Supporting Information: Effects of Core Location on the Structural Stability of Ni-Au Core-Shell Nanoparticles

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The supporting information includes an elaborated description of the molecular dynamics simulations (see section S1) and provides further details about the decentralization of the clusters, induced via electron beam damage (see section S3) as well as the modified Ni-Au phase diagram (see section S4).

**S1 Methods: Atomistic Molecular Dynamics Simulations**

All molecular dynamic (MD) simulations have been performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulation) package. The Newton’s equations of motion have been solved through numeric integration by using the velocity Verlet algorithm, with time steps ranging from 1.0 to 3.0 fs.

**S1.1 Interatomic Interaction Forces: Pair Interaction Potentials**

The potential obtained via the embedded atom method (EAM) of X. W. Zhou for metal alloys has been used to describe all pair interaction. As indicated in the cited article ”These potentials are well fitted to basic material properties such as lattice constants, elastic constants, bulk module, vacancy formation energies, and sublimation energies, and they predict reasonably well the heats of solution”. The EAM potential includes contributions for the embedding of each metal atom in the surrounding metal atoms. Therefore, it is expected to be more sensitive to surface nanoparticle effects than other additive pairwise interatomic potentials. In fact, it is one of the most popular potentials in atomistic simulations on nanomaterial properties (see, e.g., Ref. 4 for a recent overview of the EAM method). During the last few years, however, other potentials sharing similar functional forms have been developed such as the GUPTA potential. The *eam database tool* included in the LAMMPS package was used to derive the necessary alloy parameters (see appendix A of Ref. 3 for the details).
S1.2 Initial Nanoparticle Formation

The dynamic range of solid gold and nickel indicates that a time step within the range of 3–5 fs would be acceptable. However, it is recommended that a smaller time step of about 1 fs is used instead when surface effects and initial instabilities are expected to appear at the initial steps of the simulation. For comparison purposes, very recent state-of-the-art MD simulations on nickel and gold nanoparticles used a time step of 2 fs.\textsuperscript{8,9}

To create the initial nanoparticle, 900 Ni atoms were randomly located inside a sphere with a radius of 14.0 Å, cooling it down using a Berendsen thermostat at 0.001 K and allowing a maximum atomic displacement of 0.01 Å (see left-hand panel of Figure S1). The value of 14 Å was consistent with an estimated diameter $d$ of the nickel nanoparticle following the relationship $d$ [nm] = 31.72 - 282.85 $N^{-1/3}$ from Ref.\textsuperscript{8} resulting in a value of about 24 Å for a number of Ni atoms $N = 900$. Next, an annealing procedure was applied as follows: First, the Ni nanoparticle was heated up to 900 K and this temperature was kept during 5 ns. Second, the nanoparticle was cooled down to 0.4 K, resulting in the crystallization shown in the right-hand panel of Figure S1.

Figure S1: Left-hand panel: initial random configuration of the Ni$_{900}$ nanoparticle. Right-hand panel: final configuration after applying our annealing procedure.
To include the 2100 Au atoms into the nanoparticle, they were randomly localized in a hollow sphere with an internal (external) radius of 14 Å (24 Å) around the core Ni$_{900}$ nanoparticle. Keeping fixed the atoms of the Ni$_{900}$ core, we applied the same annealing procedure described above (see Figure S2), allowing the Au$_{2100}$ shell to crystallize as well.

![Figure S2](image)

Figure S2: Left-hand panel: initial random configuration of the shell Au$_{2100}$ nanoparticle. Right-hand panel: final configuration of the core-shell Ni$_{900}$Au$_{2100}$ nanoparticle after applying our annealing procedure.

**S1.3 Diffusion of Ni Atoms into the Solid Nanoparticle**

To analyze the diffusion at 900 K, Figure S3 presents the evolution vs. time of the average nickel concentration at a given radius from the center of the nanoparticle [referred to as $C_{Ni}(r)$]. The radius of the nanoparticle is 25 Å. For comparison purposes, the function $C_{Ni}(r)$ is also presented at 300 and 750 K. From $C_{Ni}(r)$ at 300 K (shown in red), it can be noticed that the Ni core is not a perfect sphere. The functions $C_{Ni}(r)$ shown in dark-blue and dark-green correspond to temperatures of 750 and 900 K, respectively. It can be observed that they are very similar, reflecting both of them the exchange of a few atoms between the Ni core and the Au shell during the heating process. After reaching the temperature of 900
K, the diffusion of the Ni atoms over the nanoparticle is much more appreciable. Up to 20 ns, the effect is much more significant (the differences in $C_{Ni}(r)$ are more pronounced). Then, the diffusion process slows down. This way, the functions $C_{Ni}(r)$ at 50 and 90 ns (shown in black and violet) are very similar.

