Noncontact Atomic Force Microscopy Investigations of Au$_{55}$ Thin Films Deposited on Gold and Graphite Substrates

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Abstract. Thin films of ligand-stabilized Au$_{55}$ clusters deposited on Au(111) and highly oriented pyrolytic graphite (HOPG) substrates have been investigated by noncontact atomic force microscopy (NC-AFM) and spectroscopy. The NC-AFM images show small size islands (consisting of one up to 20 clusters) on the Au(111) substrate which are locally ordered. In contrast, on HOPG, the clusters stick together in disordered monolayer islands of larger size. Conservative and dissipative interactions between the AFM probe and individual Au$_{55}$ clusters have been investigated for the two systems. The force as well as the dissipation curves show different behavior for the two systems.

1. Introduction
In recent years, noncontact atomic force microscopy (NC-AFM) became a powerful tool for imaging surfaces at the atomic scale as well as for imaging organic materials with molecular resolution [1]. NC-AFM was extended to noncontact atomic force spectroscopy which allows the precise detection of the tip-sample interaction force [2, 3] as a function of the tip-sample separation. Only a few references can be found in literature which deal with NC-AFM imaging of nanoclusters so far (see [4] and references therein).

Conservative and dissipative probe-sample interactions can be distinguished in NC-AFM. While the conservative tip-sample forces have been readily described by classical force laws [3], the origin of dissipative forces is still under discussion. Several studies about the energy dissipation measured in NC-AFM as the tip approaches the surface have been published [5], but a unified theoretical description of the observed phenomena is still missing.

In this paper, thin films of ligand-stabilized Au$_{55}$ clusters deposited on Au(111) and highly oriented pyrolytic graphite (HOPG) substrates have been imaged by NC-AFM with single cluster resolution. Force spectroscopy has been performed on individual clusters for the two systems. The force curves are compared to force laws of long-range, short-range and contact forces. Possible mechanisms which produce energy dissipation in the interaction between the AFM probe and Au$_{55}$ clusters are also discussed.

2. Sample Preparation and Experimental
Ligand-stabilized Au$_{55}$ clusters, such as Au$_{55}$P(C$_6$H$_5$)$_3$$_{12}$Cl$_6$ are produced by a wet chemical process as described elsewhere [6]. They contain a metallic core of 1.4 nm diameter composed
of 55 gold atoms in a two-shell closed-packed arrangement. The outer atoms are stabilized by chemical binding to organic ligands. The size of the $\text{Au}_{55}(\text{P(C}_6\text{H}_5)_3\text{Cl})_{12}$ cluster including the ligand shell is approximately 2.1 nm. HOPG and Au (111) have been used as substrate for cluster deposition. The Au (111) substrate has been prepared by depositing a 50 nm thick Au film on a freshly cleaved HOPG sample under vacuum conditions. Subsequent annealing results in large grains (around 100 nm diameter) having atomically flat (111) terraces [7]. The clusters were dissolved in dichloromethane and deposited onto freshly prepared substrates by spin coating.

Experiments have been performed at room temperature under ultrahigh vacuum (UHV) conditions ($\approx 10^{-10}$ mbar base pressure) using a commercial scanning force microscope (UHV-STM/AFM, Omicron NanoTechnology GmbH). In NC-AFM, a cantilever with eigenfrequency $f_0$ is subject to controlled positive feedback such that it oscillates with a constant amplitude $A$. Forces between tip and sample cause change in the eigenfrequency of the cantilever by $\Delta f$. For imaging, $\Delta f$ is kept constant by a feedback loop which varies the cantilever-sample distance. A feedback loop equipped with an automatic gain control (AGC) keeps the oscillation amplitude $A$ constant. The error signal of this loop yields a measure for the energy dissipated per cycle during cantilever oscillation and is called damping signal. In force spectroscopy, frequency shift and damping are recorded as a function of probe-sample separation. Locations where spectroscopy was performed have been choosen during scanning.

