Increase of the mean inner Coulomb potential in Au clusters induced by surface tension and its implication for electron scattering

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Electron holography in a transmission electron microscope was applied to measure the phase shift \( \Delta \varphi \) induced by Au clusters as a function of the cluster size. Large \( \Delta \varphi \) observed for small Au clusters cannot be described by the well-known equation \( \Delta \varphi = C_E V_0 t \) (\( C_E \): interaction constant, \( V_0 \): mean inner Coulomb potential (MIP) of bulk gold, \( t \): cluster thickness). The rapid increase of the Au MIP with decreasing cluster size derived from \( \Delta \varphi \), can be explained by the compressive strain of surface atoms in the cluster.

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Au clusters are considered as prototype material for nano-scaled electronic devices and biosensors [1]. Moreover, Au clusters exhibit an exceptional catalytic activity [2]. All these potential applications have motivated numerous studies regarding the properties of Au nano-clusters. One fundamental material property is the mean inner Coulomb potential (MIP), which plays an important role for the quantitative evaluation of experimental data obtained from electron scattering techniques, e.g. transmission electron microscopy (TEM) and electron holography (EH). The MIP is the volume-averaged electrostatic part of the crystal potential, which can be expressed [3, 4] by

\[
V_0 = \frac{\hbar^2}{2 \pi m e \Omega} \sum_i n_i f_i^e(0),
\]

with Planck’s constant \( \hbar \), the electron mass and charge \( m \) and \( e \), the unit cell volume \( \Omega \) and the occupation number \( n_i \) for the atomic species \( i \) within the unit cell. The important property in Eq. (1) is the atomic scattering factor \( f_i^e(0) \) [3] which correlates the MIP with the amplitude of the electron wave scattered in forward direction. The MIP can be determined by off-axis EH under kinematical diffraction conditions according to the relation \( \Delta \varphi = C_E V_0 t \) (\( C_E \): interaction constant) by measuring the phase shift \( \Delta \varphi \) between the electron wave passing through the sample with a known thickness \( t \) and a vacuum reference wave [2]. On the other hand, local TEM sample thicknesses can be determined by EH, if precise values of the MIP are known, but thus far only MIP values for few materials with limited accuracy are available [5, 8, 10, 11]. For instance, experimental values for the MIP of Au between 16.8 and 30.2 V were reported [8], whereas calculations yield values of 25.0 to 35.9 V [5, 8, 11]. Moreover, a strong increase of the Au MIP up to 45 V was reported for Au clusters deposited on TiO\(_2\) powder with decreasing cluster size [12]. Recently, effective carbon MIP values up to 65 V were reported for ultra-thin amorphous carbon (a-C) films compared to a bulk value of 9 V [13]. This indicates that the MIP increase for nano-scaled objects could be a general phenomenon.

In this study, we applied EH to determine 1) the MIP of bulk Au, which corresponds to the MIP of Au atoms in the cluster core and 2) the contribution of surface atoms to the overall MIP of Au clusters to elucidate the physical origin of its increase.

Samples were prepared by low-energy-beam cluster deposition of Au\(_n\) clusters with 10\( \leq n \leq 20 \) atoms on commercial a-C substrates, \( \approx 10 \) nm thick. Due to the storage of the sample, a coarsening of the particle sizes occurs, which leads to Au clusters with diameters \( D \) between 0.8\( \leq D \leq 8.0 \) nm. Off-axis transmission EH was carried out in a 200 keV Philips CM200 FEG/ST electron microscope equipped with a Möllenstedt-Düker biprism in the selected-area aperture holder. Holograms with an interference fringe distance of (0.16\( \pm 0.05 \) nm) nm and a corresponding resolution \( \Delta D = (0.32\pm 0.10) \) nm were recorded using a 2048\( \times \)2048 pixel CCD camera. The \( \Delta \varphi \) was reconstructed from the hologram sideband [14] by using the DALI program package extended for hologram reconstruction [15]. For our microscope a constant \( C_E = 7.29 \times 10^6 \) rad/(Vnm)\(^{-1}\) was determined according to Ref. [10].