![Graph of $C_{Ni}(r)$ vs radial distance](image)

Figure S3: Scans of the average nickel concentration as a function of the radial distance from the center of the nanoparticle

With the exception of the nanoparticle at $t = 15$ ns (curve shown in cyan), there is no significant concentration of Ni atoms close to the surface at 25 Å. However, it should be stressed that the concentration at the surface is never strictly zero. There is always a certain but small amount of Ni atoms exposed on the surface at any time.
Figure S4: Snapshots of a core-shell Ni–Au nanoparticle at different times of the melting process at $T=1035$ K.

Figure S5: Evolution of the pair function $G(r)$ as a function of time, corresponding to the same times considered in the snapshots of Figure S4. Left-hand panel (total), middle panel (Au-Au pairs), right-hand panel (Ni-Ni pairs).
S1.4 Melting Process

The nanoparticle was heated up to 1000 K, being still solid. However, an increase of the temperature to 1100 K lead to the melting of the particle. To estimate a more precise value of the melting temperature, the temperature was increased in steps of 1 K in 150 ps (i.e., with a heating rate of about $6.7 \times 10^9$ K s$^{-1}$). Each increased value of the temperature was kept during 7.5 ns repeatedly. Applying this fast heating process, the particle melted during the 7.5 ns of the simulation at a temperature of 1036 K. Aimed to study the phase transition while keeping reasonable simulation times, a new simulation at 1035 K was followed by starting from the previous one at 1036 K (after 7.5 ns of production run).

One way of visualizing the phase transitions is through the analysis of the time-dependent evolution of the pair function $G(r)$ (i.e., the radial distribution function). This function describes how density varies as a function of the distance between two particles. More specifically, it is defined as:

$$G(r) = \frac{1}{\rho} \left\langle \sum_{i \neq 0} \delta(r - r_i) \right\rangle$$  \hspace{1cm} (1)

where $\rho$ is the average density of the system. As discussed below, the analysis of this function clearly shows that the gold and Ni melting processes are different, with the latter being much less gradual.

Let us focus in the picture showing the snapshots at different times of the melting process at 1035 K (Figure S4) along with the graphics (see Figure S5) presenting the pair functions, $G(r)$: both total (left-hand panel) and those restricted to Au-Au (middle panel) and Ni-Ni pairs (right-hand panel). Figure S6 presents eights panels, extending Figure S5 to all possible pairs and including a second set of graphics (right-hand panels) in which the range of considered distances is larger.

The function $G(r)$ shown in red in Figure S5 (referred to as “solid”) corresponds to the snapshot taken at 15.75 ns in Figure S4. At $t = 16.089$ ns, notice that the Au phase at the
left-upper region of the nanoparticle has started to melt. About 1.5 ns later, at \( t = 17.55 \) ns, the Au–Ni phase on top of the Ni core has just melted. After 18.9 ns, almost all the allowed Au–Ni phase has melted. However, only after 19.05 ns, the Ni core becomes completely melted, experiencing a very fast homogenization. This is clearly reflected in the pair function \( G(r) \) of Ni-Ni pairs (shown in black in the middle panel of Figure S5 and referred to as “liquid”).

It is important to notice that the melting process is more evident from the \( G(r) \) function for the Ni-Ni pairs. It can be observed that, at \( t = 17.55 \) ns, the \( G(r) \) function is almost the same as for the solid phase. After 18.9 ns, the Ni core starts to destabilize so that the peak of the \( G(r) \) function located at about 4.75 Å disappears. However, the abrupt change takes place later, in between \( t = 18.9 \) and 19.05 ns (see the \( G(r) \) function shown in black and referred to as “liquid”): Notice that, due to the disappearance of the solid Ni core, the heights of the peaks of the \( G(r) \) function suddenly decrease and become shifted. While the distances between nearest and next-nearest neighbors are kept very similar, those to third-nearest neighbors (at about 7 Å) become significantly shifted, and the heights of the peaks abruptly decrease due to the transition to the liquid phase.

