2. EXPERIMENTAL AND THEORETICAL BACKGROUND

2.1 Synthesis and cluster characterization

The outline of the experimental production (synthesis) and characterization (visualization) of nanoparticles becomes important, despite this work has only focused on the computational modeling of nanoalloys. One of the most commonly known ways for the synthesis of gas-phase clusters is the so-called cluster molecular beam (see Figure 1).

![Figure 1. Experiments under collision-free conditions [18].](image)

The first step in the experimental production of this type of nanoparticle involves the evaporation of bulk material in the plate or rod by laser ablation [19]. When producing bimetallic nanoalloys, a single metal may be used, or two pure metals. Evaporation can also be performed by heavy ion sputtering, magneton sputtering or electrical discharge. This process generates a plasma which is then cooled down via collisions with a cold gas (helium or argon), which in turn results in condensation and cluster nucleation. Clusters are grown by collisions. Strong cooling takes places due to adiabatic and isenthalpic expansion, as the clusters undergo a supersonic expansion when passing from the high-pressure condensation region through a narrow nozzle into a vacuum. There are no collisions within the supersonic jet and the characteristics of isolated clusters can be easily investigated (see figure 2) [6,18,19].
Figure 2. Electron microscopy images of supported nanoalloys. (a) TEM image of Pd$_6$Pt catalyst (~ 6 nm), (b) HRTEM image of Ni-Pd nanoparticles (~ 3 nm) and (c) HAADF-STEM image of a three-layer cuboctahedral Pd-Au nanoparticle (~ 12 nm) [20,21,22].

Chemical techniques for cluster production also include chemical reduction, in which clusters are generated by reduction of different metal salt solutions in the presence of surfactant. Particle size can be controlled by the use of inverse micelles. Electrochemical synthesis involves the generation of metals such as Pt, Rh and Ru by reducing of their corresponding salts at the cathode [6].

Mass spectrometry is an experimental technique used for cluster characterization. This method allows the ionization of the cluster which in turn is deflected by an applied electric field. By changing the intensity of the electric field, cluster mass can be selected, i.e. cluster particle size. X-ray diffraction can determine the structure and crystallinity of the cluster. Z-contrast HAADF-STEM is able to reveal the internal structure of the nanoparticle. Topography of the nanoparticle can be obtained by AFM. XAS and EXAFS are both based on the fact that each element has a unique X-ray absorption spectrum [23].

It becomes evident that the appropriate combination of computational and theoretical methods, especially modeling of nanoparticles, with experimental techniques will lead to a thorough understanding of the physicochemical properties of nanoparticles.
2.2 The transmission electron microscope

There are two fundamental forms of TEM as is illustrated in a simplified schematic form in figure 3. In the conventional or fixed beam form (CTEM) the specimen is illuminated by a parallel (or nearly so) beam of electrons. An objective lens forms an image of the specimen in parallel with a fixed beam similar to a standard light optical microscope. The bright field image is typically phase contrast. In the scanning form (STEM) a small focused probe (of order 1 to 2 Å in diameter) is scanned across the specimen in raster form. The transmitted electrons that have been scattered to large angles form an ADF image that has a strong dependence on the atomic number of the atoms in the specimen (Z-contrast). The transmitted electrons that are on the optic axis form the BF image which exhibits phase contrast similar to CTEM.

**Figure 3.** Comparison of CTEM and STEM. Simplified schematic of the CTEM (left) and the STEM (right) [24].

There are a large number of things that can go wrong in an image simulation. The proposed specimen structure must be specified in some detail, usually in the form of a list of atomic coordinates and atomic numbers in a unit cell. Even less well known is the thickness of the specimen. Usually a large sequence of possible specimen thicknesses are calculated and compared to experiment.
The instrumental (optical) parameters such as the aberration constants (spherical aberration constant, etc.) and aperture size of the objective lens and lens defocus must be known. Usually defocus is not known very well (particularly in bright field phase contrast). Frequently a defocus series is calculated for comparison to experiment. There are also a variety of parameters such as defocus spread, illumination angle etc. that are hard to estimate but can influence the image [24].

