Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Appendix (I)

Details for derivation of Equation (1):

The goal of this section is derivation of an expression for probability of formation of an N-atom nanocluster containing N_A atom of metal A and N_B atom of metal B from the gas phase. Let N^*_A and N^*_B be the initial number of atoms A, and B in gas phase. Thus we have:

$$\begin{cases} N_A^* + N_B^* = N^* \\ N_A + N_B = N \end{cases} \tag{S1}$$

where N^*_A and N^*_B are constant values. Now, the random formation of an N-atom nanocluster is considered. Suppose that first N^*_A atoms of A and then N^*_B atoms of B join together to form the nanocluster. The probability of this process can be obtained as:

$$P_N = \left(\frac{N_A^*}{N^*}\right)\left(\frac{N_A^*-1}{N^*-1}\right)\left(\frac{N_A^*-2}{N^*-2}\right)\cdots\left(\frac{N_A^*-N_A+1}{N^*-N_A+1}\right)\times$$
$$\left(\frac{N_B^*}{N^*-N_A}\right)\left(\frac{N_B^*-1}{N^*-N_A-1}\right)\left(\frac{N_B^*-2}{N^*-N_A-2}\right)\cdots\left(\frac{N_B^*-N_B+1}{N^*-N_A-N_B+1}\right) \tag{S2}$$

Please note that the order of addition of atoms A and B can not affect this probability. Using Equation (S1) we have:

$$P_N = \frac{N_A^*!\,N_B^*!\,(N^*-N_A-N_B)!}{(N_A^*-N_A)!\,(N_B^*-N_B)!\,N^*!} \tag{S3}$$

As mentioned above, change in order of addition of A and B atoms does not affect P_N. Therefore, in order to find total probability of formation of a N-atom nanocluster containing N_A atom A and N_B atom B, $P(N_A,N)$, all of the probabilities P_N for all of the various orders for addition of atoms A and B should be summed. Since, all of the mentioned P_N values are equal, the ways for various orders for addition of atoms A and B is required to be considered. Then we have:

$$P\left(N_A, N\right) = \frac{N!}{N_A! N_B!} P_N \tag{S4}$$

Using Equation (S1) on can write Equation(S4) as follows:

$$P\left(N_A, N\right) = \frac{N!}{N_A!(N - N_A)!} \frac{N_A^*!(N^* - N_A^*)!(N^* - N)!}{(N_A^* - N_A)!(N^* - N_A^* - N + N_A)!N^*!} \tag{S5}$$

This equation expresses the probability of formation of a *N*-atom cluster. The advantage of this expression is introducing a random limit for cluster formation in gas phase, in such a way that various clusters obtained by molecular simulation methods can be tested by this equation in order to reach a measure of randomness in the simulated system. Also, Equation (S5) van be rewritten as:

$$P\left(N_A, N\right) = \frac{W_{clus} \times W_{res}}{W^*} \tag{S6}$$

where:

$$W_{clus} = \frac{N!}{N_A! \times N_B!} \tag{S7}$$

$$W_{res} = \frac{(N^* - N)!}{(N_A^* - N_A)! \times (N_B^* - N_B)!} \tag{S8}$$

$$W^* = \frac{N^*!}{N_A^*! \times N_B^*!} \tag{S9}$$

In above Equations, W_{clus} is the ways of distribution of A and B atoms in the solid-like cluster, W_{res} in the ways of distribution of residual A and B atoms in the gas phase if the gas phase to be considered as another solid-like cluster, and finally W^* is the ways of distribution of A and B atoms in the gas phase of initial state if the initial gas phase is assumed as a solid-like cluster containing N^*_{A} atoms of A and N^*_{B} atoms of B.

