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Interaction between atoms in a nanoparticle and the interaction of nanoparticles with surfaces presented in this report belong to the latter category. For these, interaction potentials are set up as functionals of the local electron density or of hopping integrals and parameterized on the basis of a range of microscopic and macroscopic properties of bulk materials. Obviously, the correct prediction of other properties is not warranted and comparison with experiment is necessary.

There is not a lot of systematic studies available about the consistency between *ab initio*, classical approaches and experiment, probably because of the difficulty of doing measurement on particles that are free of interaction with their environment. In [1], experimental, classical and *ab initio* modeling studies are carried on in order to determine the geometry and stability of small bimetallic silver-cobalt clusters containing at most a few ten atoms. Experimentally, the clusters are formed by laser vaporization and inert gas condensation. Photofragmentation experiments allow checking the stability of the clusters. Some geometries obtained by classical modeling were compared with *ab initio* results. The classical approach predicts 3D configurations as soon as there is more than three atoms forming the clusters. 2D configurations are however predicted *ab initio* for somewhat larger ones. Consistently with experiment and with *ab initio* calculations, classical simulations predict clusters with more than 10 atoms to form icosahedral based structures and the silver atoms locate at the cluster periphery.

Since systems with larger numbers of particles are better conveniently tractable experimentally, more comparison between experiment and with classical modeling is available. Modeling the deposition and the accumulation of particles on a surface, or the pressing of particles assemblies can be done classically for systems containing millions of atoms. Experimental positron life time measurements and quantum mechanical predictions [2], high resolution transmission electron microscopy [3-6], Mössbauer spectroscopy [7,8], and surface tunneling or atomic force microscopy [9-11] were used in combination with the modeling work reported here.

This report focuses on bi-metallic particles and nanostructured materials. Their technological interest lays in both their magnetic and optical properties. When reduced to the nanometer size, magnetic particles display one single domain and are often superparamagnetic. Some bi-metallic ones, like Co-Ag or Co-Pt, depending on their stoichiometry, may display a high coercive fields, which is interesting for storage devices. The optical properties of nanoparticles find their origin in surface plasmons which frequencies also depend on stoichiometry. While magnetic anisotropy is related to the anisotropy of the atomic lattice, the surface stoichiometry of nanoparticles depends on segregation properties. Hence the interest of controlling the properties of nanoparticles and keeping them in different environments. When assembled, nanoparticles form a nanostructured material which may display original transport properties like giant magnetoresistance, which is interesting for designing sensors. Hence the interest of learning about the properties of nanostructured materials. Fundamental problems pertaining to applications thus embody size effects on structural phases and segregation, interfaces in nanomaterials and more generally, the interaction of nanoparticles with their environment, as well as the mechanical properties of the nanostructured materials they form.

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The modelling work reviewed here focuses on structural, morphological and thermodynamic properties of bi-metallic particles when they are free of interaction with their environment, and the modification of their properties when they are deposited on surfaces (typical deposition energies range from 0.1 eV per atom to 1.5 eV per atom), when they are accumulated on a surface or condensed from the gas phase and compacted in order to form a nanostructured material. The problem of the mechanical properties of nanostructured materials is also addressed. We distinguish between the cases of clusters made of miscible elements like Cu-Au or Ni-Al and clusters made of non-miscible elements like Ag-Co.

The case of miscible free clusters is discussed elsewhere [12,13]. Structural phases and transitions known in bulk materials are retrieved in nanoparticles. One example is the first order order-disorder phase transition in Cu₃Au which takes place at temperatures decreasing with the cluster size. More intense segregation than at flat surfaces is possible and a surface segregation gradient is observed directed toward the surface. The magnitude of this gradient scales with the cluster radius. The deposition of bi-metallic miscible clusters on surfaces was also studied [14,15]. Depending on the elastic properties of the substrate and on the deposition energy, they may either form a flat perfect interface or undergo pinning. The former case is better favorable for epitaxial accommodation than the latter. For a given substrate, the quality of the epitaxy, measured by means of a long range order parameter results from a subtle interplay between deposition energy, temperature and cluster size. An interesting problem remains unsolved: The above-mentioned order-disorder transition in Cu₃Au clusters was never observed experimentally. This problem, carefully studied by combining high resolution transmission electron microscopy with modelling [6,13], raises the question of whether clusters deposited on a surface may keep in a non-equilibrium thermodynamic state. In the absence of strong enough external perturbation, to our knowledge, no atomic scale technique is presently available for predicting the possible kinetic paths from disorder to order and the time scales involved.

Molecular dynamics allows to model the deposition of a cluster layer on a surface. This requires long computing times as the slowing down of clusters has to be simulated one after the other and the time between impacts has to be kept equal or larger than, typically, 100 ps. One layer formed at room temperature by 50 clusters with size distribution relevant to typical experimental ones was modeled [16] and compared with a system formed by cluster compaction [14]. Such layers display original morphological properties and the identity of each free cluster remains after their assembling. These layers also display surprising thermal diffusion properties [17,18]. Diffusion properties at inner surfaces and interfaces of Ni₃Al nanostructured materials were investigated by means of classical Molecular Dynamics. Model samples as prepared by Low Energy Cluster Beam Deposition on a metal substrate and by compaction are used. One model sample consists in a cluster layer interacting with the substrate. The second is a fragment of the first, to which periodic boundary conditions are applied in order to approximate an infinitely thick layer and a third one is obtained by modeling the compaction of clusters with the same size distribution at 2 GPa. These samples differ in the detail. In each however, half of the atoms are either located at pore surfaces or at cluster interfaces. As a consequence of temperature, in the absence of external pressure, the model thick film undergoes strong compaction, which is identified as the result of coalescence. The effect is less pronounced for the cluster film on a substrate, suggesting the latter to contribute to the nanostructured layer stability. The compacted sample undergoes no significant coalescence because of temperature which can be detected on the time scale of a molecular dynamics simulation (of the order of the nanosecond). The comparison of the diffusion properties of these samples was made. For the three samples, atomic diffusion at surfaces and interfaces was found particularly fast and the diffusion coefficient obeys an Arrhenius law with an activation energy of 0.3 eV. This is the activation energy found for diffusion in liquid Ni₃Al. The mechanical properties of such model materials are also studied [19]. In particular, the response of the material to a uniaxial load is examined by molecular dynamics and evidence is found for a temperature dependent elastic limit and both inter- and intra- granular plastic deformation mechanisms are identified.

