Supplementary information
Coalescence of AuPd nanoalloys in implicit environments

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S-1 Introduction

Below we include other characterization quantities, a table summarising the parameters adopted in the various simulations and the graphs obtained for all quantities analysed, for all sets. For the sake of clarity, they have not been reported in the main text, but form an essential part of this work. The results obtained are ordered as follow:

- S-2 contains a table showing all sets of η_α and ρ_α parameters we chose for the MEIs.
- S-3 contains others characterization quantities used for the analysis but not reported in detail in the main text.
- S-4 contains all the figures for the simulations for the smaller systems, composed of 55 atoms of gold and 55 of palladium, both icosahedral.
- S-5 contains all the figures for the simulations for the bigger systems, composed of 561 atoms of gold and 561 of palladium, both icosahedral.

S-2 MEI-Set selection

In the table S1 are reported all the sets of simulation performed for Au_{55}^{Ih} - Pd_{55}^{Ih}. Referring to the main text of this article: set0 represents simulations performed in vacuum. Sets 1 to 34 environments of type AP, sets 101 to 134 environments of type P, and set 201 to 234 environments of type A. For Au_{561}^{Ih} - Pd_{561}^{Ih} simulations only: `set0, set1, set2, set3, set4, set21, set24, set31, set34, set134`, has been performed, due to the large computational time required, highlighted in violet in the table.

S-3 Supplementary characterization methods: PDDF in `Sapphire`

In `Sapphire`[1], the PDDF is calculated via a Kernel function, $K\left(d_{ij},d;h\right)$ over the d_{ij} variable, constructed from n observations:

$$\mathrm{PDDF}\left[K\left(d_{ij},d;h\right)\right]=\frac{1}{Nh}\sum_{i}^{N}\sum_{j\neq i}K\left(\frac{d_{ij}-d}{h}\right) \quad , \tag{S1}$$

where d_{ij} is the pair-distance between atom i and j in Cartesian coordinates, $d_{ij}=\sqrt{\left(x_i-x_j\right)^2+\left(y_i-y_j\right)^2+\left(z_i-z_j\right)^2}$. The parameter h is the bandwidth that defines the tightness of the kernel function. Setting the bandwidth is a delicate step.[1,2] We select $h=0.05$ of the bulk lattice as it has been proven to be sufficiently broad to smooth the sharp Dirac peaks from having a finite sample, and to sufficiently resolve key features. A detailed discussion is available elsewhere[1,3].

Set name	ρ_{Au}	ρ_{Pd}	η_{Au}[eV]	η_{Pd}[eV]
set 0	Vacuum			
set 1	0.5	0.5	0.02	0.02
set 2	0.5	0.5	0.02	0.04
set 3	0.5	0.5	0.02	0.06
set 4	0.5	0.5	0.02	0.08
set 11	0.5	0.75	0.02	0.02
set 12	0.5	0.75	0.02	0.04
set 13	0.5	0.75	0.02	0.06
set 14	0.5	0.75	0.02	0.08
set 21	0.5	1.0	0.02	0.02
set 22	0.5	1.0	0.02	0.04
set 23	0.5	1.0	0.02	0.06
set 24	0.5	1.0	0.02	0.08
set 28	1.0	1.0	0.02	0.2
set 31	0.5	1.5	0.02	0.02
set 32	0.5	1.5	0.02	0.04
set 33	0.5	1.5	0.02	0.06
set 34	0.5	1.5	0.02	0.08
set 201	0.5	0	0.02	0
set 204	0.5	0	0.08	0
set 221	1.0	0	0.02	0
set 224	1.0	0	0.08	0
set 231	1.5	0	0.02	0
set 234	1.5	0	0.08	0
set 101	0	0.5	0	0.02
set 104	0	0.5	0	0.08
set 106	0	0.5	0	0.2
set 121	0	1.0	0	0.02
set 124	0	1.0	0	0.08
set 126	0	1.0	0	0.2
set 131	0	1.5	0	0.02
set 133	0	1.5	0	0.06
set 134	0	1.5	0	0.08

Table S1 Sets of simulations at 400K performed for both nanoalloys composed of 55 atoms of gold and 55 of palladium and in light purple for nanoalloys composed of 561 atoms of gold and 561 of palladium at 600K. In the first columns, we reported the set name corresponding to the chosen parameters ρ_{Au}, ρ_{Pd}, η_{Au}, η_{Pd} given in columns 2,3,4,5 respectively.

S-4 Au_{55}^{Ih}-Pd_{55}^{Ih}

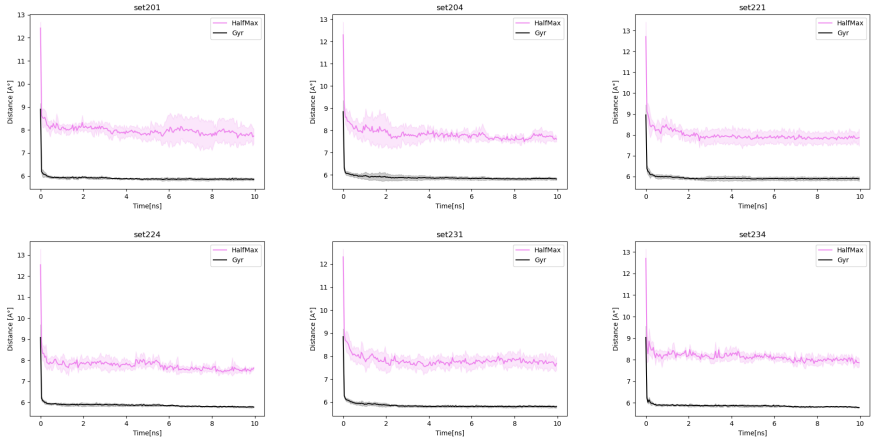

Fig. S1 Time evolution of radius of gyration of the whole cluster (in black) and half maximum pair distance $R_{max} = D_{max}/2$ (in pink), for Au_{55}^{Ih}-Pd_{55}^{Ih} in vacuum (set0) and in the environment (all the others sets) with ρ_{Au}, ρ_{Pd}, η_{Au} eV and η_{Pd} eV varing with associated set names as in table S1. Each graph represents the average over four independent simulations of the quantities mentioned. The mean value is represented by the solid line, while the shadow represents the standard deviation.

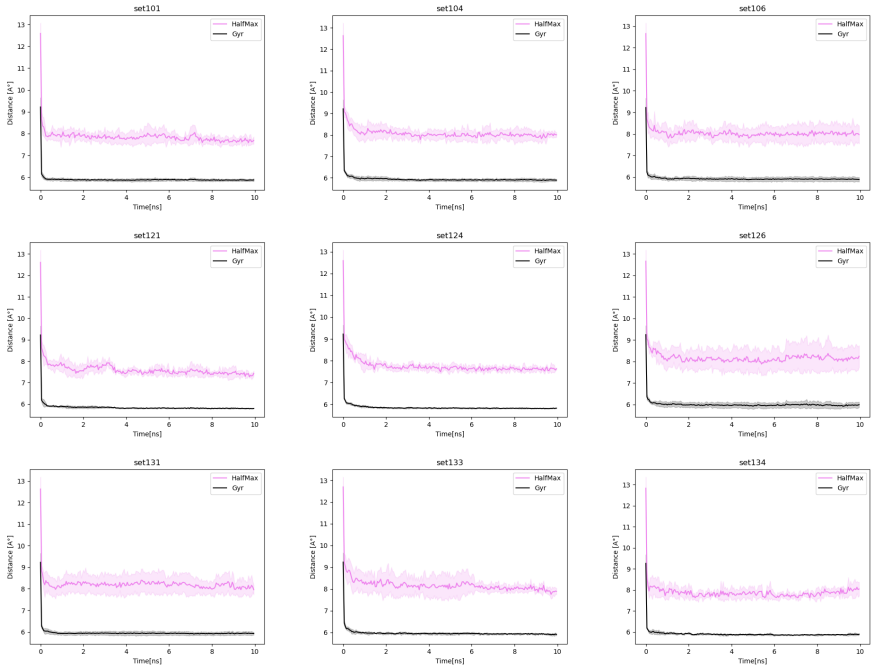

Fig. S2 Time evolution of the radius of gyration of the whole cluster (in black) and half maximum pair distance $R_{max} = D_{max}/2$ (in pink), for Au_{55}^{Ih}-Pd_{55}^{Ih} in vacuum (set0) and in the environment (all the others sets) with ρ_{Au}, ρ_{Pd}, η_{Au} eV and η_{Pd} eV varing with associated set names as in table S1. Each graph represents the average over four independent simulations of the quantities mentioned. The mean value is represented by the solid line, while the shadow represents the standard deviation.