Fig. 1a shows the reconstructed phase shift for an Au cluster with \( D = 6.9 \) nm. The total phase shift of the electron wave in the bright region of Fig. 1a is given by the phase shift induced by the cluster and the supporting a-C film, whereas the gray background represents the phase
shift due to the a-C film only. We use the following procedure to extract the integrated phase shift induced by the Au cluster $\Delta \varphi_{Au}^{int}$, first, the integration of the phase shift along the y-direction of the integration domain (black frame in Fig. 1a)) was performed according to: $\varphi^{int}(x) = \int_0^{R_{cl}} \varphi(x, y) dy$ (see Fig. 1b)). To eliminate the substrate contribution $\varphi_{sub}^{int}(x)$, the background is linearly interpolated (straight line in Fig. 1b)) on both sides of the cluster. Finally, $\Delta \varphi_{Au}^{int}$ is obtained by integration along the x-direction: $\Delta \varphi_{Au}^{int} = \int_{x_i}^{x_i+D} (\varphi^{int}(x) - \varphi_{sub}^{int}(x)) dx$. In Fig. 1) $\Delta \varphi_{Au}^{int}$ of 123 Au clusters is plotted versus the radius of cluster projection $R$.

To analyze the experimental $\Delta \varphi_{Au}^{int}$ we propose a new expression for the MIP of Au clusters which distinguishes between surface and core atoms. Generally, the atoms in a cluster are compressed due to surface tension. Previously observed compressive strain in metallic clusters (Au, Cu, Ni, Pt) was attributed to the sole contraction of atoms at the cluster surface [16, 17, 18, 19], which is essential for the explanation of the lattice vibrations in small particles [20]. Considering that the strain is confined entirely to the cluster surface, surface atoms are under uniform compressive strain, whereas core atoms are unstrained. The strain $\varepsilon$ leads to a decrease of the atomic volume for surface atoms to $(1+\varepsilon)^3 \Omega_{at}$, where $\Omega_{at}$ is the volume of unstrained core atoms, which is identical to the volume of bulk atoms. The inverse dependence of the MIP on the volume ($V_0 \sim 1/\Omega$) requires accordingly the distinction between the surface and core atoms with different atomic volumes. The MIP of Au in Au clusters $V_0^{cl}$ can then be expressed by

$$V_0^{cl} = \left(1 - \frac{N_S}{N_T}\right) V_0 + \frac{N_S}{N_T} \frac{V_0}{(1+\varepsilon)^3}, \quad (2)$$

with the number of surface atoms $N_S$ and the total number of atoms within the cluster $N_T$. $V_0$ is the MIP value of core atoms, which is equal to the MIP of the bulk material. As expected, $V_0^{cl}$ approaches $V_0$ for bulk material, if $N_S/N_T \rightarrow 0$ and $\varepsilon \approx -0.02$. However, large differences can be anticipated for nano-scaled objects, which are characterised by increased $N_S/N_T$ ratios and significant strain $\varepsilon$. A theoretical $\Delta \varphi_{Au}^{int}$ can then be calculated on the basis of Eq. (2) as

$$\Delta \varphi_{Au}^{int} = C_E V_0^{cl} \int_{\Sigma} t(x, y) = C_E V_0^{cl} \Omega_{cl}, \quad (3)$$

where $t(x, y)$ is the cluster thickness at a given position within the area of the cluster projection $\Sigma$ on the (x,y) hologram (image) plane and $\Omega_{cl}$ denotes the geometrical cluster volume.

To interpret the measured $\Delta \varphi_{Au}^{int}$ using Eq. (3), the cluster shape and structure needs to be known. According to Fig. 1b) the area of the Au-cluster projection corresponds in a good approximation to disks with radii $R$ suggesting that the clusters could be spheres. To verify this assumption, high-resolution TEM (HRTEM) images of Au clusters with $0.6 \leq R \leq 3.4$ nm were recorded at normal illumination (0°) and after tilting the samples by ±22°. The projected cluster area increases by about 5% in the tilted position, which excludes spherical clusters. Vertical facets are required with a ratio $h/R \approx 0.4$ of the vertical facet height ($h$) with respect to the apparent radius $R$ of the cluster projection.