The sudden disappearance of the Ni core can also be observed in the \( G(r) \) function for Ni-Au pairs (see third panel from the top in Figure S6). Thus, from Figure S6, a sudden jump in the average height of the \( G(r) \) function is clearly discernible in between 18.9 and 19.05 ns along with an increase of the \( G(r) \) value at distances shorter than 10 Å. However, the modification in the position and width of the peaks in the \( G(r) \) function is happening more gradually than for the Ni-Ni pairs due to the more progressive nature of the melting process for the Ni-Au alloy. For instance, we can notice the disappearance of the shoulder in the \( G(r) \) function at 4.0 Å as well as a progressive regrouping of two peaks (at 6.5 and 7.5 Å, respectively) in just one peak localized at about 7 Å.

The progressive nature of the melting process for the Au-Ni alloy is also reflected in the time-
dependent evolution of the G(r) function for Au-Au pairs (see middle panel in Figure S5). The only relatively abrupt change is the jump in the average values of G(r) for distances larger than 10 Å. Once again, such modification arises from the disappearance of the Ni core and the associated hole in the gold structure.

Altogether, the G(r) functions shown in Figures S5 and S6 are consistent with those reported for pure gold and nickel nanoparticles as well as for bulk gold. In particular, the G(r) function for the gold shell of the nanoparticle shows there major peaks at 2.8, 5.1, and 7.6 Å, and two minor peaks at 4 and 6.5 Å. These peaks are very close to those reported for the G(r) function in bulk gold (FCC packing), with the three major peaks located at 2.8, 5.1 and 7.8 Å (see Ref. 9). Similarly, it has been shown that these major peaks in the G(r) function drop while the minor peaks disappear at the melting temperature (1350 K for bulk gold).

It is also interesting that the G(r) function for the nickel core of the solid nanoparticle reflects a multi-domain structuring, with a mixing of FCC and HPC phases. As discussed in Ref. 8 for a pure nickel nanoparticle, this can be deducted from the fact that secondary peaks are made of several overlapping maxima. The first major peak is located at a distance, 2.5 Å (see Figures S5 and S6), which is a distance very similar to that found in Ref. 8 for a pure Ni4000 particle (2.45 Å). The same holds true for the second and third maxima localized at 4.5 and 7.0 Å, as well as for the minor peak at about 3.8 Å. However, the heights and widths of the peaks are rather different: the Ni900 core has a higher mixing degree of FCC and HPC structures than the pure Ni4000 particle (see Figure 4 of Ref. 8). Work is in progress to study the relative weights of FCC and HPC structures in the Ni900 core using the common neighbor analysis (CNA) method.
Figure S6: Evolution of the pair function $G(r)$ as a function of time, corresponding to the same times as for the snapshots presented in Figure S4.


S1.5 Discussion

Although some diffusion can be observed over the solid nanoparticle at a temperature as low as 550 K, it is not significant enough to be studied within the time scales accessible in classic simulations up to a temperature of about 900 K. Initially (at 900 K and during 50 ns), the diffusion into the solid nanoparticle is a fast process. After 50 ns, however, the Ni concentration changes very slowly, with that located in the surface of the nanoparticle being negligible. The Ni core would be either kept almost unmodified or fully mixed at macroscopic time scales. The final outcome will depend on the size of the nanoparticle and thermal conditions (i.e., heating rates).

At 1000 K the core-shell Ni$_{900}$Au$_{2100}$ nanoparticle is still solid and, under very fast heating conditions (a heating rate of about $6.7 \times 10^9$ K s$^{-1}$), a melting temperature of 1035 K can be estimated. This melting temperature is much lower than that of either bulk gold (1336 K) or bulk nickel (1728 K). As previously shown in MD simulations of pure Ni nanoparticles, the melting temperature increases with heating rate and decreases with nanoparticle size, scaling with the number of atoms as $N^{-1/3}$. Melting temperatures in the range of 1460–1375 K have been reported for nickel nanoparticles containing from 4000 to 8788 nickel atoms, applying higher heating rates in the range from $2 \times 10^{12}$ K s$^{-1}$ to $4 \times 10^{12}$ K s$^{-1}$ (see Ref. 8). For comparison purposes, molecular dynamics simulations on gold nanoparticles (from 675 to 5425 atoms) indicated melting temperatures from 615 to 1115 K (see Ref. 9). For instance, a melting temperature of 1075 ± 5 K was reported for a gold nanoparticle having a diameter (4.89 nm) similar to that studied in our work (5.0 nm).