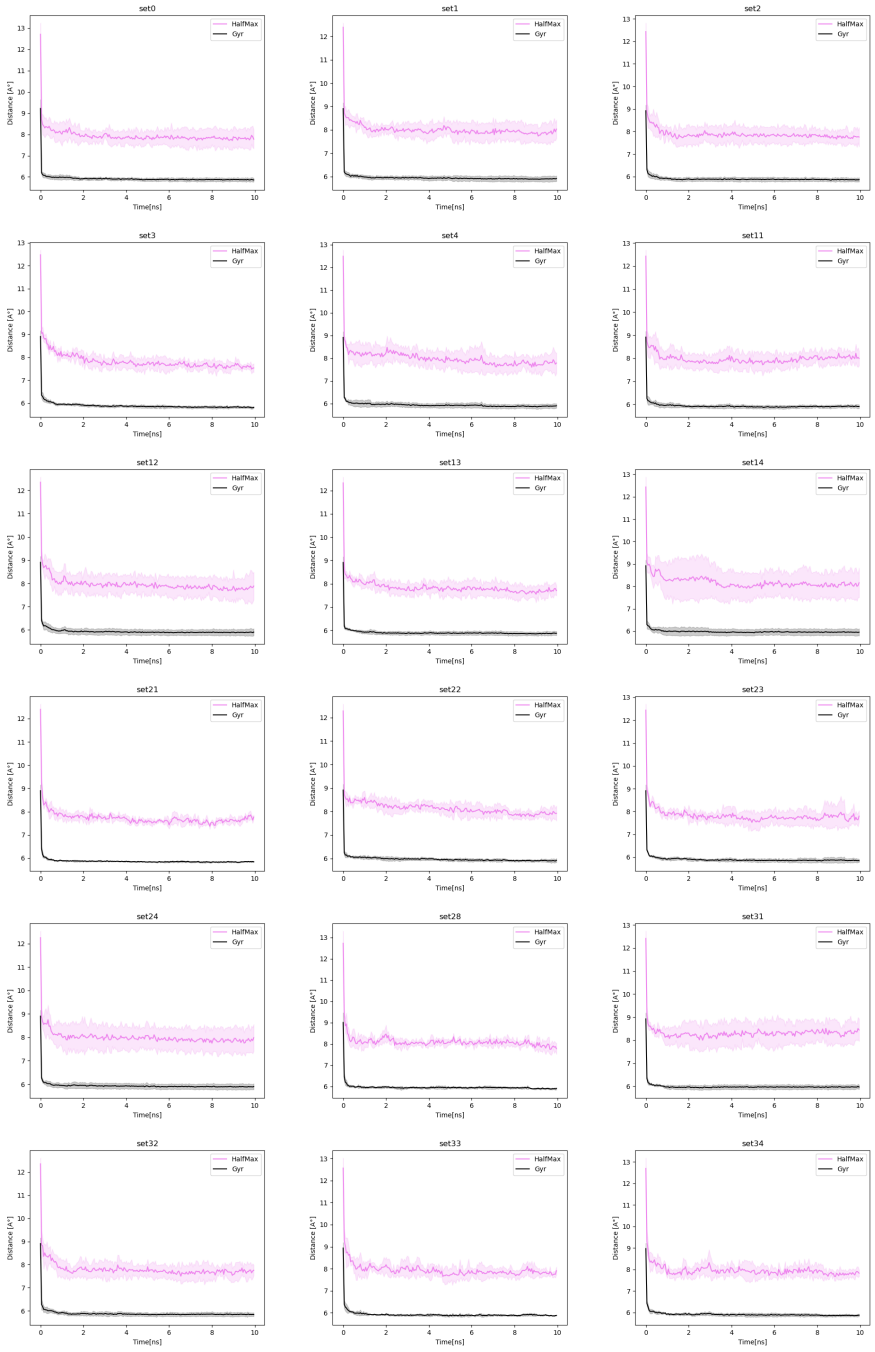

Fig. S3 Time evolution of radius of gyration of the whole cluster (in black) and half maximum pair distance $R_{max} = D_{max}/2$ (in pink), for Au_{55}^{Ih}-Pd_{55}^{Ih} in vacuum (set0) and in the environment (all the others sets) with ρ_{Au}, ρ_{Pd}, η_{Au} eV and η_{Pd} eV varing with associated set names as in table S1. Each graph represents the average over four independent simulations of the quantities mentioned. The mean value is represented by the solid line, while the shadow represents the standard deviation.

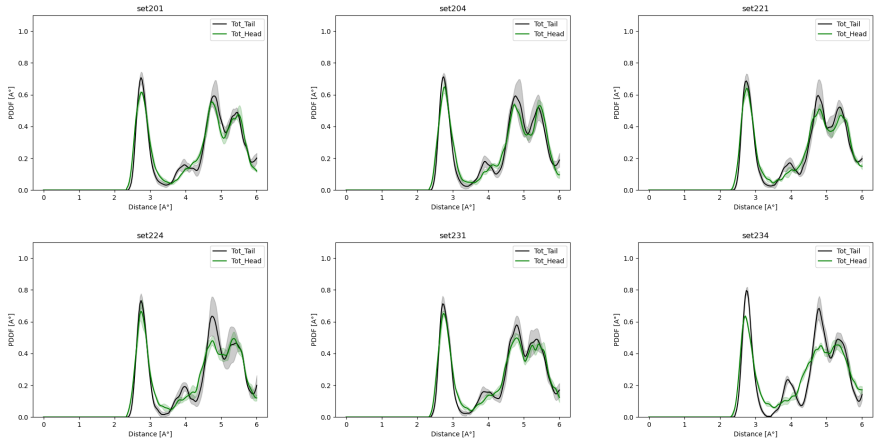

Fig. S4 Pair distance distribution function mean of whole cluster. In black is represented the PDDF at initial time (equal to the contact time) while in green is represented the PDDF at final time. Final time is equal to 10 ns.

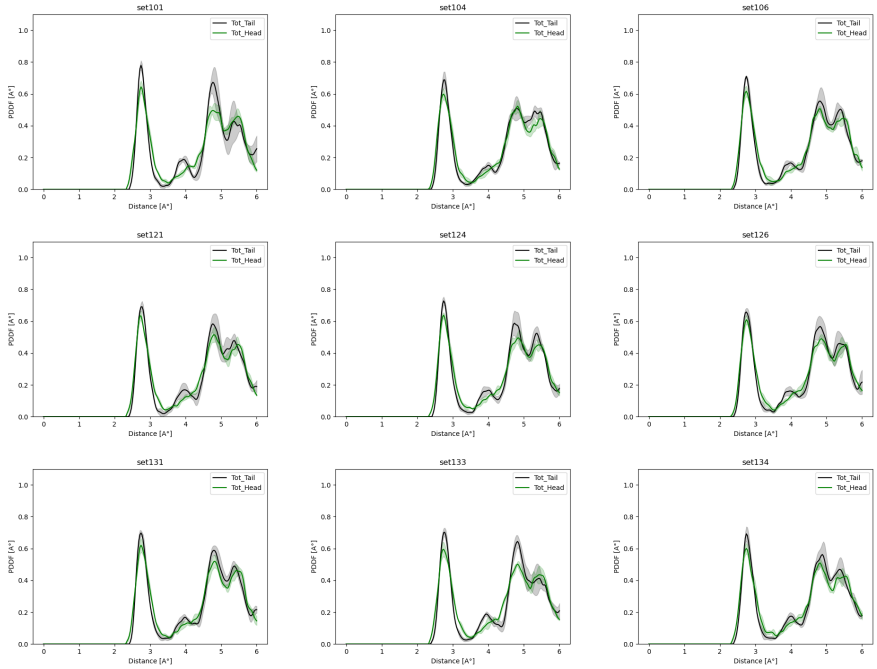

Fig. S5 Pair distance distribution function mean of whole cluster. In black is represented the PDDF at initial time (equal to the contact time) while in green is represented the PDDF at final time. Final time is equal to 10 ns.

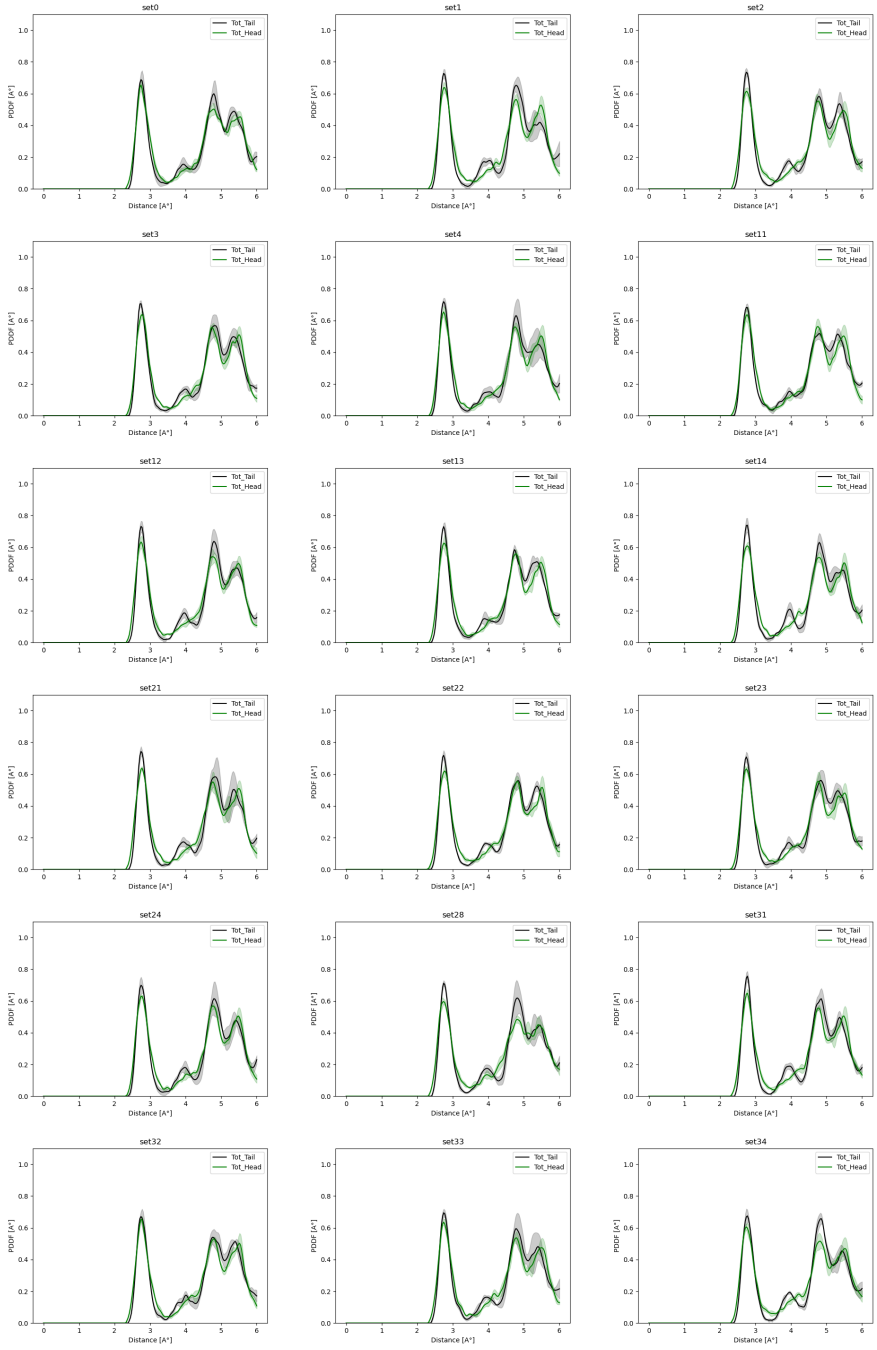

Fig. S6 Pair distance distribution function mean of whole cluster. In green is represented the PDDF at initial time (equal to the contact time) while in black is represented the PDDF at final time. Final time is equal to 10 ns.

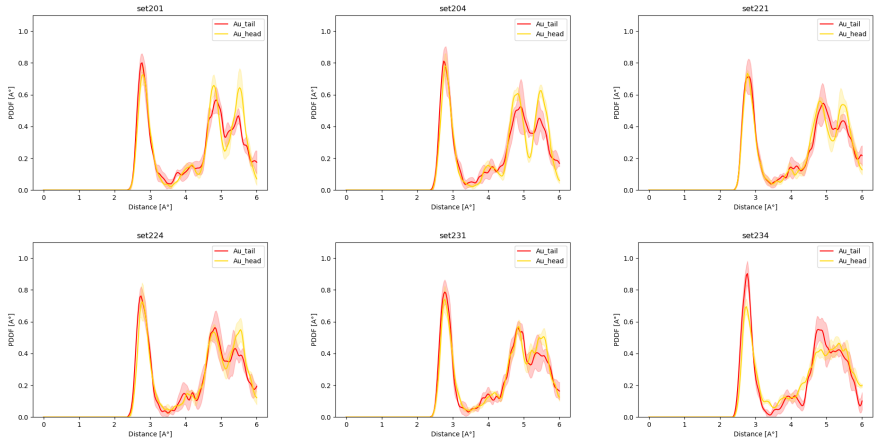

Fig. S7 Pair distance distribution function mean of Au atoms. In yellow is represented the PDDF at initial time (equal to the contact time) while in red is represented the PDDF at final time. Final time is equal to 10 ns.