Appendix (II)

Details for derivation of Equation (3):

In this section, formation of a *N*-atom nanocluster in a thermodynamic viewpoint is discussed. Suppose that the system contains N^*_A atoms of type A, N^*_B atoms of type B and N_C atoms of inert gas C in constant temperature (*T*) and total volume (*V*). Since, total number of atoms is constant, thermodynamic potential of the system is Helmholtz function (*F*). The formation of a N-atom cluster from atoms A and B can be considered as the following simple reaction:

$$nA^{(g)} + mB^{(g)} \rightarrow A_nB_m{}^{(g)} \qquad \text{(S10)}$$

where (g) superscript represents the gas phase. The total Helmholtz free energy of the system before and after cluster formation (*F*1, and *F*2) can be expressed as:[40]

$$F_1 = N^*_A\mu^*_A + N^*_B\mu^*_B + N_C\mu_C \qquad \text{(S11)}$$

$$F_2 = \left(N^*_A - n\right)\mu_A + \left(N^*_B - m\right)\mu_B + N_C\mu_C + F_{clus} + 4\pi r^2\gamma \qquad \text{(S12)}$$

where μ_A, μ_B, and F_{clus} are the chemical potentials A, B, and Helmholtz energy of the created nanocluster, respectively. Also, star(*) superscript represents the initial state in the gas phase. In Equation (S12) the nanocluster assumed to be spherical with radius *r*, and γ is surface tension between the nanocluster and C gas. Hence, Helmholtz free energy for formation of A_nB_m nanocluster, $\Delta F(n,m)$, can be obtained as:

$$\Delta F(n,m) = \left(N^*_A - n\right)\mu_A + \left(N^*_B - m\right)\mu_B + F_{clus}(n,m) + 4\pi r^2\gamma - N^*_A\mu^*_A - N^*_B\mu^*_B \qquad \text{(S13)}$$

In this relation, $F_{clus}\,(n,m)$ should be determined. The Helmholtz free energy of the nanocluster can be obtained by characteristic function of canonical ensemble:[41]

$$F_{clus} = -kT\ln Q_{clus} + U_0(\rho) \qquad \text{(S14)}$$

where k is the Boltzmann constant and U_0 is total intermolecular potential of the nanocluster which is a function of cluster density (ρ). Q_{clus} is total partition function of the *N*-atom nanocluster which can be expressed as:

$$Q_{clus} = \frac{N!}{n!m!} Q_{ele} Q_{vib} \tag{S15}$$

Please note that $N = n + m$. In this equation "ele" and "vib" subscripts represent electronic and vibrational contributions in Q_{clus}. Also, the first term of equation (S15) is the ways of distribution of n atoms of A and m atoms of B in a solid-like nanocluster. The vibrational partition function of the nanocluster can be written as:

$$\ln Q_{vib} = -\int_0^{\infty} \left[\ln\left(1 - e^{-h\nu/kT}\right) + \frac{h\nu}{2kT} \right] g(\nu) d\nu \tag{S16}$$

where v is the phonon frequency and $g(v)$ is its dispersion function. The simplest way to obtain vibrational partition function of the nanocluster is using of Einstein's theory of solid phonons:[41]

$$g(\nu) = 3N\delta(\nu - \nu_E) \tag{S17}$$

In this relation $\delta(v\text{-}v_{\text{E}})$ is Dirac delta-function and v_{E} is the Einstein frequency. Substitution of Equation (S17) in Equation (S16) and using the integration properties of Dirac delta function one obtains:

$$\ln Q_{vib} = -N \left[\ln\left(1 - e^{-h\nu_E/kT}\right) + \frac{h\nu_E}{2kT} \right] \tag{S18}$$

Hence, using Stirling's approximation Helmholtz free energy of the nanocluster can be written as:

$$\begin{aligned} F_{clus}(n,m) = -kT\{&(n+m)\ln(n+m) - m\ln m - n\ln n - \\ &(n+m)\ln\left(1 - e^{-h\nu_E/kT}\right) - (n+m)\frac{h\nu_E}{2kT}\} + U_0(\rho) \end{aligned} \tag{S19}$$