There are also many parameters that are solely related to the calculation and have very little to do with the microscope or specimen but can dramatically affect the calculation. These parameters include the sampling size (pixel size) in the image and slices and the slice thickness itself.

Multi-slice almost always uses an FFT to reduce the total CPU time. The FFT is a discrete Fourier transform which repeats the image infinitely in all directions. Although the image is only displayed as a single image one should remember that it is really an infinite array of identical side-by-side images. This produces a strange effect called the wrap-around error. The left side of the image in essence touches the right side of the image (and vice versa) and the top of the image touches the bottom of the image (see fig. 6.10 and 6.11 in reference 24). To use the FFT each image and slice must obey periodic boundary conditions or be an integer number unit cells of the specimen (called a super cell). Interfaces and defects must be embedded inside a large super cell (brief discussion in section 6.8 of reference 24).

In summary, some of the things that need to be specified correctly are:

- Specimen parameters: atomic coordinates and numbers of the specimen and thickness of specimen
- Instrumental parameters: defocus, Cs, objective aperture, etc.
- Sampling size: number of pixels in the image and slice and the slice thickness. Ensure that the total integrated intensity is at least 0.9 or higher (1.0 to start). Calculations with slightly higher or lower sampling should yield the same result if the sampling is adequate.
- Slice thickness: usually the slices should correspond to the existing atomic layers in the specimen.
2.2.1 STEM Simulation

Computer simulation of images has become a routine tool of high-resolution transmission electron microscopy (conventional and scanning) of materials. The resolution of high resolution CTEM or STEM graphs of materials are primarily limited by the aberrations of the lenses in the microscope and multiple scattering in the specimen [25].

Even for very thin specimens, the imaging electrons will likely interact strongly enough with the specimen to be scattered more than once while traveling through the specimen. This multiple scattering may influence the image in unexpected ways such that the image is no longer related to the specimen structure in a simple manner. The goal of image simulation is to understand this image structure better. In summary the main goals of image simulation are:

Understanding: Image simulation may help to understand the detailed structure in the image to separate what is due to the specimen, what is due to the instrument and to help unravel the effects of multiple scattering.

Improvement: Image simulation may help to understand how the image is formed and generate intuition on ways to improve the image and instrumentation [24].

There are a variety of image calculation programs in existence. Many have been written for private use only. Some have been made available commercially and some are available as a free download. A partial list of some programs is shown in table 1.
Table 1. Some image simulation software packages appearing in the literature or on-line. Type M is multi-slice and type B is Bloch-Wave. Some of the listed programs may be commercial. Many other private programs likely exist [24].

<table>
<thead>
<tr>
<th>Program</th>
<th>Author</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>SHRLI</td>
<td>O’Keefe and Buseck</td>
<td>1978</td>
</tr>
<tr>
<td>TEMPAS</td>
<td>Kilaas</td>
<td>1987</td>
</tr>
<tr>
<td>EMS</td>
<td>Stadelmann</td>
<td>1987</td>
</tr>
<tr>
<td>NCEMSS</td>
<td>O'Keefe and Kilaas</td>
<td>1988</td>
</tr>
<tr>
<td>TEMSIM</td>
<td>Kirkland</td>
<td>1998</td>
</tr>
<tr>
<td>JEMS</td>
<td>Stadelmann</td>
<td>2004</td>
</tr>
<tr>
<td>WebEMAPS</td>
<td>Zuo</td>
<td>2005</td>
</tr>
<tr>
<td>HAADF-STEM</td>
<td>Logsdail, Li and Johnston</td>
<td>2012</td>
</tr>
</tbody>
</table>