Two types of cantilevers have been used. Silicon cantilevers having a diamond-like high aspect ratio extratip at the apex have been used to image $\text{Au}_{55}$ thin films deposited on the Au substrate. Tip curvature radius of the extratip given by the manufacturer is $R < 1$ nm. For imaging the $\text{Au}_{55}$ thin films deposited on the HOPG substrate Cr-Au-coated silicon cantilevers were used. A typical curvature radius with the coating is $R < 50$ nm. The resonant frequency of the cantilevers was $f_0 \approx 300$ kHz and the spring constant $k = 40$ N/m.

3. Experimental Results and discussion

3.1. Thin Film Topography

For low enough cluster concentration in the solution, islands of single cluster height are obtained on both substrates. On the Au substrate the clusters form small islands consisting of one up to 20 clusters (Fig. 1(a)). For a larger cluster concentration in the solution, a monolayer covering the Au substrate is obtained [8]. In contrast, on HOPG, the clusters stick together in larger size islands (Fig. 1(b)). For larger cluster concentration, the cluster islands are connected to each other giving rise to monolayers with pores of varying size [9].

Formation of small islands indicates a stronger cluster-substrate interaction compared to the cluster-cluster interaction in the case of the Au substrate. Additional, the clusters appear to be arranged within many local areas in a 2D closest packing (as observed in high-resolution images which are not shown here). On the HOPG substrate, the cluster-cluster interaction dominates the cluster-substrate interaction and the clusters are dense packed in disordered monolayer islands.

3.2. Force Spectroscopy

In order to get insight into the tip-sample interaction, force spectroscopy has been performed on individual clusters as well as on the bare substrate. The tip-sample interaction force has been calculated from the experimental frequency shift-versus-distance curves using a numerical inversion method introduced by Giessibl [10] further slightly modified by Pfeiffer [11]. The energy dissipation has been calculated from the experimental damping-versus-distance curves like in reference [2].

It is easier to represent the interactions between tip and sample by dividing the tip into two parts: a macroscopic part and a nanotip. The forces involving the macroscopic part of the
Figure 1. NC-AFM images of Au$_{55}$ monolayer islands deposited by spin coating on Au(111) (a) and HOPG (b) substrates. The size of the images is 80 nm × 76 nm (a) and 300 nm × 300 nm (b). (a) $f_0 = 290$ kHz; $A = 3$ nm; $\Delta f = -19$ Hz; $U_{\text{bias}} = 0.3$ V. (b) $f_0 = 300$ kHz; $A = 6$ nm; $\Delta f = -15$ Hz; $U_{\text{bias}} = 0$ V.

Tip are referred to as long-range forces whereas the ones involving the nanotip as short-range forces. The resulting force curves from spectroscopy data taken on an individual Au$_{55}$ cluster on Au (111) are shown in Fig. 2(a). The long-range part of the two curves is the same and can be fit by a van der Waals force with a sphere-plane geometry (red curve in Fig. 2(a)):

$$F_{\text{vdW}} = \frac{HR}{6s^2},$$

where $H$ is the Hamaker constant, $R$ the tip radius and $s$ the separation between tip and sample. A value of $HR = 3 \cdot 10^{-27}$ Jm was obtained from the fit.

The short-range interaction is obtained by subtracting the long-range fit from the experimental curve [12]. The resulting curve is shown in Fig. 2(b). Two minima are observed separated by a distance of 4.5 Å. Force curves taken on five different clusters (in total 32 curves) have been analyzed and the distance between the two minima has been determined to be between 3.5 and 5 Å. We assume that the first minimum is given by the interaction of the nanotip with a phenyl molecule ($C_6H_5$) and the second one with the Au core. At the point marked with the circle in the figure, the phenyl molecule is mechanically bend down. The distance of 3.5 up to 5 Å between the two minima in the force curve is in good agreement with the length of the phenyl molecule (3.5 Å). A larger value compared to the length of the phenyl molecule can be explained by simultaneously deformation of the ligand molecules situated between the Au
core and the substrate. Mechanical bending of the phenyl molecule was also observed in STM measurements [13].