If volume of the initial system to be large enough, distances between atoms are faraway and with a good approximation, various gas particles can be viewed as ideal gases. Therefore, chemical potentials of particle i in gas phase and its partial pressure, P_{i} can be expressed as:

$$\mu_i = \mu_i^{\theta} + kT \ln\left(\frac{P_i}{P^{\theta}}\right) \tag{S20}$$

$$P_i = \frac{N_i kT}{V} \tag{S21}$$

where θ superscript indicates the standard conditions. Now, using Equations (S13), (S19), (S20), and (S21) Helmholtz free energy for formation of the nanocluster becomes:

$$\begin{aligned}
\Delta F(n,m) = {} & \left(N_A^* - n\right)\left(\mu_A^\theta + kT\ln\frac{\left(N_A^* - n\right)kT}{VP^\theta}\right) + \left(N_B^* - m\right)\left(\mu_B^\theta + kT\ln\frac{\left(N_B^* - m\right)kT}{VP^\theta}\right) - \\
& kT\{(n+m)\ln(n+m) - m\ln m - n\ln n - (n+m)\ln\left(1 - e^{-h\nu_E/kT}\right) - (n+m)\frac{h\nu_E}{2kT}\} + \\
& 4\pi\gamma r^2 + U_0(\rho) - N_A^*\left(\mu_A^\theta + kT\ln\frac{N_A^* kT}{VP^\theta}\right) - N_B^*\left(\mu_B^\theta + kT\ln\frac{N_B^* kT}{VP^\theta}\right)
\end{aligned} \tag{S22}$$

Here, differentiation of $\Delta F(n,m)$ with respect to n and m can give us the composition of the nanocluster with minimum free energy:

$$\begin{cases} \left(\dfrac{\partial \Delta F}{\partial n}\right)_m = 0 \\ \left(\dfrac{\partial \Delta F}{\partial m}\right)_n = 0 \end{cases} \tag{S23}$$

In order to differentiation of Equation (S22) respect to n and m, dependency of r to m and n should be determined. If the volume of the cluster, V_{clus} is considered as a linear function of its total number of atoms:

$$V_{clus} = \alpha N \tag{S24}$$

and using the relation between the volume and surface of a sphere one can obtain:

$$4\pi r^2 = 4\pi\left[\frac{3\alpha}{4\pi}(n+m)\right]^{3/2} = \alpha'(n+m)^{3/2} \tag{S25}$$

Also, by considering:

$$f(T) = \left(1 - e^{-h\nu_E/kT}\right)e^{h\nu_E/2kT} \tag{S26}$$

Then using Equations (S22), (S23), (S25), and (S26) the following expressions are obtained:

$$-\mu_A^\theta - kT\ln\left[\frac{(N_A^* - n)(n+m)kT}{nf(T)VP^\theta}\right] + \frac{3}{2}\gamma\alpha'(n+m)^{1/2} = 0 \tag{S27}$$

$$-\mu_B^\theta - kT\ln\left[\frac{(N_B^* - n)(n+m)kT}{mf(T)VP^\theta}\right] + \frac{3}{2}\gamma\alpha'(n+m)^{1/2} = 0 \tag{S28}$$

or another form:

$$\frac{(N_A^* - n)(n+m)kT}{nf(T)VP^\theta} = e^{-\mu_A^\theta/kT} \times e^{\frac{-3}{2kT}\gamma\alpha'(n+m)^{1/2}} \tag{S29}$$

$$\frac{(N_B^* - m)(n+m)kT}{mf(T)VP^\theta} = e^{-\mu_B^\theta/kT} \times e^{\frac{-3}{2kT}\gamma\alpha'(n+m)^{1/2}} \tag{S30}$$

by dividing Equation (S29) to Equation (S30) the following simple equation is obtained:

$$\frac{m(N_A^* - n)}{n(N_B^* - m)} = \exp\left\{\frac{-(\mu_A^\theta - \mu_B^\theta)}{kT}\right\} = \beta(T) \tag{S31}$$

Rearrangement of Equation (29) leads to a simple relation between n and m at constant N^*, V, and T conditions:

$$m = \frac{\beta N_B^* n}{(N_A^* - n + \beta n)} \tag{S32}$$

where β is an adjustable parameter.