2.3 Nanoalloys

Metallic nanoparticles have been the subject of study for around three decades, while only during the past fifteen years there has been a boom in the interest in bi- and multimetallic clusters, known as nanoalloys. Nanoalloys are unique materials with special characteristics, as they represent a type of finite-size objects. By controlling the size, composition and degree of chemical ordering (degree of mixing) [1,5,6,7,8] the chemical and physical properties of these novel materials can be modified. Catalytic conversion in the treatment of exhaust gases (e.g. CO) represents one of the main industrial applications of metal nanoparticles and nanoalloys. These gases are generated as products of incomplete combustion in car engines and other industrial processes, contributing to air pollution, acid rain and global warming effects.

2.3.1 Homotops

The term *homotop* was coined by Julius Jellinek [8,9] to describe alloy cluster isomers \( (A_mB_n) \) with a fixed number of atoms \( N = m+n \) and composition \( m/n \) ratio that is the case of bimetallic nanoalloys (e.g. Pd-Pt, Pd-Au, Ag-Pt, Cu-Pt, Ag-Au). These isomers possess the same
geometrical disposition of their atoms but differ in the way in which A and B type atoms are arranged. The number of homotops is defined by the next expression:

\[ N_H = \frac{N!}{N_A!N_B!} = \frac{N!}{N_A!(N - N_A)!} \]

\(N_H\) is maximum when \(N_A = N_B\), in other words for the 50:50 mixture. Therefore, the number of homotops increases combinatorially, making the global optimization search a difficult endeavor.

2.4.2 Segregation in nanoalloys

The chemical ordering of the atoms A (in red) and B (in yellow) within the nanoalloy structure will create a characteristic mixing pattern. Figure 4 shows different possible ways in which these two types of atoms can be arranged, according to mixed or segregated behavior.

**Figure 4.** Different segregation arrangements found in nanoalloys [6].
2.3.2.1 Segregated configurations

Segregation in bimetallic nanoalloys can be found in different arrangement of atoms:

- **Core-shell**: One element (A) occupies core positions in the nanoparticle, while a shell, created of B atoms, completely surrounds the core.
- **Onion-like**: Usually found in medium-large clusters, in which clusters present a layered A-B-A alternating shell pattern.
- **Layered**: These structures (aka. Janus particles) minimize the number of A-B bonds. They are in contact only at a small interface.
- **Random mixing**: The so called “alloyed” nanoparticles possess randomly mixed patterns, corresponding to bulk solid solutions.
- **Ordered mixing**: Pseudo-crystalline regular arrangements of A-B atoms.

The type of segregation present on a specific nanoalloy depends on many factors such as:

- Bond strength. This relates to the relative strengths of A-A, B-B and A-B bonds between metal atoms. If the homonuclear bonds are stronger segregation is preferred, while stronger A-B bonds will favor mixing.
- Surface energy. The metal with the lowest surface energy will segregate to nanoparticle surface sites.
- Atomic size. This is related to the release of strain effects in the nanoparticle itself, with the smaller atom tending to occupy core positions.
- Charge transfer. This means that the most electronegative atom will tend to occupy surface sites.
- Strength of binding to ligands. The metal which binds more strongly to the ligand will prefer to occupy surface sites (especially true for passivated clusters).
- Specific electronic effects. For certain metals, specific electronic effects may play an important role in determining segregation.
For a given size and composition for a specific nanoalloy, in terms of their geometrical disposition and chemical ordering and electronic structure, a problem arises when trying to determine the most stable cluster (GM) [10-17]. Once this issue is cleared up, structure-property relations can be investigated.

