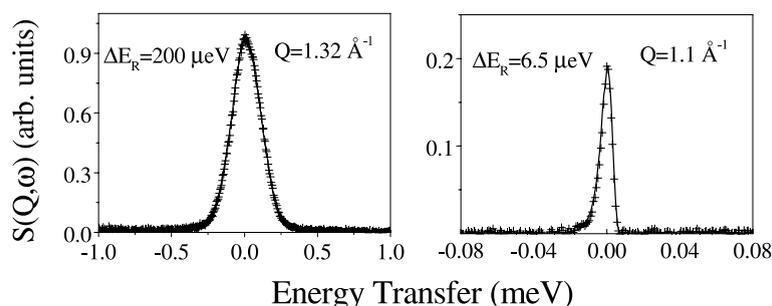


Fig. 2. Typical QENS spectra (+) along with the instrumental resolution function (solid line) for Ag-ODT at RT taken using two spectrometers with different energy resolutions. Quasielastic broadening is absent in both the spectra.

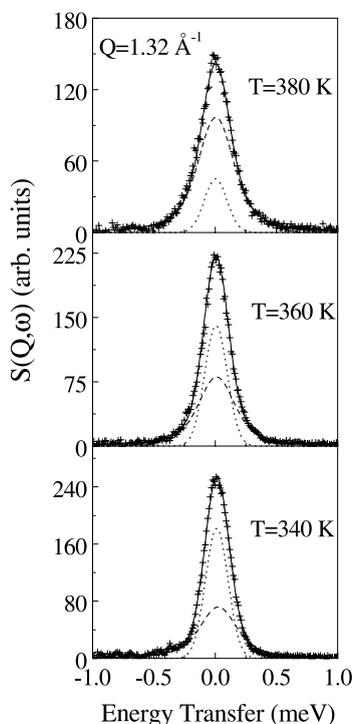


Fig. 3. QENS spectra of Ag-ODT ($\text{Ag-SC}_{18}\text{H}_{37}$) at different temperatures at a typical value of $Q = 1.32 \text{ \AA}^{-1}$. Experiments carried out using QENS spectrometer ($\Delta E_R = 200 \text{ \mu eV}$) at Trombay. Evolution of the alkyl chain dynamics with increase of temperature is evident. The separated quasielastic and elastic components are shown by dashed line and dotted line, respectively.

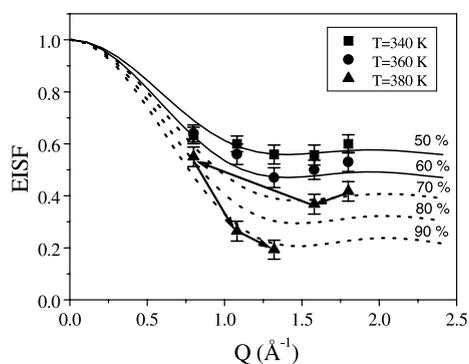


Fig. 4. Variation of EISF with Q for Ag-ODT at different temperatures. Lines are the calculated EISF as defined in Eq. (3) with p_x as parameter assuming uniaxial rotational diffusion model. Values of p_x are written along the calculated curves.

defined as the ratio of the quasielastic to total scattering intensities, $(I_{\text{el}}/(I_{\text{el}} + I_{\text{qel}}))$, at different temperatures are extracted from the fit of the data using Eq. (1). It is found that the value of EISF (Fig. 4) is quite large even at large Q ($\sim 2 \text{ \AA}^{-1}$). Large EISF at large Q values implies that some hydrogen atoms are not participating in the dynamics. The component of the static/dynamic proportion has been estimated by least squares fit to the data. If p_x is the fraction of hydrogen atoms in the system participating in the dynamics then the modified scattering law can be written as

$$S_{\text{inc}}(Q, \omega) \propto (1 - p_x)\delta(\omega) + p_x[A_0(Q)\delta(\omega) + \{1 - A_0(Q)\}L(\Gamma, \omega)] \quad (2)$$

and $A_0(Q)$ is the EISF which depends on the model, the effective elastic fraction can be written as

$$\text{EISF}_{\text{eff}} = [p_x A_0(Q) + (1 - p_x)]. \quad (3)$$

As reported in our earlier paper [7] that the rotational dynamics of alkyl chains in MPCs was very well described by uniaxial rotational diffusion model and accordingly $A_0(Q)$ is presumed which can be written as [22]

$$A_0(Q) = \frac{1}{N} \sum_{n=1}^N j_0 \left(2Qa \sin \frac{n\pi}{N} \right); \quad N \geq 6, \quad (4)$$

where j_0 is the spherical Bessels function of the zeroth order, a is the radius of gyration.

In the least squares fit of the experimentally extracted EISF with Eq. (3) there were two parameters: p_x and a . At 340 K, $p_x = 0.5$ and $a = 2.1 \text{ \AA}$ are obtained, suggesting that only 50% of the chains are contributing to the dynamics and the hydrogen atoms lie on the average on a cylinder of radius 2.1 \AA . It may be noted that the Ag-ODT exist in the superlattice structure as the chains among neighbouring clusters are interdigitated which makes the clusters fixed. For a simple cubic lattice and assuming nearly spherical cluster geometry (in reality it is a truncated icosahedron), only those chains along the unit cell axes are interdigitating and that would amount to about half of the chains to be free. Thus, the 50% correspond to the fraction of chains, which take part in

interdigitation. At 360 K, EISF is found to reach a lower limit indicating that more protons start contributing to the dynamics. The value of p_x was 0.6 at 360 K. However, at 380 K, the behaviour of the EISF showed that even at a constant temperature, the proportion of chains contributing to the dynamics increases slowly with time. Some kind of annealing effect is observed. The lines in Fig. 4 represents the least squares fit to the experimental EISF using Eq. (3) at different temperatures. In Fig. 4 we have also indicated the order in which the spectra were recorded at different Q -values at 380 K. At 380 K, initially about 70% of the chains were contributing to the dynamics and afterwards it went up to 90%. It may be noted that the calorimetry data showed a transition ca. 400 K which was related to the superlattice melting [20]. The increasing contribution of the alkyl chain towards dynamics, clearly indicate that the system approaches towards the melting as indicated in the calorimetry measurements.

4. Conclusions

Dynamical behaviour of the alkyl chains in MPC superlattice systems has been studied by the quasielastic neutron scattering (QENS) technique. The studies have definitively established that MPCs, isolated ones (Au-ODT, Au-OT and Au-HT) as well as superlattice one (Ag-ODT), are rotationally frozen at room temperature and dynamics evolve upon increase in temperature. The absence of rotator phase has been verified over a wide range of time scale (10^{-9} – 10^{-12} s). The rotator phase is absent even in much smaller chain length systems. Dynamical behaviours are very different in isolated and superlattice MPC systems. In case of isolated MPCs the dynamics is in common for all the chains whereas the dynamics are first initiated in the non-interdigitated ones and then the others take part at elevated temperatures for superlattice MPC systems. Uniaxial rotational

diffusion has been found to describe the alkyl chain dynamics in the MPC systems.

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