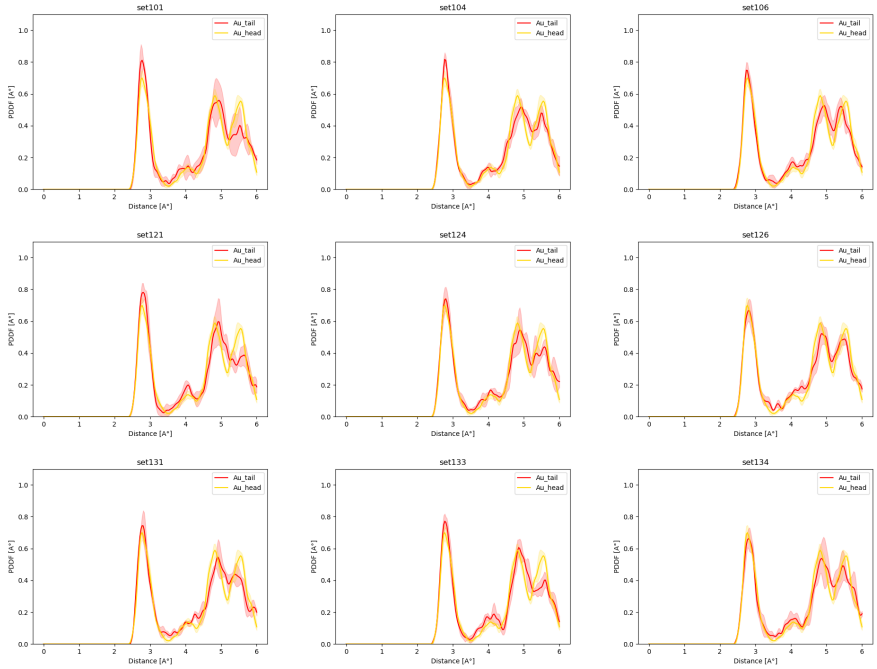

Fig. S8 Pair distance distribution function mean of Au atoms. In yellow is represented the PDDF at initial time (equal to the contact time) while in red is represented the PDDF at final time. Final time is equal to 10 ns.

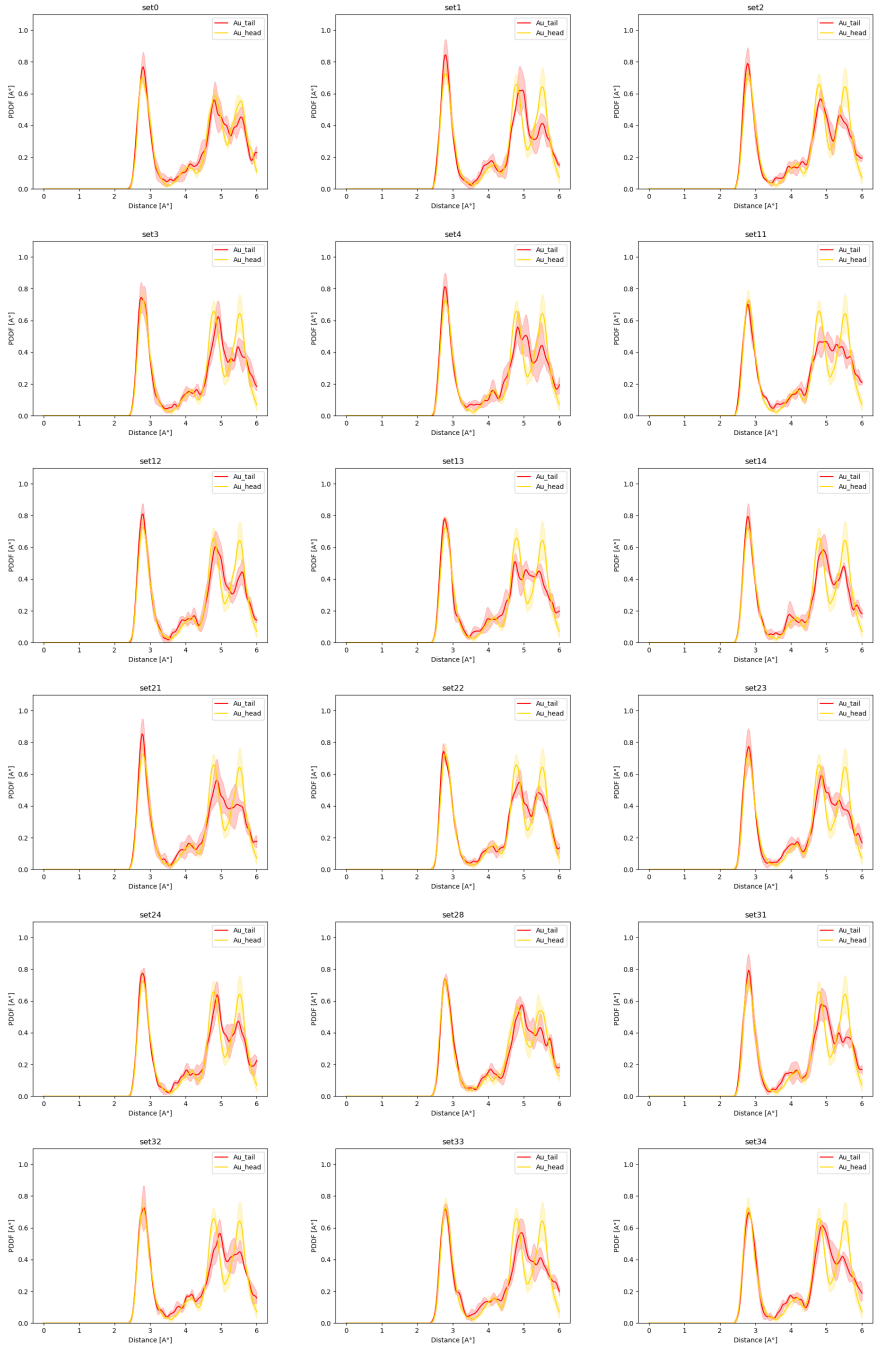

Fig. S9 Pair distance distribution function mean of Au atoms. In yellow is represented the PDDF at initial time (equal to the contact time) while in red is represented the PDDF at final time. Final time is equal to 10 ns.

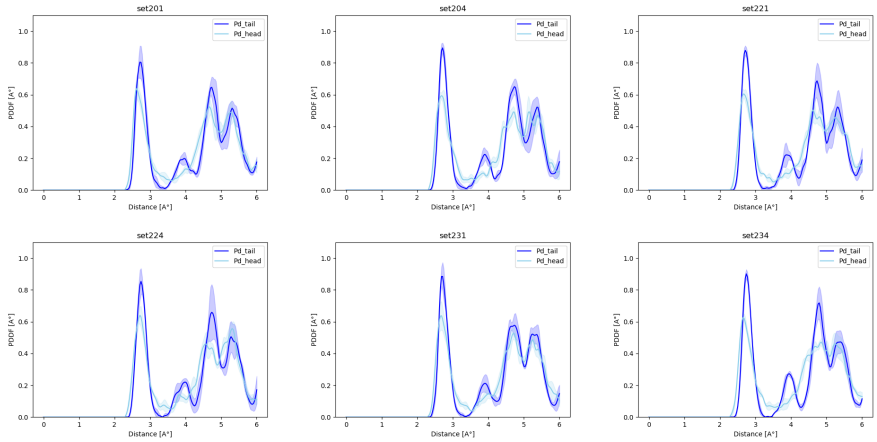

Fig. S10 Pair distance distribution function mean of Au atoms. In light blue is represented the PDDF at initial time (equal to the contact time) while in blue is represented the PDDF at final time. Final time is equal to 10 ns.

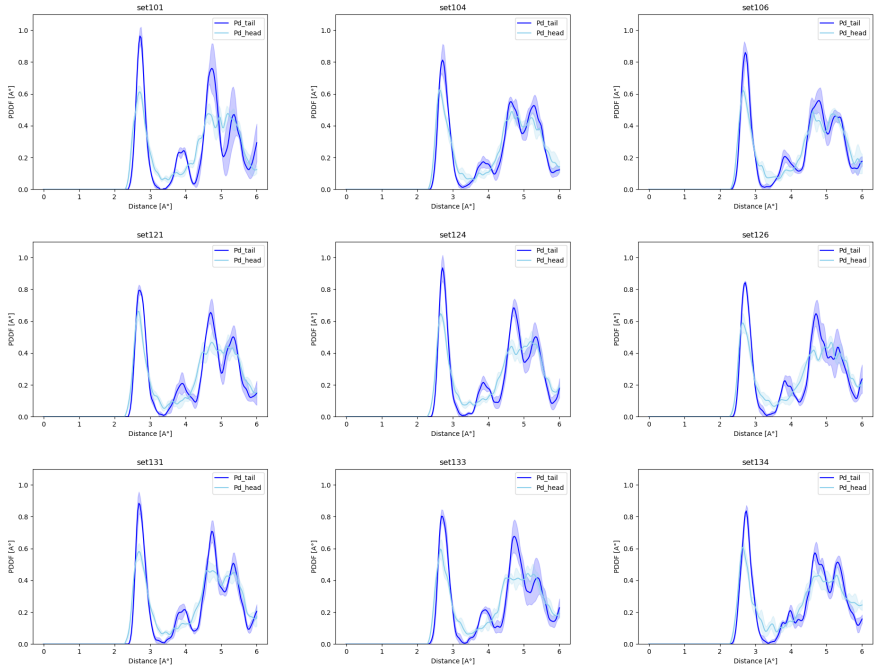

Fig. S11 Pair distance distribution function mean of Au atoms. In light blue is represented the PDDF at initial time (equal to the contact time) while in blue is represented the PDDF at final time. Final time is equal to 10 ns.