2.4.1 Cu monometallic properties

Copper nanoparticles play an important role in several relevant technological applications, for example in metallurgical and petrochemical applications, being significant in automobile exhaust purification as a substitute for the more expensive transition metal (Pt and Ru) components of catalytic converters. Carbon monoxide (CO) chemisorption on high purity copper has been the subject of several investigations. There are reports showing that CO adsorption takes place on top of the three fold Cu(111) hollow and Cu(001) bridge-sites. For the Cu(111) hollow, the C-O bond stretching frequency of the CO changes upon adsorption from $2145 \text{ cm}^{-1}$ to $2070 \text{ cm}^{-1}$ [26]. It is observed that as the coordination number of Cu increases the Cu-CO bond also increases. On the other hand, during Cu-CO bonding, the inward relaxation of the top layer and the buckling amplitudes are reduced. Spin unrestricted DFT has been used to predict the most stable spin multiplicity for Cu$_2$-CO [27]. This spin multiplicity was found to be $2S + 1 = 1$ (singlet). The vibrational stretching frequency of CO is $2161 \text{ cm}^{-1}$ and the adsorption energy of the Cu-CO is 17.2 kcal/mol, which is in agreement with the experimental value reported by Zeinalipour et al [27]. The latter researchers also showed that Cu$_4$-CO clusters relax into a planar structure with C$_s$ symmetry.

2.4.2 Pt monometallic properties

Platinum (Pt) makes an excellent catalyst when used as an anode in pure H$_2$ in fuel cells. The presence of CO in the mixture, however makes Pt unsuitable because it binds strongly to the metal when its concentration is 20 ppm or higher. Pt (111) shows a theoretical adsorption energy of CO-Pt of -1.39 eV (experimental value: -1.49 eV) when binding to the top Pt sites [28].
2.4.3 Comparison of Cu and Pt monometallic clusters

The correlation between transition metals and vibrational frequencies of the CO bonding stretching ($V_{CO}$) adsorption is shown on Figure 5. For Cu$_2$-CO the bridging C-O stretching frequency is higher at around 2115 cm$^{-1}$ than Pt$_2$-CO which is around 2090 cm$^{-1}$. The increasing population of the d-shell of any given quantum number, n, significantly augments the adsorption energies of CO (see figure 6). In this case, Cu$_2$-CO adsorption energy has a value of around 18 kcal/mol lower than that for Pt (42 kcal/mol). This means that Cu binds more weakly to CO, reducing the chance of Pt poisoning in the bimetallic alloy [29].

![Figure 5](image1.png) ![Figure 6](image2.png)

**Figure 5.** The vibrational C-O stretching frequency of M$_2$-CO transition metalcarbonyl clusters [27].

**Figure 6.** Experimental and calculated CO adsorption energies on transition metal clusters. The open white squares represent M$_2$-CO, the solid squares represent M$_4$-CO and the triangles represent experimental values [27].

2.4.4 Cu-Pt bimetallic properties

Differences in Cu-Pt alloys come about due to the fact that Cu is a third-row quasi-noble metal and Pt is a fifth-row noble metal. Another notable distinction is electronegativity, Pt = 2.28, Cu = 1.90, which explains Pt’s propensity to attract electrons towards it.
The synthesis of Cu-Pt nanoclusters includes a variety of methods [30,31,32]. One of these procedures includes the immersion of the CuPt in a solution of glycol and water in the presence of PVP. This is a reduction method. When formed experimentally, Cu-Pt clusters contain different molar ratios, possess fcc structure [33], are spherical, elongated [34] and have a mean particle size of 8 nm [6]. Cu-Pt NSAs could potentially facilitate highly selective hydrogenation reactions at low temperatures. The use of Cu-Pt NSAs facilitates H₂ dissociation due to the weak atomic hydrogen bonding [36]. This makes Cu-Pt nanoalloys good potential anodes in fuel cells. Computational studies of Cu-Pt nanoparticles have used structures with symmetries C₃ᵥ, D₂d, D₄h. The absorption of ethylene in Cu₁₂Pt₂ clusters has been investigated [35]. The relative stability of the different isomeric structures follows the order: C₃ᵥ>D₂d>D₄h [34]. One of the reasons for this addition of Pt to Cu is because it modifies the valence spd-band of the cluster improving its catalytic characteristics [36].