Appendix (III)

Equations for calculation of Order parameter Q6 used in this study:

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_l^m(r_{ij}) \tag{S33}$$

$$q_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{+l} \left| q_{lm}(i) \right|^2} \tag{S34}$$

$$Q_l(i) = \frac{1}{\tau_\alpha} \int_{t_0}^{t+\tau_\alpha} q_l(i) dt \tag{S35}$$

where i'th atom is surrounded by $N_\mathrm{b}(i)$ atoms within the cutoff distance, r_ij is the distance between i'th atom and one of the surrounding atoms (j), $Y_{lm}(r_\mathrm{ij})$ is the spherical harmonic within distance, and $q_\mathrm{lm}(i)$ is the average of spherical harmonics around atom i within the cutoff range. Also, t_0 is a reference time and τ_α is the time interval.

Tables

Table S1: N, N_{Ag}, N_{Au}, and Q_6 parameter for pure Ag nanoclusters (N^*_{Ag}=2000 system) obtained from MD simulations at 5, 7.5, 10, 15, 20, 25, and 30 ns of simulation time.

time (ns)	N_{Ag}	N_{Au}	N	x_{Ag}	Q_6
5	1458	0	1458	1	0.664
5	89	0	89	1	0.63
5	453	0	453	1	0.65
7.5	1547	0	1547	1	0.66
7.5	453	0	453	1	0.65
10	2000	0	2000	1	0.663
15	2000	0	2000	1	0.663
20	2000	0	2000	1	0.663
25	2000	0	2000	1	0.663
30	2000	0	2000	1	0.663

Table S2: The same as Table S1 accompanied by $P(N_{\mathrm{Ag}},N)$ for N^{*}_{Ag}=400 system in .

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6	$P(N_{\mathrm{Ag}},N)$
5	29	28	1	0.03	0.65	0.029
5	133	121	12	0.09	0.61	0.002
5	417	314	103	0.25	0.58	0.03
5	193	150	43	0.22	0.59	0.713
5	114	84	30	0.26	0.65	0.244
5	56	37	19	0.34	0.65	0.047
5	241	197	44	0.18	0.58	0.767
5	206	170	36	0.17	0.58	0.624
5	611	499	112	0.18	0.58	0.46
7.5	1087	894	193	0.18	0.57	0.024
7.5	56	37	19	0.34	0.65	0.047
7.5	664	519	145	0.22	0.58	0.354
7.5	193	150	43	0.22	0.59	0.713
10	1807	1450	357	0.2	0.58	0.713
10	193	150	43	0.22	0.59	0.713
15	1807	1450	357	0.2	0.58	0.713
15	193	150	43	0.22	0.58	0.713
20	1807	1450	357	0.2	0.58	0.713
20	193	150	43	0.22	0.58	0.713
25	1807	1450	357	0.2	0.58	0.713
25	193	150	43	0.22	0.58	0.713
30	2000	1600	400	0.2	0.58	0.713

Table S3: The same as Table S2 for N^*_{Ag}=800 system.

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6	$P(N_{\mathrm{Ag}},N)$
5	57	41	16	0.28	0.65	0.162
5	171	106	65	0.38	0.6	0.857
5	211	128	83	0.39	0.58	0.979
5	547	324	223	0.41	0.58	0.912
5	172	118	54	0.31	0.58	0.051
5	61	32	29	0.48	0.65	0.48
5	781	451	330	0.42	0.58	0.258
7.5	443	266	177	0.4	0.58	0.999
7.5	172	118	54	0.31	0.58	0.051
7.5	604	365	239	0.4	0.58	0.967
7.5	780	450	330	0.42	0.58	0.243
10	604	365	239	0.4	0.58	0.967
10	1396	835	561	0.4	0.58	0.967
15	604	365	239	0.4	0.58	0.967
15	1396	835	561	0.4	0.58	0.967
20	604	365	239	0.4	0.58	0.967
20	1396	835	561	0.4	0.58	0.967
25	604	365	239	0.4	0.58	0.967
25	1396	835	561	0.4	0.58	0.967
30	2000	1200	800	0.4	0.58	0.967

Table S4: The same as Table S2 for N^{*}_{Ag}=1000 system.