For further analysis of the short-range interaction, a Lenard-Jones (LJ) pair potential has been chosen:

\[ F_{\text{LJ}} = \frac{12E_0}{\lambda} \left[ \left( \frac{\lambda}{s} \right)^{13} - \left( \frac{\lambda}{s} \right)^7 \right], \]  

(2)

where \( E_0 \) is the binding energy and \( \lambda \) is the equilibrium distance. A fit of this equation to the data from the first minimum is plotted in Fig. 2(b) by a red line. From the fit parameters a binding energy of \( E_0 = 0.2 \text{ eV} \) and an equilibrium distance of \( \lambda = 5 \text{ Å} \) have been obtained. At the beginning of the attractive part of the force curve, the fit does not match well the experimental curve. A reason can be the influence of several neighbouring molecules on the interaction before finally only one molecule interacts with the nanotip. The repulsive part of the first minimum in Fig. 2(b) can be approximated by a linear fit with a linear stiffness of 0.34 N m\(^{-1}\) (black line in Fig. 2(b)). Dissipation curves not shown here show that energy dissipation takes place by the interaction between an individual phenyl molecule and the nanotip.

High resolution images of a location on the larger island in Fig. 1(b) show single cluster resolution. Force and dissipation curves taken on two different clusters are shown in Fig. 3. During recording of the curves in Fig. 3(b) the tip is approached 0.7 nm closer to the sample surface compared to the situation of the curves in Fig. 3(a). A long-range interaction followed by a rapid increase of the tip-sample force as being characteristic for the short-range interaction can be recognized in Fig. 3(a). By further approach of the tip to the sample surface by 0.7 nm (Fig. 3(b)), the interaction force remains attractive. The steep increase of the attractive force takes place on a distance of 2 nm in Fig. 3(b). The minimum of the force is reached after a further approach by approximately 0.2 nm. The distance of 2.2 nm is large compared with the decay length of the short-range forces normally found in experiments (0.1 - 0.4 nm).

NC-AFM images taken after performing spectroscopy show a changed topography of the cluster monolayer. Clusters on which spectropscopy has been performed seems to have a deeper location within the cluster monolayer than before performing spectroscopy. We believe that the tip pushes the cluster into the monolayer when recording the spectroscopy curve. Pushing of the cluster by the AFM probe starts at a certain distance between tip and cluster (solid line in Fig. 3). The attractive force regime is thus extended until no movement of the cluster is possible anymore and the minimum of the force is reached. Fit of the long-range part of the force curves in Fig. 3 with equation 1 gives \( HR = 0.36 \cdot 10^{-27} \text{ J m} \).

Energy dissipation starts with the onset of the rapid increase of the attractive force (dashed line in Fig. 3(a)). The dissipation curve in Fig. 3(a) can be fit by an inverse power law \( (1/s^n) \) with an exponent of \( n = 3.5 \). In Fig. 3(b), the dissipation curve can be fit by the same power law until the point marked by the solid line. The same value of \( n = 3.5 \) was predicted by Counturier et al. [14] for dissipation associated with viscoelastic deformation of sample under the action of the oscillating tip. Small displacement of the cluster out of the cluster monolayer is believed to take place at the beginning of the force curve. No permanent deformation of the cluster monolayer takes place in this regime. The energy dissipation starts to increase monotonically with decreasing the tip-sample distance at the point marked by the solid line in Fig. 3(b). Contact between tip and cluster is believed to take place at this point. Further approach of the tip to the cluster causes displacement of the cluster into the monolayer and a permanent deformation of the cluster monolayer takes place.

4. Conclusion
Disordered Au\(_{55}\) monolayer islands on top of a HOPG substrate as well as locally ordered ones on top of a Au(111) substrate have been imaged with high resolution by NC-AFM. Conservative and dissipative interactions between tip and individual clusters were investigated for the two
Figure 3. Force and dissipation curves taken on two individual clusters on HOPG. During recording of the curves in (a) the tip was approached 0.7 nm closer to the sample surface compared to the situation in (b).

systems. Interaction of the tip with an individual phenyl molecule is observed in the force curves taken on individual Au$_{55}$ clusters on the Au substrate. Bending of the phenyl molecule under the action of the tip is assumed to take place. This process is accompanied by energy dissipation. On the HOPG substrate, tip induced displacement of the clusters within the cluster monolayer has been observed. This is attributed to a lower cluster-substrate interaction compared to the cluster-tip interaction in the case of the HOPG substrate. Energy dissipation takes place also. Deformation of the cluster monolayer under the action of the oscillating tip is a possible mechanism of energy dissipation.

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5. References
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