Calculations indicate that clusters with a pentagonal decahedral (Dh) structure variant called Marks-Dh (M-
Dh) \cite{21} and the face-centered-cubic (fcc) truncated octahedral (TO) clusters are energetically the most stable structures for \(Au_N\) clusters (50\(\leq N\leq5000\) atoms) \cite{16, 22, 23}. A growth study of small Au particles (size 4-25 nm) produced by gas evaporation in flowing Ar has shown that, after condensation of the clusters on a substrate, the growth of Au particles with icosahedral (Ih) or Dh structures is favored with respect to fcc ones \cite{24}. Accordingly, the Au clusters may have Ih or M-Dh structures. But except for the smallest Au clusters, it was shown that the Ih structures are energetically noncompetitive as compared with the M-Dh ones \cite{16, 22}. We therefore assume the M-Dh morphology for Au clusters in our experimental size range. This assumption is confirmed by HRTEM images showing the typical fivefold symmetry (insert in Fig. 1b). The M-Dh Au clusters are characterized by \(h=0.4R\), derived from the tilt experiments, and an apparent diameter of \(D=2R\) (see the insert in Fig. 1b)). The latter relation is assumed to be valid because the cluster projections are almost circular.

To evaluate Eqs. (2) and (3), \(N_S/N_T(R)\) and \(\varepsilon(R)\) for Au clusters with our shape are required. For the theoretical estimation of these properties we distinguish between: a) ideal M-Dh Au clusters with closed-shell structures \cite{20} and corresponding ideal radii \(R_{id}\) and b) M-Dh Au clusters without closed-shell structures and intermediate radii \(R\). We calculate first \(N_S/N_T\) and \(\varepsilon\) for the ideal clusters. The total number of Au atoms in ideal M-Dh clusters, i.e. the “magic numbers”, \(N_{T id}\), can be described by the number of atoms \(n\), \(m\) and \(p\) \cite{16, 27} as shown in the insert in Fig. 1b). We use only \(p=2\) to approximate the observed circular cluster cross section. For a given \(m\), \(n\) is calculated on the basis of the experimental ratio \(h/R\). Then, the difference of \(N_{T id}\) in clusters with \((i+1)\) and \((i)\) closed shells, \(N_{T id}^{(i+1)}-N_{T id}^{(i)}=N_{S id}^{(i+1)}\), corresponds to the number of surface atoms of an ideal cluster with \((i+1)\) shells.

The following considerations yield estimates for the strain \(\varepsilon\) and cluster radii \(R_{id}\) which depend themselves on \(\varepsilon\). Imposing that \(\varepsilon\) is confined completely to the cluster surface, an ideal M-Dh Au cluster with \((i+1)\) closed shells and radius \(R_{id}^{(i+1)}\) is formed by a) an unstrained M-Dh cluster core with \((i)\)-closed shells and radius \(R_{id}^{(i)}\) consisting of \(N_{T id}^{(i)}\) core atoms and b) the \((i+1)\)-closed shell, formed by \(N_{S id}^{(i+1)}\) surface atoms with radii \(R_{Au-S} < R_{Au}\). We assume that the unstrained M-Dh cluster core consists of unstrained core Au atoms with a diameter \(d_{Au}=2R_{Au}=0.288\) nm, which is given by the minimum bond length between Au atoms in bulk gold. The strain \(\varepsilon^{(i+1)}\) is proportional to the reduction of the minimum bond lengths between \(Au\) and \(core\) atoms as compared to \(d_{Au}\): \(\varepsilon^{(i+1)} = [(R_{Au} + R_{Au-S}) - 2R_{Au}]/2R_{Au}\). However, a more useful expression for \(\varepsilon^{(i+1)}\) is given by: \(\varepsilon(R_{id}^{(i+1)}) \approx (R_{id}^{(i+1)} - R_{id}^{(i)}) - 2R_{Au}/2R_{Au}\). \(R_{id}^{(i)}\) can be estimated by constructing unstrained M-Dh clusters with closed-shell structure using only geometrical considerations and \(Au\) atoms with \(R_{Au}\). To estimate \(R_{id}^{(i)}\), we define the atom density of clusters as \(\rho(R_{id})=N_{T id}/\Omega_{id}(R_{id})\). For M-Dh Au clusters with our experimental shape, an analytical expression of \(\Omega_{id}(R_{id})\) can be derived. The lower boundary for \(R_{id}\) (and the upper boundary for \(\varepsilon\) ) is calculated considering that \(\rho(R_{id})\) cannot be larger than the atom density of \(fcc\) bulk Au \(\rho_{bulk}=58.9\) atoms/nm\(^3\) by solving \(N_{T id}^{(i+1)}/\Omega_{id}(R_{id}^{(i)}))=\rho_{bulk}\). The upper boundary for \(R_{id}\) (and the lower boundary for \(\varepsilon\) ) is given by \(\rho_{id}=48.0\) atoms/nm\(^3\) obtained for a cluster with two closed shells from \(ab\) initio density functional theory calculations, which yields \(\varepsilon = -15.9\%\). The atom density of large Au clusters with \(\geq10^6\) atoms is \(\rho_{cl}\approx\rho_{bulk}\) and the strain \(\varepsilon\) in these clusters converges towards the strain of surface atoms in bulk Au between -1\% and -2\% for low-index metal surfaces \cite{28}. The strain \(\varepsilon(R_{id})\) in ideal M-Dh Au clusters approximated by the average values on the basis of \(\rho_{bulk}\) and \(\rho_{cd}\) is plotted in Fig. 2. The error bars represent strain values deduced from \(\rho_{bulk}\) and \(\rho_{cd}\). We note that \(R_{id}\) differences associated with maximum and minimum strain are smaller than the spatial resolution in our experiment.