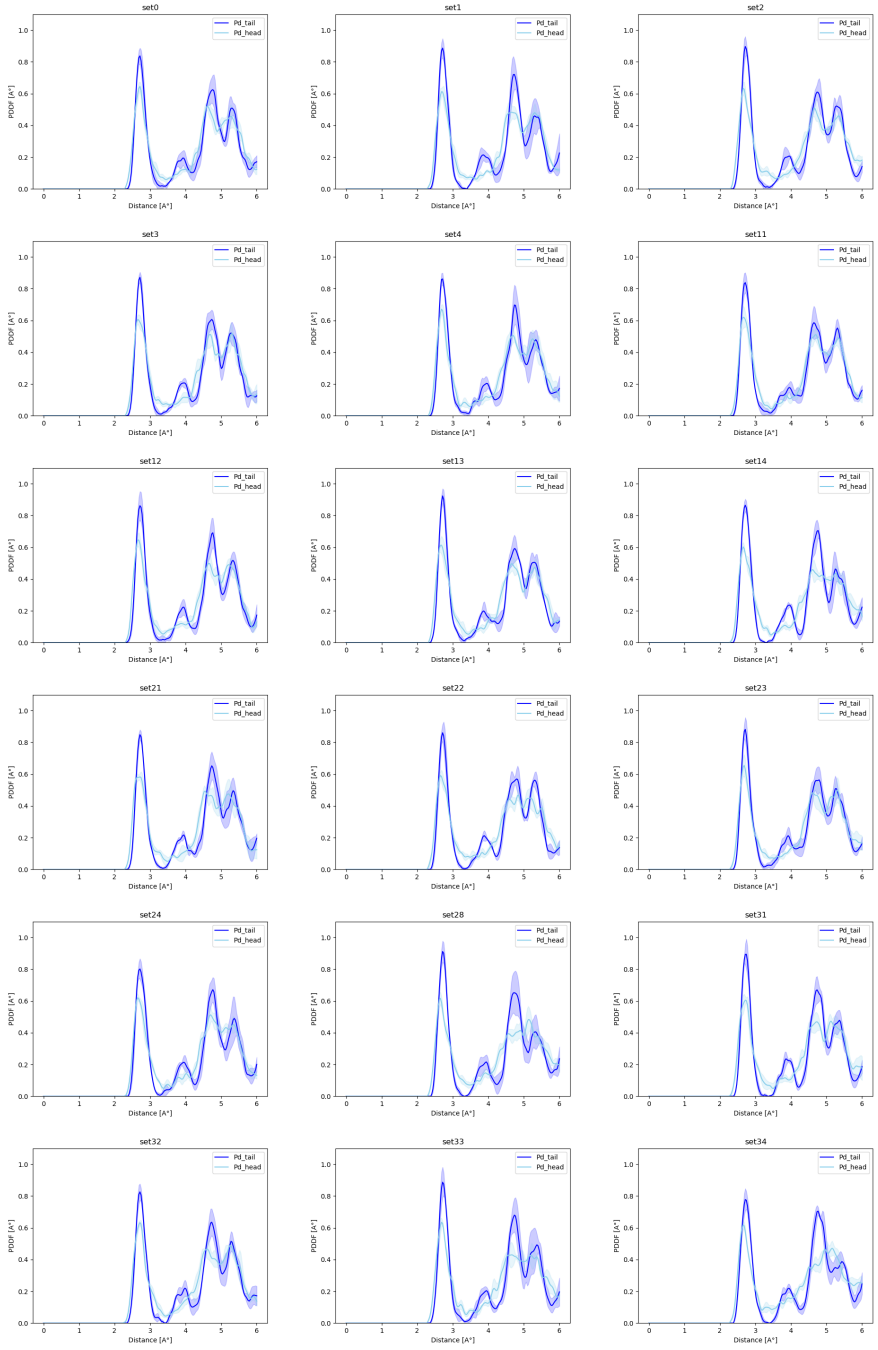

Fig. S12 Pair distance distribution function mean of Au atoms. In light blue is represented the PDDF at initial time (equal to the contact time) while in blue is represented the PDDF at final time. Final time is equal to 10 ns.

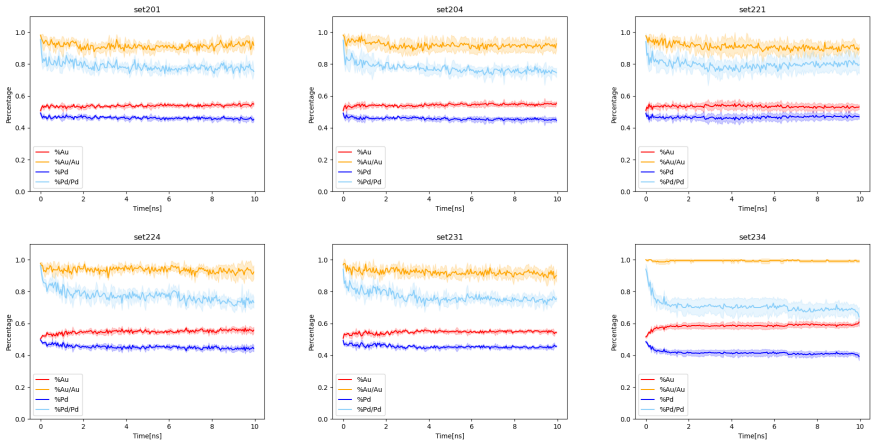

Fig. S13 Time evolution percentage of Au atoms (in red) and Pd atoms (in dark blue), compared to the total number of surface atoms. Surface atoms were identified by their atop generalized coordination number. The shaded areas correspond to the variations on the simulations, while the solid line represents the average of the percentages. Also shown in light blue is the percentage of surface palladium atoms to the total number of palladium atoms and in orange the percentage of gold on the surface compared to the total number of atoms of gold.

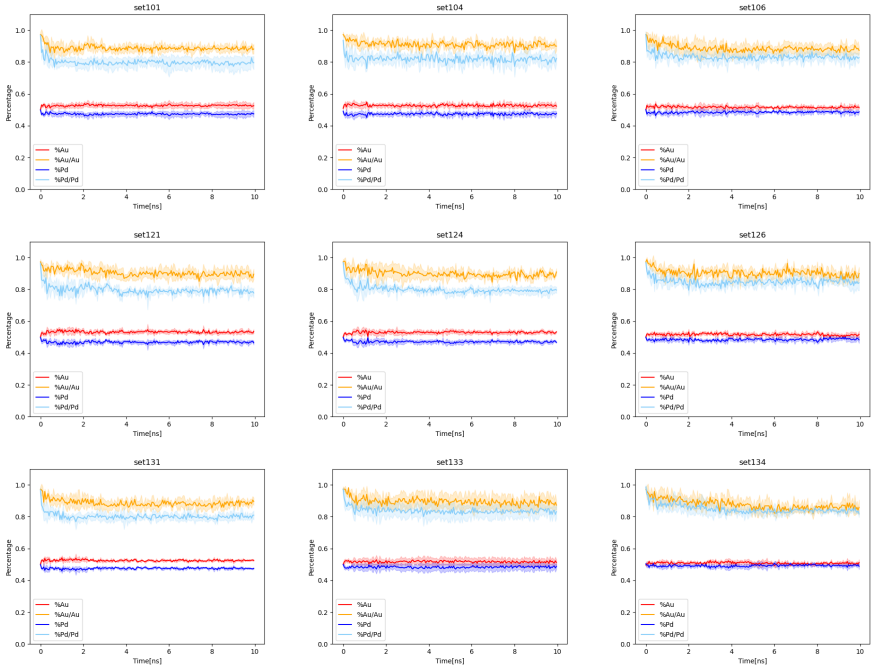

Fig. S14 Time evolution percentage of Au atoms (in red) and Pd atoms (in dark blue), compared to the total number of surface atoms. Surface atoms were identified by their atop generalized coordination number. The shaded areas correspond to the variations on the simulations, while the solid line represents the average of the percentages. Also shown in light blue is the percentage of surface palladium atoms to the total number of palladium atoms and in orange the percentage of gold on the surface compared to the total number of atoms of gold.

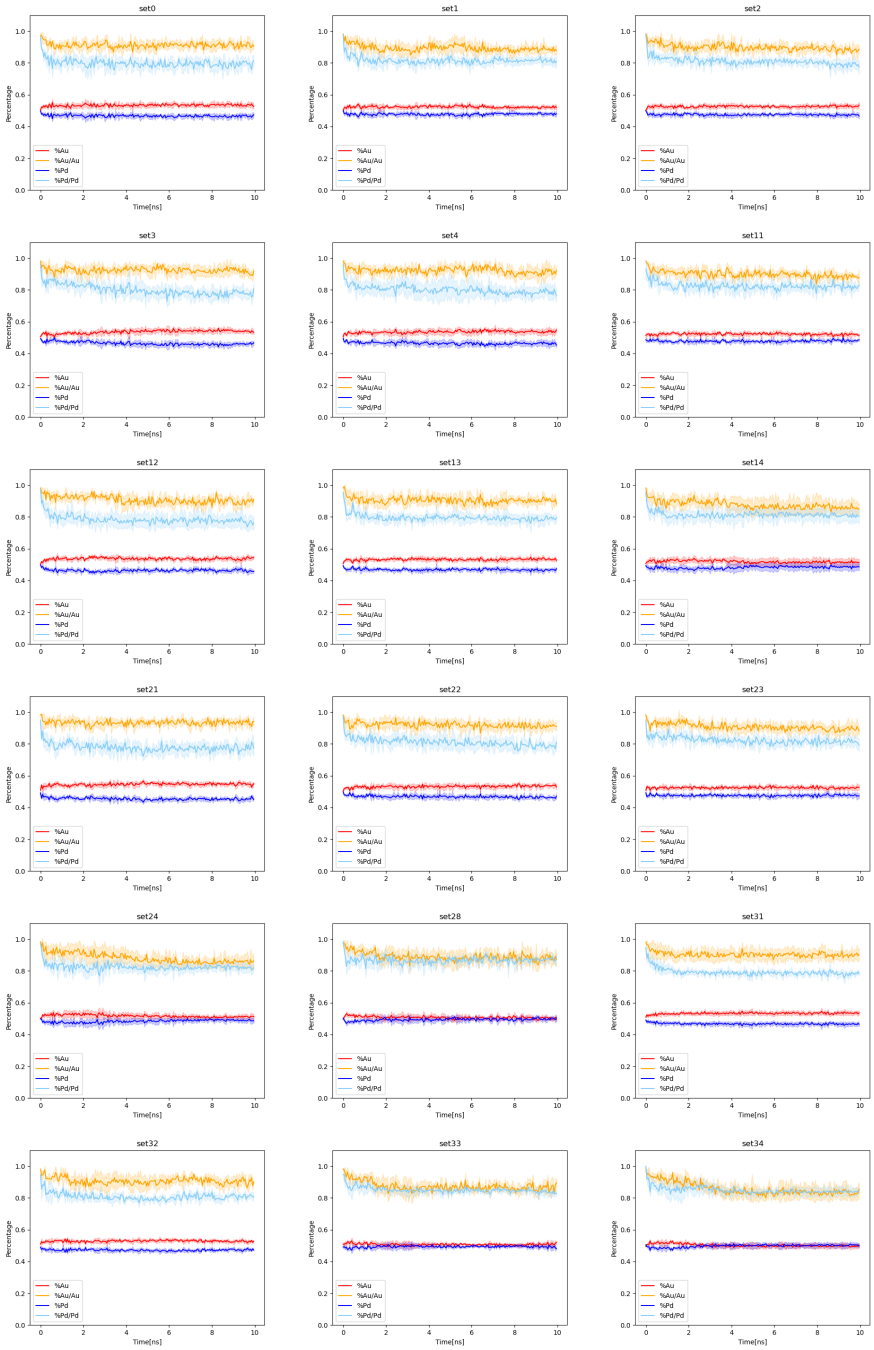

Fig. S15 Time evolution percentage of Au atoms (in red) and Pd atoms (in dark blue), compared to the total number of surface atoms. Surface atoms were identified by their atop generalized coordination number. The shaded areas correspond to the variations on the simulations, while the solid line represents the average of the percentages. Also shown in light blue is the percentage of surface palladium atoms to the total number of palladium atoms and in orange the percentage of gold on the surface compared to the total number of atoms of gold.

