In Summer 2003, three Stern College students (Dana Glasner, Avital Merl and Pesia Soloveichik) were awarded summer research internship by the Vice President of Academic Affairs.

Dana Glasner:

Geometrical Properties of Metal Nanoparticles

Dana Glasner, Anatoly Frenkel, and Fredy Zypman

The purpose of this project was to determine the geometric properties of gold nanoparticles. Results from Extended X-Ray Absorption Fine-Structure (EXAFS) experiments gave the average coordination numbers of the first through the fifth nearest neighbors in the samples containing thiol-stabilized gold nanocluters. To determine the size and shape of the clusters of different sizes, we developed the following modeling strategy that was used to fit the experimental data. Namely, the three theoretically most probable shapes for metal nanoparticles are the cuboctahedron, icosahedron, and the truncated octahedron. Programs were written to generate 3D cluster coordinates of these three shapes for any cluster order. These coordinates were then processed by another program that calculated the radial distribution function (RDF) for all the clusters, that is, the average change in the number of atoms per radial distance from the absorbing atom. The area under each RDF peak determined the average number of the first through the n^{th} nearest neighbors. The structural model that matched the

EXAFS data would thus provide both the correct size and shape of the cluster.

Another way to establish the shape of the cluster is to determine which cluster geometry is characterized by the least cohesive energy for a given size cluster. Out of several models that we compared, the configuration of atoms that has the least cohesive energy, must best approximate the actual cluster. A program was written using Equivalent Crystal Theory (ECT) to calculate the cohesive energy of any cluster. The cohesive energies of the cuboctahedron, icosahedron, and truncated octahedron were compared for various sizes, and the structures that are characterized by the least cohesive energy were obtained for each cluster size. Our conclusion is that the combination of ECT and EXAFS methods allows to reproduce many geometric features in small gold clusters that are predicted by ab initio theories.

Pesia Soloveichik:

Time-Resolved X-Ray Absorption Spectroscopy Study of CuO Reduction with Carbon Monoxide

Pesia Soloveichik, Anatoly Frenkel, Xianqin Wang, Jonathan Hanson, and Jose Rodriguez.

This study investigated nucleation of reaction intermediates during the reduction of CuO to Cu with carbon monoxide at elevated temperatures. The technique of Extended X-ray Absorption Fine Structure (EXAFS) was used to observe changes in the structure around Cu atoms in the sample during the reaction. This procedure was repeated at 250, 270 and 280º C. EXAFS scans of CuO differ greatly from those of Cu. Moreover, we observed no evidence of isosbestic points (where the EXAFS curves cross each other at different stages of the reaction), thus indicating the presence of intermediate phase(s) during the reaction. The technique of Principle Component Analysis (PCA) formally confirmed the existence of an intermediary phase and identified it as Cu_2O. This technique also allowed us to quantify the mixing fractions of all three phases – CuO, Cu_2O, and Cu – as functions of time. The time-dependent mixing fractions were analyzed by Mehl-Avrami Equation, that relates the dimensionality of nucleation of the product of a reaction to time dependence of the mixing fraction of a new phase forming in the reaction. The fit of the Mehl-Avrami Equation to the experimental data produced consistent nucleation numbers at different temperatures for the formation of Cu_2O, and these nucleation numbers indicated that Cu_2O grows via two-dimensional surface nucleation. This equation, however, produced consistently high, nonsensical values of the nucleation number for the formation of Cu, demonstrating that the underlying approximations are two crude for Cu nucleation studies.

The rate of the reactions increased as temperature increased, in accordance with the Arrhenius Rate Law. Using this Law, we obtained the activation energy of the second half of the reaction, the Cu_2O transformation to Cu.

Avital Merl:

X-ray Absorption Fine Structure Analysis of Gold Nanoclusters

Avital Merl, Dana Glasner, Yuan Sun, Miriam Rafailovich, Anatoly Frenkel

Gold catalysis has sprung interest in the last years due to its catalytic activity with a number of important reactions. One key factor which influences its catalytic activity is the size of the gold particles, which must be in the nanometer range. This presentation describes the use of the technique of Extended X-ray Absorption Fine-Structure spectroscopy (EXAFS) to study the local structure of thiol-stabilized gold nanoparticles. Three nanocluster samples of different average particle sizes were synthesized for this experiment by adding $LiB(C_2H_5)_3H$ to a THF solution of H[Aucl4]·$3H_20$ to reduce the ions of $[AuCl_4]^{-1}$ to gold nanoparticles stabilized by thiol chains. Then this mixture was poured into a large amount of ethanol to precipitate the nanoparticles. X-ray absorption coefficient was measured as a function of photon energy for each sample by using beamline X16C at the National Synchrotron Light Source at Brookhaven National Laboratory. Afterwards, several computer programs used the experimental data to best fit the theoretical EXAFS equation and obtain the unknown structural variables. Among the unknown variables were the coordination numbers of the gold atoms in the particle. Different scattering paths (including multiple scatterings) of the electrons away from the central atom were chosen for the fit. Finally, through the use of a new computer program generating 3D coordinates of the cuboctahedron, truncated octahedron, and icosahedron clusters, the first five nearest neighbor coordination numbers were generated for any given cluster order for a given cluster geometry and kept fixed in the fits of theory to the data. The fits were performed repeatedly until the lowest chi squared was obtained. This procedure allowed us to obtain the best geometrical model of the gold nanocluster as a function of its size. We obtained that for the smallest size (38 atoms), the structure is truncated octahedral, for the intermediate size (55 atoms): icosahedral, and for the largest size (147 atoms): icosahedral, in a qualitative agreement with theoretical predictions.