It should also be stressed that our estimation of the melting temperature (1035 K) is consistent with the phase diagram reported by Jopoušek et al. using the CALPHAD method. Thus, from Figure 2 of Ref. 10, melting temperatures of about 1150 and 1100 K can be estimated for AuNi nanoparticles with sizes of 20 and 13 nm, respectively (keeping a Ni to Au ratio of 3:7).
It is also interesting to note that the melting process starts from surface defects and, later, it is expanded through the Au-Ni alloy while keeping the Ni core almost intact. Of course, the melting process might depend on the particular heating procedure. For instance, if the heating is indirect through the nanoparticle support, the melting process would obviously start from the surface side closest to the support. Finally, the Ni core also experiences a very fast melting. The sudden nature of the melting for the Ni core could be a signal of instability due to its small size. Therefore, it is possible that, for a larger nanoparticle having also a larger Ni core, it is kept stable while the Au-Ni alloy becomes melted.

S1.6 Decentralized core-shell Ni–Au nanoparticle

Figure S7: Picture illustrating the decentralized core-shell Ni–Au nanoparticle formed by applying our annealing procedure in MD simulations.

By applying the same procedure discussed above, we have also performed the simulations for the decentralized core-shell Ni–Au nanoparticle shown in Figure S7. The total energies of the centralized and decentralized nanoparticles were $-11793.101$ and $-11694.488$ eV, respectively. The estimated melting temperature is a little bit lower for the decentralized nanoparticle (in between 900 and 1000 K) for the centralized one. It should be also stressed that there are many possibilities of structuring for the decentralized nanoparticle.
Figure S8: Picture illustrating how much the total energy is modified upon increasing the distance from the Ni core center-of-mass to the center-of-mass of the total core-shell NiAu nanoparticle.

Finally, Figure S8 illustrates how much the total energy is modified upon increasing the distance from the Ni core center-of-mass to the center-of-mass of the total core-shell NiAu nanoparticle. As indicated, the origin corresponds to the centralized NP (energy of $-11793.101 \text{ eV}$) while, at the largest distance, the energy is that of the decentralized nanoparticle (energy of $-11694.488 \text{ eV}$). The annealing procedure was applied as before but moving and constraining the distance between the center-of-mass of the Au shell and the Ni core. At any geometry, the atoms from the Au shell were allowed to relax but not those of the Ni core. Using Zhou’s potential, the energy differences between centralized and decentralized structures are minimal (within 1%) and there is no barrier, with the energy increasing slowly up to ca. 8 Å and then rapidly up to ca. 11 Å. The sudden increase occurs
at the distance for which the Ni core starts to deform the outer surface of the Au shell.

S1.7  Further Insights into the Reasons Why Ni Atoms Prefer Not to Go Further the Subsurface Region

Lastly, in order to get further insights into the reasons why Ni atoms prefer not to go further the subsurface region, we have represented the energy per atom as a function of the distance to the nanoparticle surface for both Ni (red line) and Au (blue line) cases. In general, for distances larger than 0.3 and smaller than 2 Å, the nickel location in the nanoparticle is favored. However, as can be clearly seen in Figure S9, the energy per atom of nickel goes down very rapidly up to about 5 Å from the surface but, then, it stabilizes around $-4.1$ eV/atom (with some noise around that value). In stark contrast, for the gold case, the energy per atom continue to decrease further even at distances larger than 17 Å. It nicely shows the preferential gold (nickel) location on the surface (subsurface) region of the nanoparticle.

S1.8  MD Simulations on Larger Centralized and Decentralized Nanoparticles

Finally, we have repeated the simulation using the nanoparticles composed by 6266 atoms. Our calculations provided values of $-24849.154$, $-24847.141$, and $-24901.512$ eV for random, centralized, and decentralized arrangements of the Ni core. Hence, agreeing well with experimental observations, the decentralized nanoparticle is the most stable. Analysing the behaviour of centralized and decentralized nanoparticles as a function of temperature, the most interesting different was found in the diffusion of Ni atoms trough the solid at a temperature of 900 K. As can be observed in Figure S10, the nickel atoms diffuse through the gold solid towards the subsurface region in the centralized nanoparticle but not in the decentralized one. In the latter case, the diffusion of Ni atoms is via the Ni core itself. The different behaviour can be understood by considering the tendency of the nickel atoms to be located
in the subsurface region of the nanoparticle. For the case of the decentralized particle, the nickel atoms are already in contact with this sub-surface area and, then, they diffuse primarily throughout the area. Contrarily, the centralized nanoparticle needs to diffuse through the bulk of the gold phase to reach the sub-surface region. A similar phenomenon can be observed for the smaller nanoparticles considered in previous sections but it is less evident because of the spherical shape of the particles and the larger ratio between the sub-surface area and the gold bulk phase.
Figure S9: Energy per atom as a function of the distance to the nanoparticle surface for both Ni (red line) and Au (blue line) cases. A binning of 0.3 Å was used.
Figure S10: Snapshots showing the different diffusion process of Ni atoms through the solid for centralized (upper panels) and decentralized (lower panels) nanoparticles at 900 K.
S2  Particle Overview Scan