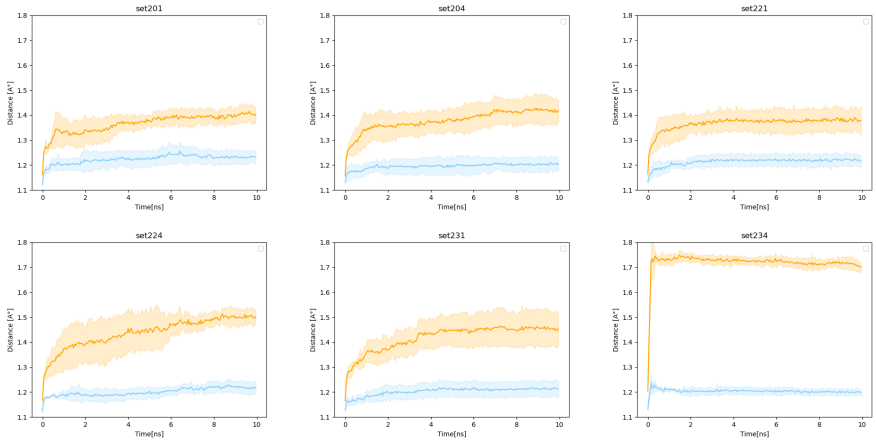

Fig. S16 Time evolution radius of gyration of the two chemical species: in orange is represented the mean radius of gyration of Au and in blue that of Pd.

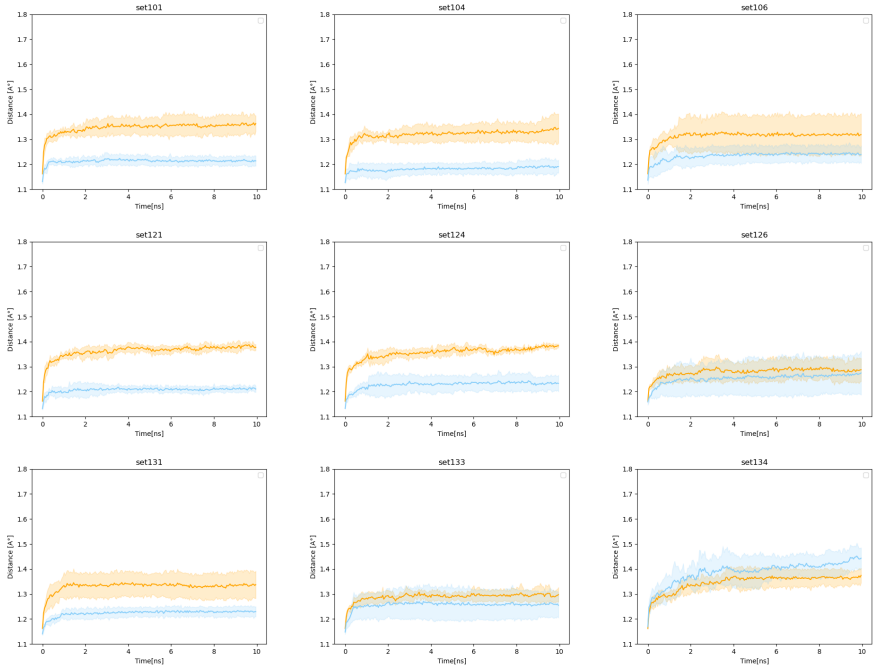

Fig. S17 Time evolution radius of gyration of the two chemical species: in orange is represented the mean radius of gyration of Au and in blue that of Pd.

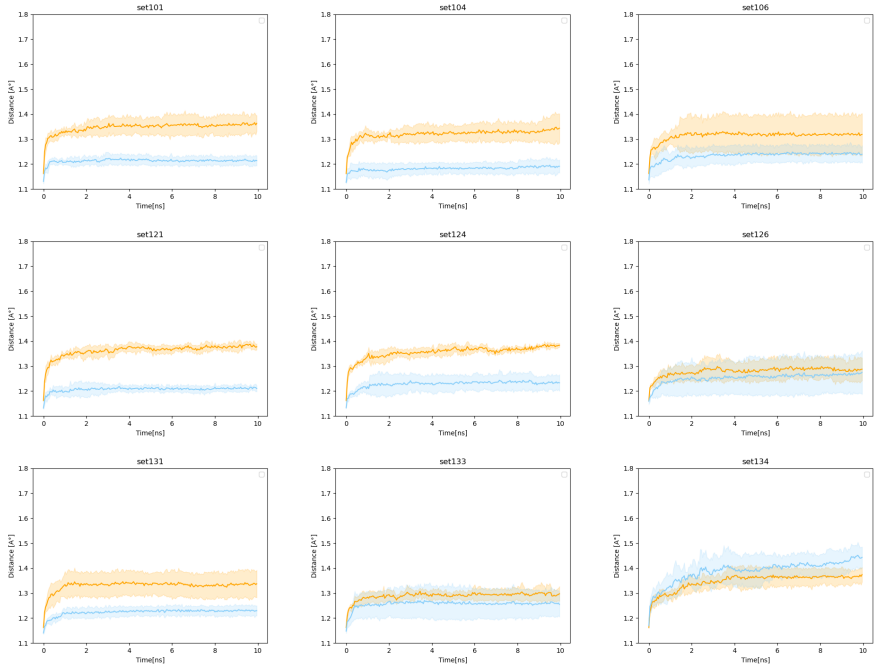

Fig. S18 Time evolution radius of gyration of the two chemical species: in orange is represented the mean radius of gyration of Au and in blue that of Pd.

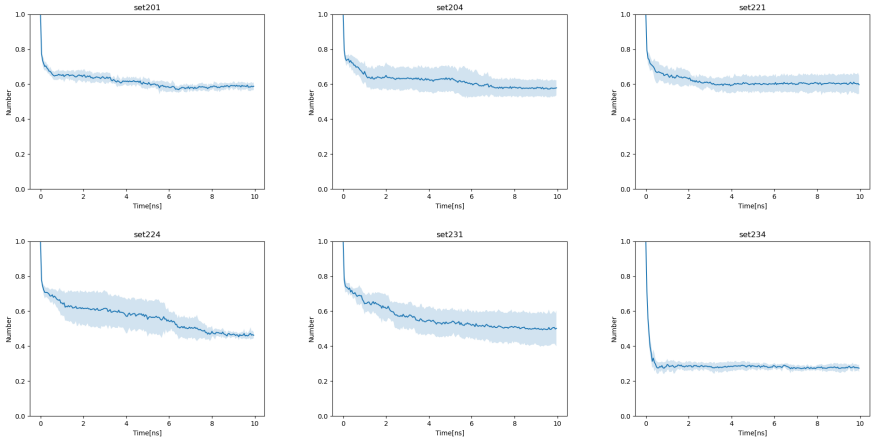

Fig. S19 Time evolution mixing parameter μ.

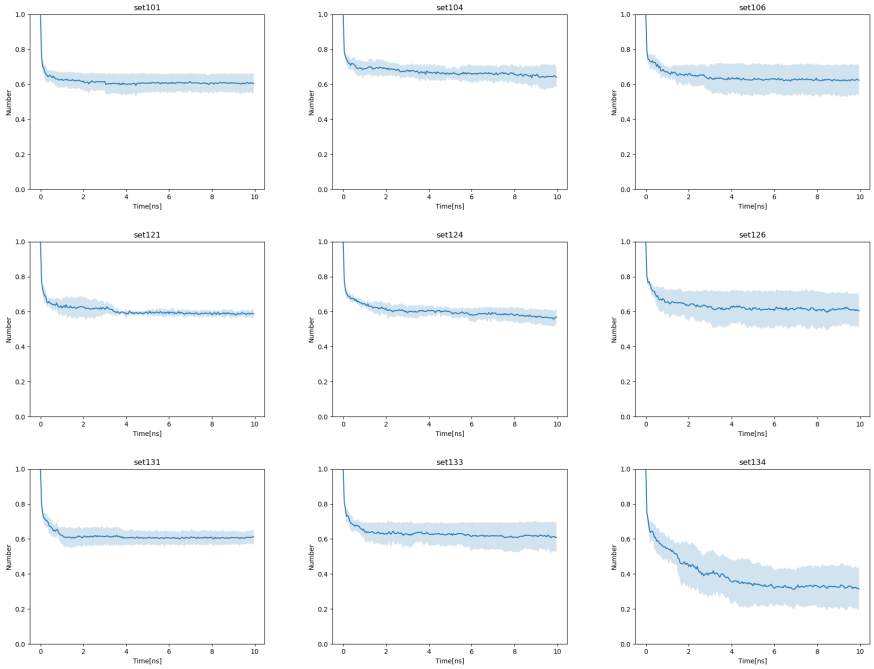

Fig. S20 Time evolution mixing parameter μ.