The existence of a linear correlation between near-surface transition metal alloys and H and CO binding energies has been proved. This is shown in Figure 7. In the diagram, Cu/Pt is in the middle with a CO binding energy of around -1.5eV and a H binding energy of around -2.75 eV. This means H bonding and CO bonding are both in the middle of the range and so neither is strongly preferred, therefore both association and dissociation can take place [28].
Puig-Molina et al. reduced and re-oxidized Cu-Pt nanoalloys. XANES was used to observe the change in structure. These researchers found that upon reduction the XANES showed the CuPt cluster was not metallic Cu, Cu/Pt nor Cu₃Pt. They concluded it probably formed another alloy. It was also shown that upon re-oxidation the Cu/Pt structure was different from the fresh sample [37].

The CuPt phase diagram shows ordered phases: CuPt, Cu₃Pt, CuPt₃ and a 1D-LPS [38] (see figure 8). The preferred structures and types are given in Table 2. Figure 8 also shows the amount of mixing between the Cu and Pt atoms. CuPt has 50% Pt as is expected and becomes a liquid at around 1085 K. Cu₃Pt has around 15% Pt which is lower than expected and becomes a liquid around 1005 K. 1D-LPS around 30% Pt and becomes a liquid at around 691 K.
**Figure 8.** The bulk phase diagram of CuPt [38].

**Table 2.** CuPt crystal structures and lattice parameters [38].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure</th>
<th>Type</th>
<th>a[nm]</th>
<th>c[nm]</th>
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<tr>
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<tr>
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<tr>
<td>CuPt₃</td>
<td>cub</td>
<td></td>
<td></td>
<td>0.38492</td>
</tr>
</tbody>
</table>
2.5 Genetic algorithms and the optimization of cluster geometries

Genetic algorithms (GA) were proposed by John Holland in the 70s. They have been used in diverse areas such as chemistry, physics, economy and computer science. These algorithms were inspired in the biologic process of evolution [82].

The search for the lowest potential energy configuration of an atomic nanocluster is a global optimization problem. One of the key aspects of the study of cluster potential energy surfaces (PES), is the number of local minima—that is, of stable configurations—that lie on the PES. This number increases exponentially with the cluster size. The number of local minima on the PES of a Lennard-Jones (LJ) cluster with size \( N = 100 \), according to the last estimates [84], should be larger than 10 [40].

The global optimization of clusters consists in finding, size and chemical composition being fixed, the structural and chemical arrangement of the lowest lying minimum on the PES [41-46]. To our purposes we may refer to clusters as individuals represented by its atomic coordinates which in biological terms would be its chromosomes [82]. With these elements we produce an initial population that will iterate throughout the following steps:

Selection. It is how the individuals are selected for crossover. Random selection methods can be used such as the roulette wheel which assigns a probability of being selected proportionally to the individual fitness.

Mating. Defines how the parent's chromosomes are combined to produce offspring. Figure 9 shows two examples of commonly techniques for mating.
**Figure 9.** Schematic representation of the crossover operation in a generic GA. (a) One-point crossover—two parents are cut at the same point and offspring are formed by combining complementary genes from parents. (b) Two-point crossover—two parents are cut at the same two points [47].

*Mutation.* Mating does not introduce new genetic material into the population. This can lead to an optimization that always converges to the same non-optimal solution. Mutation consists on making a few random changes in selected genes of a randomly chosen individual [48].

*Natural selection.* These two variation generating processes do not always yield individuals which are better adapted according to the fitness criteria and therefore a selection mechanism is also needed to pick up better solutions from a pool of new born individuals [83].
2.6. DFT

Density functional theory is an extremely successful approach for the description of ground state properties of metals, semiconductors, and insulators. The main idea of DFT is to describe an interacting system of fermions via its electronic density and not via its many-body wave function. For N electrons in a solid, which obey the Pauli principle and repulse each other via the Coulomb potential, this means that the basic variable of the system depends only on three spatial coordinates x, y, and z—rather than 3*N degrees of freedom.