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6	$P(N_{\mathrm{Ag}},N)$
5	737	363	374	0.51	0.65	0.878
5	633	320	313	0.49	0.65	0.945
5	204	98	106	0.52	0.65	0.84
5	100	47	53	0.53	0.65	0.827
5	132	67	65	0.49	0.65	0.984
5	194	105	89	0.46	0.58	0.481
7.5	633	320	313	0.49	0.65	0.945
7.5	941	461	480	0.51	0.65	0.696
7.5	426	219	207	0.49	0.65	0.807
10	1363	680	683	0.5	0.65	0.99
10	632	320	312	0.49	0.65	0.929
15	1367	680	687	0.5	0.66	0.945
15	633	320	313	0.49	0.66	0.945
20	2000	1000	1000	0.5	0.66	1
25	2000	1000	1000	0.5	0.66	1
30	2000	1000	1000	0.5	0.66	1

Table S5: The same as Table S2 for N^{*}_{Ag}=1200 system.

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6	$P(N_{\mathrm{Ag}},N)$
5	268	106	162	0.6	0.65	0.987
5	439	156	283	0.64	0.66	0.094
5	381	170	211	0.55	0.65	0.126
5	475	199	276	0.58	0.66	0.629
5	250	107	143	0.57	0.65	0.629
5	187	62	125	0.67	0.66	0.128
7.5	268	106	162	0.6	0.66	0.987
7.5	381	170	211	0.55	0.65	0.126
7.5	439	156	283	0.64	0.65	0.094
7.5	250	107	143	0.57	0.65	0.629
7.5	662	261	401	0.61	0.65	0.934
10	1088	432	656	0.6	0.65	0.958
10	250	107	143	0.57	0.66	0.629
10	652	260	392	0.6	0.65	0.997
15	250	107	143	0.57	0.65	0.629
15	998	375	623	0.62	0.66	0.087
15	752	318	434	0.58	0.65	0.27
20	1997	799	1198	0.6	0.66	1
25	2000	800	1200	0.6	0.66	1
30	2000	800	1200	0.6	0.66	1

Table S6: The same as Table S2 for N^{*}_{Ag}=1600 system.

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6	$P(N_{\mathrm{Ag}},N)$
5	199	20	179	0.9	0.66	0.0004
5	172	47	125	0.73	0.66	0.053
5	643	142	501	0.78	0.65	0.281
5	415	72	343	0.83	0.66	0.307
5	571	119	452	0.79	0.66	0.839
7.5	571	119	452	0.79	0.66	0.839
7.5	415	72	343	0.83	0.65	0.307
7.5	1014	209	805	0.79	0.65	0.786
10	415	72	343	0.83	0.66	0.307
10	568	119	449	0.79	0.66	0.801
10	1014	209	805	0.79	0.66	0.786
15	1207	237	970	0.8	0.65	0.882
15	777	161	616	0.79	0.65	0.814
15	16	2	14	0.88	0.65	0.728
20	2000	400	1600	0.8	0.66	1
25	2000	400	1600	0.8	0.66	1
30	2000	400	1600	0.8	0.66	1

Table S7: The same as Table S1 for pure Au nanoclusters (N^{*}_{Au}=2000 system).