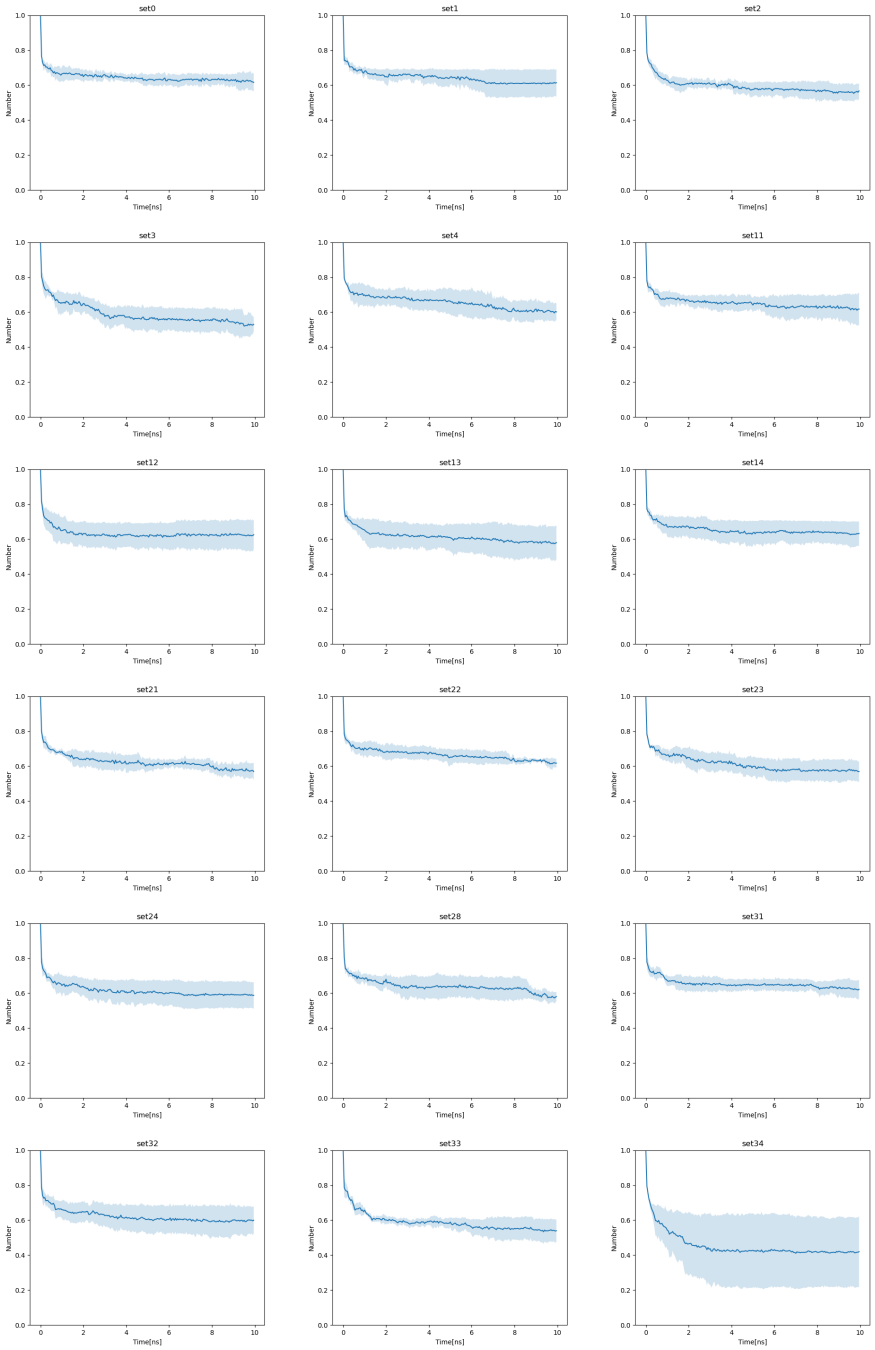

Fig. S21 Time evolution mixing parameter μ.

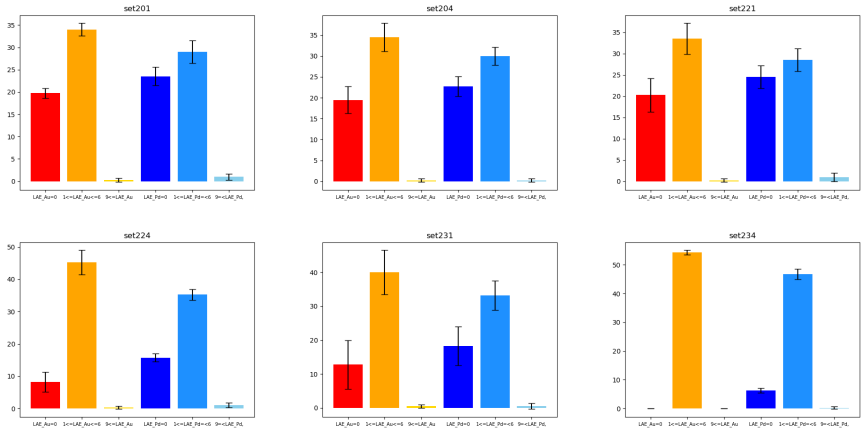

Fig. S22 LAE distribution for $Au_{55}Pd_{55}$ after 10 ns in MEIs where only Au interacts. Local atomic environments for Au atoms are in red-orange-yellow; while Pd-LAE are in blue-light-blue-cyan.

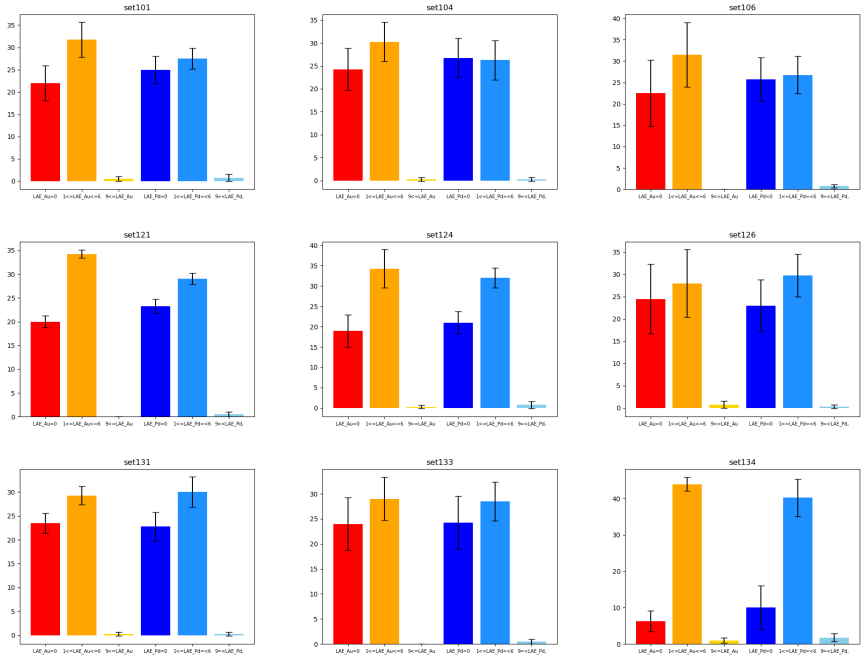

Fig. S23 LAE distribution for $Au_{55}Pd_{55}$ after 10 ns in MEIs where only Pd interacts. Local atomic environments for Au atoms are in red-orange-yellow; while Pd-LAE are in blue-light-blue-cyan.

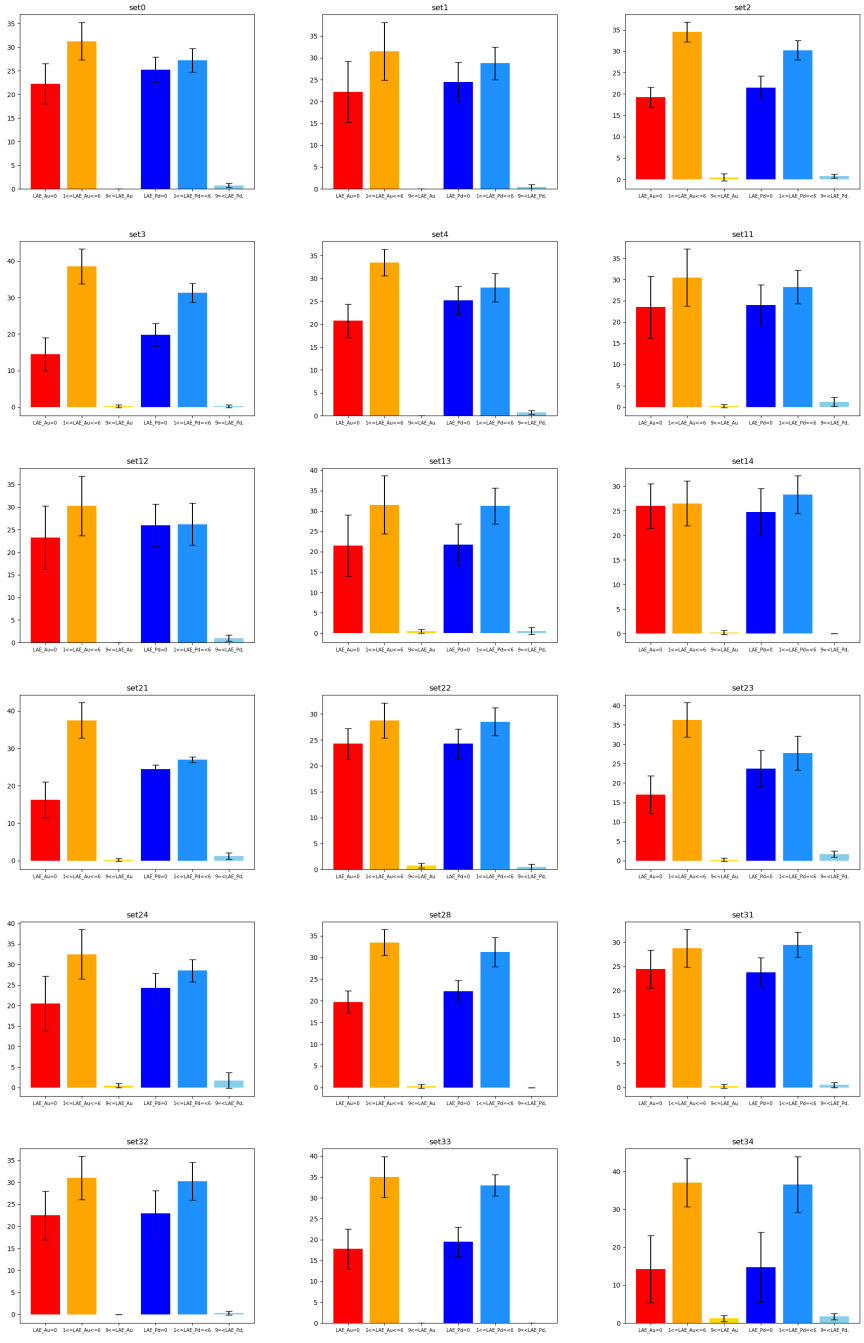

Fig. S24 LAE distribution for $Au_{55}Pd_{55}$ after 10 ns in MEIs where both Au and Pd interacts. Local atomic environments for Au atoms are in red-orange-yellow; while Pd-LAE are in blue-light-blue-cyan.