The particles synthesized with the helium droplet approach were log-normally distributed with an average diameter of $6.2 \pm 1.3 \text{nm}$. An overview at room temperature $T_0$ is depicted in Fig. S11.

![Overview of the three starting configurations at $T_0 = 300$ K. a.) centralized, b.) spinodal decomposed, c.) partially decentralized.](image)

S3  Electron Beam Damage - Decentralization

We note that demixing is not only limited to temperatures close to the melting point, but can be triggered also at lower temperatures already if longer electron beam exposure or higher electron energies are applied. Obviously, the TEM investigation itself can enhance the observed diffusion processes. Taking advantage of this influence, these intriguing demixing effects can be be studied at arbitrary time scales (see Fig. S12).
Figure S12: Electron beam induced demixing. A total dose dose of $1.5 \cdot 10^6$ electrons was necessary at 700 K to fully demix the cluster.

S4 Calphad

We observed, that starting at 300°C the clusters undergo a transition from separated to alloyed clusters. The temperature necessary to form an alloy is reduced in comparison the bulk alloying temperatures. One possible way to describe this phenomena of reduced alloying as well as melting temperature is the CALPHAD method. This method is based on the reduction of Gibbs free energy as a consequence of increasing surface to size effects.

We also note that the reduced melting temperatures for NPs of various sizes in Figure [10] correlates very well with that calculated via MD simulations for one NP of diameter close to 5 nm (about 1035 K, see section 1.4 above).

References

(1) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. J. Comp. Phys. 1995, 117, 1 – 19.
Figure S13: Diagram showing the reduced alloying and melting temperatures calculated with the CALPHAD method from Ref. [10].

(2) Verlet, L. Computer “Experiments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Phys. Rev.* **1967**, *159*, 98.

(3) Zhou, X. W.; Johnson, R. A.; Wadley, H. N. G. Misfit-Energy Increasing Dislocations in Vapor-Deposited CoFe/NiFe Multilayers. *Phys. Rev. B* **2004**, *69*, 10.

(4) Rossoulenejad-Mousavi, S. M.; Zhang, Y. Interatomic Potentials Transferability for Molecular Simulations: A Comparative Study for Platinum, Gold and Silver. *Scientific Reports* **2018**, *8*, 2424.

(5) Gupta, R. P. Lattice Relaxation at a Metal Surface. *Phys. Rev. B* **1981**, *23*, 6265–6270.

(6) Cleri, F.; Rosato, V. Tight-binding Potentials for Transition Metals and Alloys. *Phys. Rev. B* **1993**, *48*, 22–33.

(7) Rosato, V.; Guillope, M.; Legrand, B. Thermodynamical and Structural Properties of f.c.c. Transition Metals using a Simple Tight-Binding Model. *Philosophical Magazine A* **1989**, *59*, 321–336.

(8) Nguyen, T. D.; Nguyen, C. C.; Tran, V. H. Molecular Dynamics Study of Microscopic
Structures, Phase Transitions and Dynamic Crystallization in Ni Nanoparticles. *RSC Adv.* 2017, 7, 25406–25413.

(9) Qiao, Z.; Feng, H.; Zhou, J. Molecular Dynamics Simulations on the Melting of Gold Nanoparticles. *Phase Transitions* 2014, 87, 59–70.

(10) Sopoušek, J.; Kryštofová, A.; Premović, M.; Zobač, O.; Polsterová, S.; Brož, P.; Buršík, J. Au-Ni Nanoparticles: Phase Diagram Prediction, Synthesis, Characterization, and Thermal Stability. *Calphad* 2017, 58, 25–33.

(11) Kattner, U. R. The Calphad Method and its Role in Material and Process Development. *Tecnol. Metal. Mater. Miner.* 2016, 13, 3–15.