Values for \(\varepsilon\) and \(N_S/N_T\) for M-Dh Au clusters without closed shell of surface atoms are obtained by interpolation between the properties of the ideal ones. The MIP value of \(core\) Au atoms, identical to the MIP of bulk Au, is then calculated by a least-square fit of the experimental \(\Delta\varepsilon_{Au}^{int}(R)\) and calculated phase shift on the basis of Eq. (3) with \(V_0\) as the only free parameter (solid line in Fig. 1c)). We obtain \(V_0=\{32.2 \pm 3.6\} \) V, which agrees well with calculated MIP values of bulk Au \cite{2, 8} and reach, within the error bar, the upper limit of the previous experimental MIP data \cite{8}.

The experimental MIP values of Au in Au clusters are estimated from the measured \(\Delta\varepsilon_{Au}^{int}(R)\) by using \(V_0^\delta(R) = \Delta\varepsilon_{Au}^{int}(R)/C_E\Omega_{id}(R)\) (see Fig. 2). The solid line in Fig. 2 is calculated using Eq. (2) with \(V_0=32.2\)
FIG. 3: Experimental (○) and calculated (solid line) Au MIP values in M-Dh Au clusters $V_0^{cl}(R)$. The hatched region represents the maximum error of the $V_0^{cl}$ values induced by the upper and lower strain estimates.

$V_0^{cl}$, which is the fitted MIP of core Au atoms. Despite the scattering of $V_0^{cl}$ for 1.5$\leq$R$\leq$2.2 nm, Eq.[2] describes adequately the behavior of the MIP. The description is particularly reasonable for small clusters with $R \approx 0.5$ nm where $V_0^{cl}$=85 V is obtained. Data points exceeding the error limits indicated in Fig. 3 can be attributed to Au clusters with different h/R ratios, the estimation of the background phase shift or a tilted position of the cluster on the a-C substrate. The errors associated with different possible cluster structures (M-Dh or Ih) on the resulting MIP are smaller than the error limits.

To explain the MIP increase in Au clusters and thin a-C films, permanent electrical charging or adsorbate molecules with a large electrical dipole have been considered up to now [4, 12, 13]. Ichikawa et al. [12] attributed the increase of the Au MIP in Au clusters to the electronic structure, resulting MIP are smaller than the error limits. In our case, the increase of the Au MIP in Au clusters can be well explained by the compressive strain $\varepsilon$ of surface atoms. This effect is present but can not be measured in bulk samples, where $N_S/N_T$ is negligible and $\varepsilon$ is small. In contrast, surface contributions dominate and relaxations are important in small clusters.

In summary, we used EH to reconstruct the phase shift $\Delta\varphi$ induced by small Au clusters. $\Delta\varphi$ is determined by the MIP, which can be modeled by distinguishing between surface and core atoms with different atomic volumes. MIP values of 85 V are measured for Au clusters with $R=0.5$ nm, in contrast to the derived MIP value of Au core atoms of $V_0=(32.2 \pm 3.6)$ V in good agreement with previous calculations for bulk Au. Significant compression of surface atoms (reduction of bond length) yields a high surface potential contribution to the MIP of clusters. An essential additional ingredient of the model, which is generally applicable, is the increasing ratio $N_S/N_T$ in nano-scaled objects. The effect of the MIP increase in Au clusters and in many nano-scaled objects has important consequences for the quantification of electron scattering data in general because the amplitude of the electron wave scattered in forward direction can be much higher than expected from atomic scattering factors given e.g. in [2]. Modified scattering factors should be considered for the evaluation of images and diffraction patterns of nano-scaled objects from techniques based on electron scattering.

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