S-5 Au^{Ih}_{561}-Pd^{Ih}_{561}

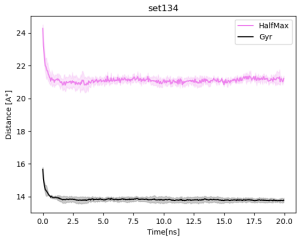

Fig. S25 Time evolution radius of gyration of the whole cluster (in black) and half maximum pair distance $R_{max} = D_{max}/2$ (in pink), for Au^{Ih}_{55}-Pd^{Ih}_{55} in the environment with ρ_{Au}, ρ_{Pd}, η_{Au} eV and η_{Pd} eV varying as in table S1. Each graph represents the average over four independent simulations of the quantities mentioned. The mean value is represented by the solid line, while the shadow represents the standard deviation.

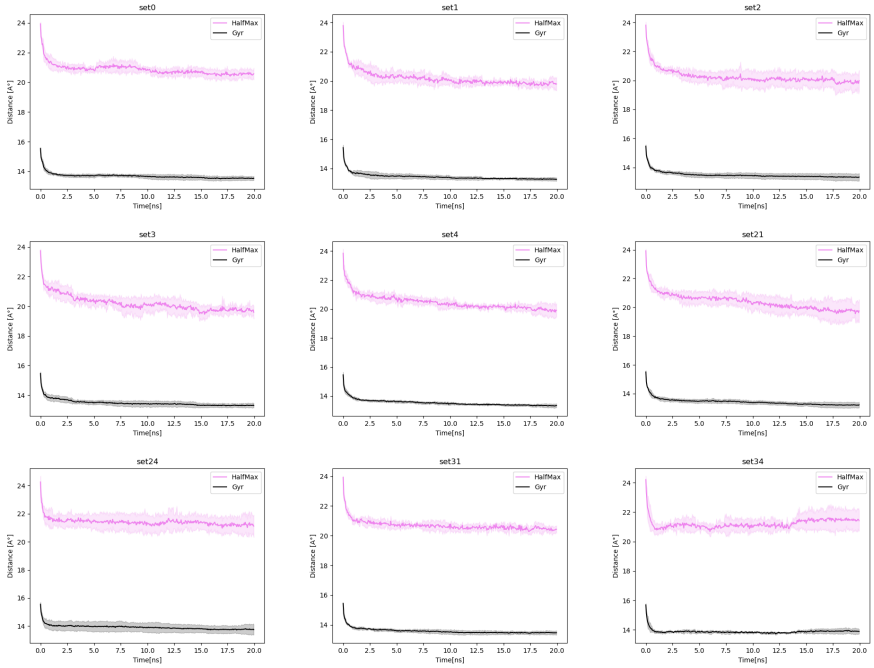

Fig. S26 Time evolution radius of gyration of the whole cluster (in black) and half maximum pair distance $R_{max} = D_{max}/2$ (in pink), for Au^{Ih}_{55}-Pd^{Ih}_{55} in the environment with ρ_{Au}, ρ_{Pd}, η_{Au} eV and η_{Pd} eV varying as in table S1. Each graph represents the average over four independent simulations of the quantities mentioned. The mean value is represented by the solid line, while the shadow represents the standard deviation.

References

1 M. Jones, Robert, K. Rossi, C. Zeni, M. Vanzan, I. Vasiljevic, A. Santana-Bonilla and F. Baletto, *Faraday Discuss.*, 2023, **242**, 326–352.

2 L. Delgado-Callico, K. Rossi, R. Pinto-Miles, P. Salzbrenner and F. Baletto, *Nanoscale*, 2021, **13**, 1172–1180.

3 R. M. Jones, *PhD thesis*, King's College London, 2022.

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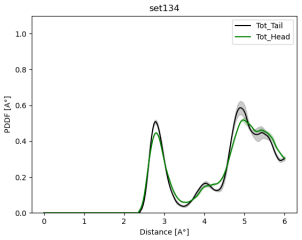

Fig. S27 Pair distance distribution function mean of whole cluster. In green is represented the PDDF at initial time (equal to the contact time) while in black is represented the PDDF at final time. Final time is equal to 20 ns

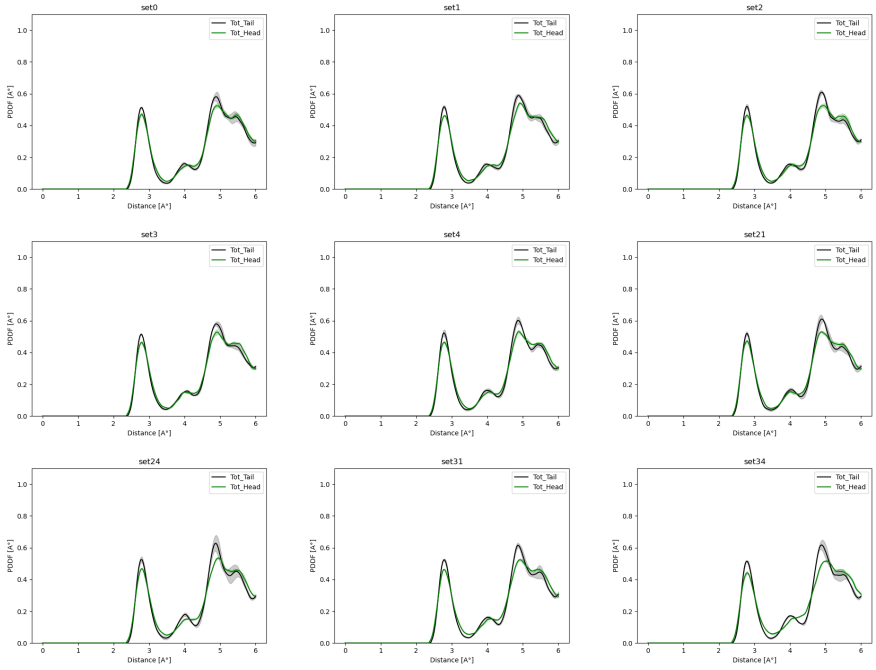

Fig. S28 Pair distance distribution function mean of whole cluster. In green is represented the PDDF at initial time (equal to the contact time) while in black is represented the PDDF at final time. Final time is equal to 20 ns

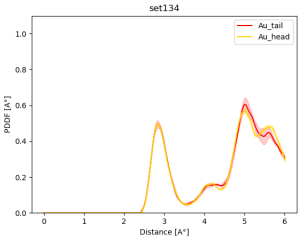

Fig. S29 Pair distance distribution function mean of Au atoms. In yellow is represented the PDDF at initial time (equal to the contact time) while in red is represented the PDDF at final time. Final time is equal to 20 ns

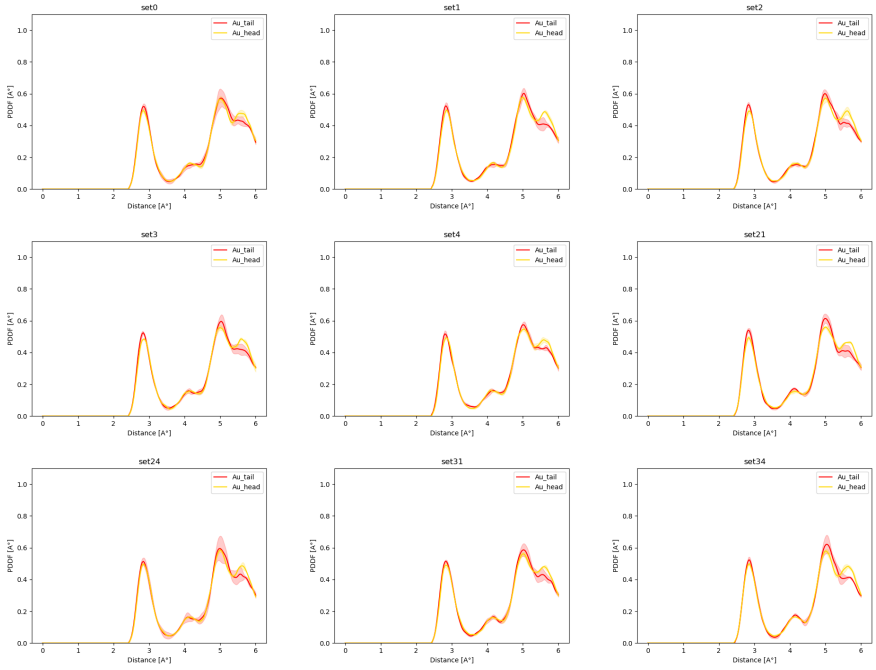

Fig. S30 Pair distance distribution function mean of Au atoms. In yellow is represented the PDDF at initial time (equal to the contact time) while in red is represented the PDDF at final time. Final time is equal to 20 ns

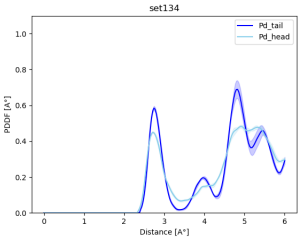

Fig. S31 Pair distance distribution function mean of Pd atoms. In light blue is represented the PDDF at initial time (equal to the contact time) while in blue is represented the PDDF at final time. Final time is equal to 20 ns.

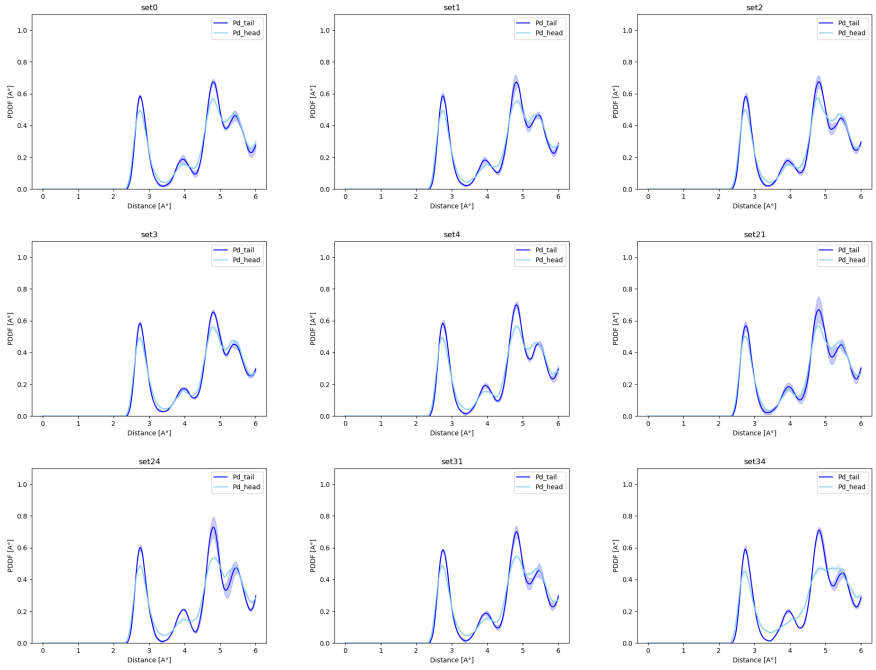

Fig. S32 Pair distance distribution function mean of Pd atoms. In light blue is represented the PDDF at initial time (equal to the contact time) while in blue is represented the PDDF at final time. Final time is equal to 20 ns.