Non-miscible clusters are quite different as they form separate phases in bulk materials and the consequences at the scale of nanoclusters are studied. In a first step, Co_xAg_{201-x} clusters containing

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201 atoms are studied by Metropolis Monte Carlo [20]. The ideal truncated octahedral configurations at thermodynamic equilibrium are explored for $0 < x < 201$ by means of Metropolis Monte Carlo sampling in the (NPT) canonical ensemble at zero pressure and at temperatures from 100K to 1000K. Remarkable configurations are predicted in this temperature range. As a consequence of a competition between strain and Co binding at low temperature, for $x < 20$, Co is distributed just below the cluster surface layer into groups of no more than 5 atoms, favouring well-defined positions, and the cluster central area is avoided. To increase the temperature favours the clustering of these small groups. Their dissolution is predicted at temperatures higher than the melting temperature of the cluster. For $x > 50$, Co regroups at the centre of the cluster and intersects {111} facets when Ag atoms are not numerous enough to form an entire surface shell. At these stoichiometries, temperature is not sufficient to mix Ag and Co, even above the melting point. At still smaller Ag concentrations, the Ag atoms are distributed at lowest coordination sites, along the edges of the cluster, avoiding the cluster facets as well as inner sites. At intermediate stoichiometries ($20 < x < 50$), either oblate Co groups below the surface or a compact group at the centre of the cluster are possible.

The second step is still more ambitious and is in progress [21]. The investigation is generalized to clusters with sizes up to 3000 atoms, covering this way the range of sizes experimentally available for low energy cluster beam deposition. The atomic scale modeling is carried on by both Molecular Dynamics and Metropolis Monte Carlo. This represents a huge series of simulations (175 cases) to which further calculations are added by spot when finer tuning of the parameters is necessary. Analyzing the results is a major task which is still in progress. This way, not only a realistic range of sizes is covered, but also the whole range of compositions and the temperature range relevant to the solid and the liquid states. Of particular interest are the conditions to fulfill in order to get core-shell structures, the factors governing the clusters morphology, those governing the short and long range order in the clusters as a whole as well as of the silver and cobalt subsystems, the conditions for melting as well as the order of the solid-liquid phase transition in the clusters, and the conditions for Co dissolution in the Ag-Co clusters. A comprehensive study is in progress which aims at capturing all the possible thermodynamic states of Co-Ag clusters and the transitions from one state to another. Phenomena about which understanding may already been put forward are the energetic and stoichiometric conditions for the precipitation of clusters into a core-shell structure, the wetting of cobalt cores by silver in clusters containing mainly cobalt, the stoichiometric conditions for a roughening transition of spherical clusters (and vice-versa), the disordering of silver shells, the role of the cluster surface and of the internal Co/Ag interface in the dynamics of melting, the occurrence of a solid-liquid coexistence temperature and the condition for Co dissolution in clusters containing mainly silver.

Clusters of the same size range are employed to model their slowing down on surfaces [22]. The slowing down of $\text{Co}_{10}\text{Ag}_{191}$ and $\text{Co}_{285}\text{Ag}_{301}$ nanoclusters on a Ag (100) surface is studied at the atomic scale by means of classical Molecular Dynamics simulations. The slowing down energy, 0.25 to 1.5 eV/atom, is characteristic of low energy cluster beam deposition and aerosol focused beam techniques. The two clusters differentiate by their size, stoichiometry and structure. While Co forms one or several groups just beneath the cluster surface in $\text{Co}_{10}\text{Ag}_{191}$, $\text{Co}_{285}\text{Ag}_{301}$ displays a core-shell structure where Ag forms one complete monolayer around the Co core. As a consequence of the impact, the smallest cluster undergoes deep reorganization and becomes fully epitaxial with the substrate. The larger one only undergoes partial accommodation and partially retains the memory of its initial morphology. For both, after impact, the Co forms one group covered by Ag. The substrate damage is significant and depends on the slowing down energy. It results in a Ag step surrounding the cluster which may be more than one atomic layers high and isolated add-atoms or small monolayer islands apart from the step. The latter originate from the cluster and the former from the substrate. Further detail in the consequences of the impact is given, concerning the cluster penetration, its deformation and lattice distortions, with emphasis on the cluster size and stoichiometry.

This is the current state of the art. Following the same line as for miscible clusters, comparison with experiment is foreseen. Large scale computations are also undertaken in order to model nanostructured Ag-Co materials synthesized by cluster deposition and to study their thermodynamic

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and mechanical properties. Molecular dynamic codes are developed therefore to run on parallel computers. Preliminary results are readily available and will be presented.

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