Despite recent improvements, there are still difficulties in using density functional theory to properly describe intermolecular interactions, especially van der Waals forces; charge transfer excitations; transition states, global potential energy surfaces and some other strongly correlated systems; and in calculations of the band gap in semiconductors. Its incomplete treatment of dispersion can adversely affect the accuracy of DFT in the treatment of systems which are dominated by dispersion [53] or where dispersion competes significantly with other effects [54]. The development of new DFT methods designed to overcome this problem, by alterations to the functional [55] or by the inclusion of additive terms [56,57,58] is an important research topic.

This technique is based on the Hohenberg and Kohn theorem [59,60], which states that the energy for a given type of Hamiltonian operator may be described by a unique functional of the density. Since the electronic energy is a unique functional of the electronic density $\rho(r)$, the electronic energy $E_e[\rho]$ of a system of interacting ions and electrons may be expressed as a unique functional $F[\rho]$:

$$E_e[\rho] = F[\rho] + \int \rho(r) v_{\text{ext}}(r) \, dr + E_{\text{ion}}(\{R_I\}),$$

where $v_{\text{ext}}(r)$ is an external potential of the electron gas, $E_{\text{ion}} (\{R_I\})$ is the ion–ion interaction energy of the ions at fixed positions $R_I$, and $F[\rho]$ is the universal functional of $\rho$ independent of $v_{\text{ext}}(r)$. Thus $F[\rho]$ is the same functional for electrons in atoms, molecules, polymers or solids. Unfortunately, the exact form of this functional $F[\rho]$ is unknown. However, reasonable approximations to it are now available such as the LDA, the GGA and, so called, hybrid methods [59].
In general, DFT is the most cost effective method for achieving a high degree of accuracy at the quantum-mechanical level. The reliability of DFT results (when calculating properties) depends sensitively on how well the property is described by the electron density, or how the property relates to the electron density.

One way of reducing the computational complexity of DFT, and making large systems (or heavy elements) or longer simulations more practical, is to use a combination of basis sets and inner-core pseudopotentials [61].

The foundations of modern DFT were published in the classic papers of Hohenberg and Khon in 1964, and Kohn and Sham one year later [60,62]. They developed an exact variational principle formalism in which ground state properties, such as: total electronic energy, equilibrium positions and magnetic moments are expressed in terms of the total electronic density. The two fundamental theorems state that:

Hohenberg and Kohn Theorem: The ground state density of a bound system of interacting electrons in some external potential determines this potential uniquely, as well as the ground state wave function. Also since electronic density determines both, the total number of electrons, N and the external potential; it also provides a full description of all the ground-state observables, which are functional of the electron density [63].

The second statement of the Hohenberg-Kohn theorems states: the ground state energy and the ground-state density of a system characterized by an external potential, can be obtained by using the variational principle. In other words, the ground state energy can be expressed as a functional of the ground state density [59].
So, this theory established the existence of a universal functional, which is independent of the external potential i.e. which has the same functional form for any system considered. From the Hohenberg-Kohn theorems are derived the Kohn-Sham equations [64]. These equations solve the problem of the complex many electron Schrödinger equations, by transforming them into a set of N single-electron equations, which need to be solved self-consistently.

\[ \left[-\frac{1}{2} \nabla^2 + V(\vec{r}) + \int \frac{\rho(\vec{r})}{|\vec{r} - \vec{r}'|} q^3 \frac{\hat{r}'}{q} + V_{xc}[n(\vec{r})]\right] \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r}) \]

with an electronic density:

\[ \rho(\vec{r}) = \sum_{i=1}^{N} |\psi_i(\vec{r})|^2 \]