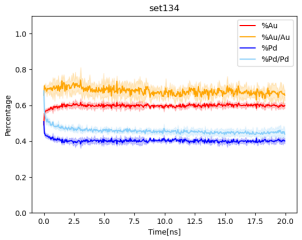

Fig. S33 Time evolution percentage of Au atoms (in red) and Pd atoms (in dark blue), compared to the total number of surface atoms. Surface atoms were identified by their atop generalized coordination number. The shaded areas correspond to the variations on the simulations, while the solid line represents the average of the percentages. Also shown in light blue is the percentage of surface palladium atoms to the total number of palladium atoms and in orange the percentage of gold on the surface compared to the total number of atoms of gold.

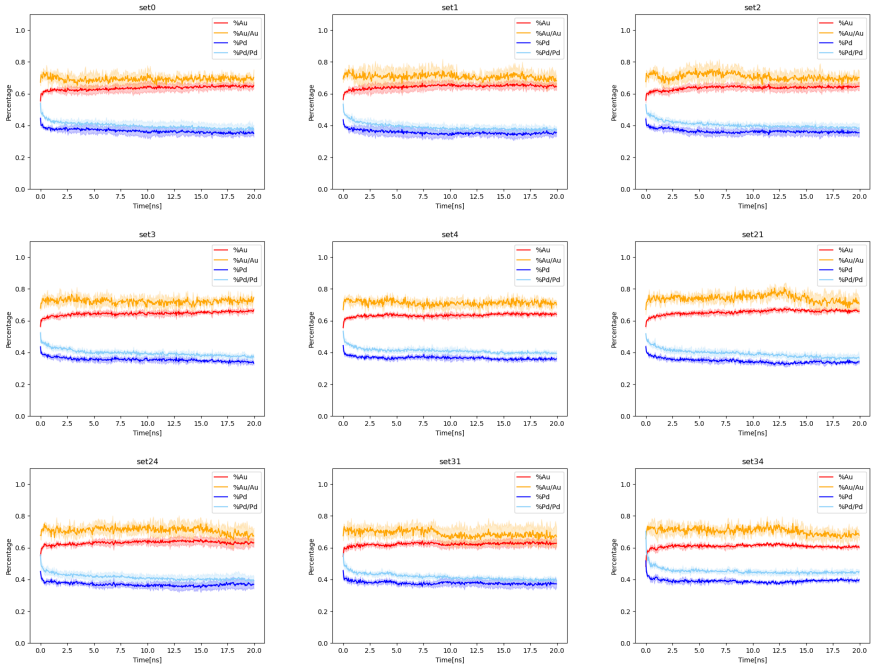

Fig. S34 Time evolution percentage of Au atoms (in red) and Pd atoms (in dark blue), compared to the total number of surface atoms. Surface atoms were identified by their atop generalized coordination number. The shaded areas correspond to the variations on the simulations, while the solid line represents the average of the percentages. Also shown in light blue is the percentage of surface palladium atoms to the total number of palladium atoms and in orange the percentage of gold on the surface compared to the total number of atoms of gold.

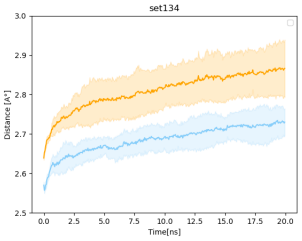

Fig. S35 Time evolution radius of gyration of the two chemical species: in orange is represented the mean radius of gyration of Au and in blue that of Pd.

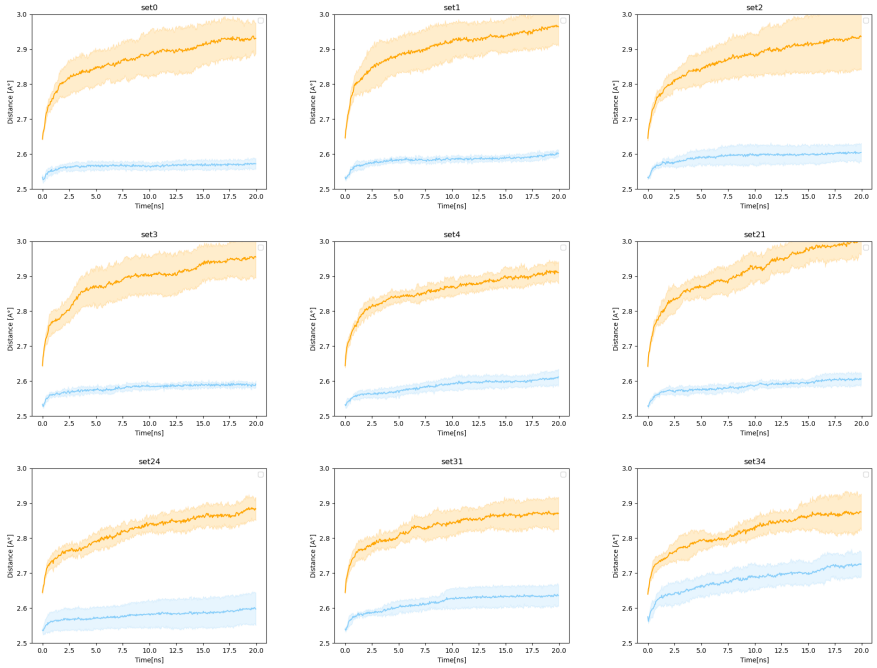

Fig. S36 Time evolution radius of gyration of the two chemical species: in orange is represented the mean radius of gyration of Au and in blue that of Pd.

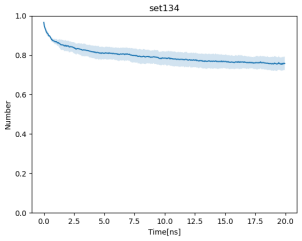

Fig. S37 Time evolution mixing parameter μ.

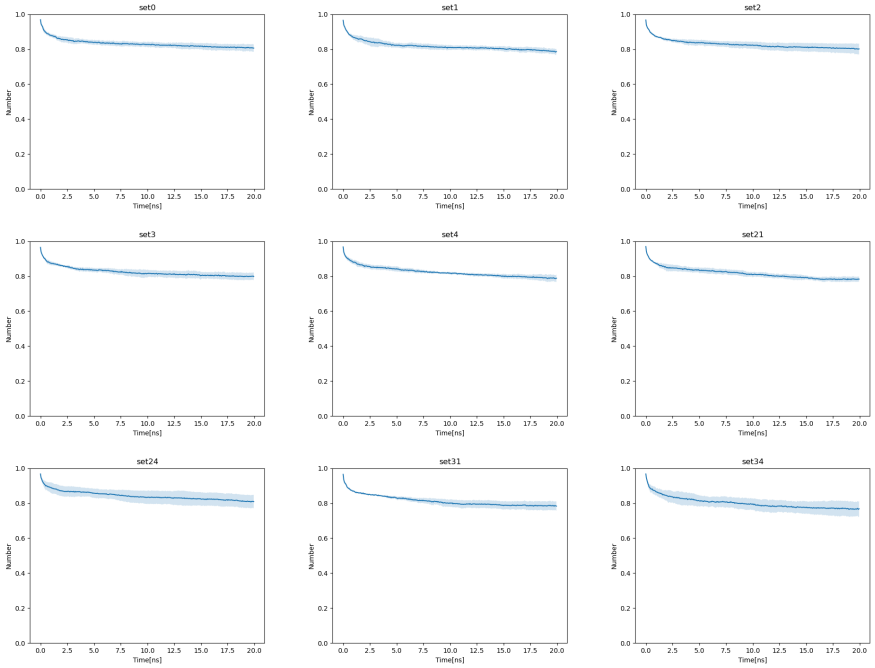

Fig. S38 Time evolution mixing parameter μ.

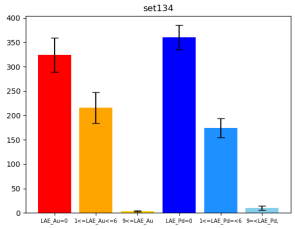

Fig. S39 LAE distribution for $Au_{561}Pd_{561}$ after 20 ns in MEIs where only Au interacts. Local atomic environments for Au atoms are in red-orange-yellow; while Pd-LAE are in blue-light-blue-cyan.

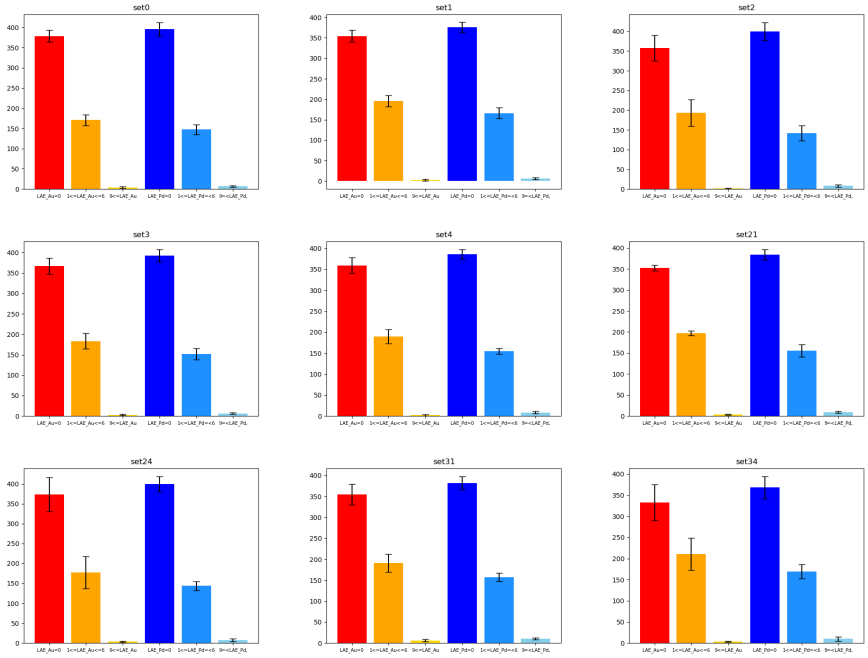

Fig. S40 LAE distribution for $Au_{561}Pd_{561}$ after 20 ns in MEIs where only Au interacts. Local atomic environments for Au atoms are in red-orange-yellow; while Pd-LAE are in blue-light-blue-cyan.