time (ns)	N	N_{Au}	N_{Ag}	x_{Ag}	Q_6
5	441	441	0	0	0.58
5	400	400	0	0	0.58
5	85	85	0	0	0.65
5	18	18	0	0	0.65
5	120	120	0	0	0.66
5	334	334	0	0	0.58
5	127	127	0	0	0.61
5	185	185	0	0	0.58
5	196	196	0	0	0.58
5	90	90	0	0	0.65
7.5	127	127	0	0	0.61
7.5	85	85	0	0	0.65
7.5	189	189	0	0	0.58
7.5	1127	1127	0	0	0.58
7.5	472	472	0	0	0.58
10	559	559	0	0	0.58
10	1127	1127	0	0	0.58
10	85	85	0	0	0.65
10	189	189	0	0	0.58
15	1212	1212	0	0	0.58
15	189	189	0	0	0.59
15	599	599	0	0	0.58
20	1401	1401	0	0	0.58
20	599	599	0	0	0.58
25	2000	2000	0	0	0.57
30	2000	2000	0	0	0.57

Appendix (IV)

Details for chemical reactions occurred during MD simulation:

For N^*_{Ag}=400 system during time interval from 5 to 7.5 ns, the following reactions are occurred:

$$Ag_{112}Au_{449} + Ag_{44}Au_{197} + Ag_{36}Au_{170} + Ag_{1}Au_{28} \rightarrow Ag_{193}Au_{844} \qquad \text{(S36)}$$

$$Ag_{12}Au_{121} + Ag_{103}Au_{314} + Ag_{30}Au_{84} \rightarrow Ag_{145}Au_{519} \qquad \text{(S37)}$$

where $Ag_{193}Au_{844}$ and $Ag_{145}Au_{519}$ nanoclusters are stable at 7.5 ns. Now, going from 7.5 ns to 10 ns, $Ag_{43}Au_{150}$ nanocluster is stabilized and the others join together by the following reaction:

$$Ag_{193}Au_{894} + Ag_{19}Au_{37} + Ag_{145}Au_{519} \rightarrow Ag_{357}Au_{1450} \qquad \text{(S38)}$$

Here, $Ag_{357}Au_{1450}$ and $Ag_{43}Au_{150}$ nanoclusters are formed with the same $P(N_{\mathrm{Ag}},N)$ and they remain stable for a longer time. For N^*_{Ag}=800 system from 5 to 7.5 ns, the following reactions are taken place:

$$Ag_{65}Au_{106} + Ag_{83}Au_{128} + Ag_{29}Au_{32} \rightarrow Ag_{177}Au_{266} \qquad \text{(S39)}$$

$$Ag_{16}Au_{41} + Ag_{223}Au_{324} \rightarrow Ag_{239}Au_{365} \qquad \text{(S40)}$$

where $Ag_{177}Au_{266}$ and $Ag_{239}Au_{365}$ nanoclusters are present in the system at 7.5 ns. From 7.5 to 10 ns the reaction is:

$$Ag_{177}Au_{266} + Ag_{54}Au_{118} + Ag_{330}Au_{450} + Au_{(g)} \rightarrow Ag_{561}Au_{835} \qquad \text{(S41)}$$

Here, $Ag_{561}Au_{835}$ and $Ag_{239}Au_{365}$ nanoclusters are present in the system with the same $P(N_{\mathrm{Ag}},N)$ value and remain stable for a longer time. The reactions for N^*_{Ag}=1000 system from 5 to 7.5 ns are:

$$Ag_{374}Au_{363} + Ag_{106}Au_{98} \rightarrow Ag_{480}Au_{461} \qquad \text{(S42)}$$

$$Ag_{53}Au_{47} + Ag_{65}Au_{67} + Ag_{89}Au_{105} \rightarrow Ag_{207}Au_{219} \qquad \text{(S43)}$$

Also, from 7.5 to 10 ns the reactions are:

$$Ag_{480}Au_{461} + Ag_{207}Au_{219} \rightarrow Ag_{683}Au_{680} + 4Ag_{(g)} \qquad \text{(S44)}$$

$$Ag_{313}Au_{320} \rightarrow Ag_{312}Au_{320} + Ag_{(g)} \qquad \text{(S45)}$$

Then, form 10 to 15 ns the reactions are:

$$Ag_{683}Au_{680} + 4Ag_{(g)} \rightarrow Ag_{687}Au_{320} \qquad \text{(S46)}$$

$$Ag_{312}Au_{320} + Ag_{(g)} \rightarrow Ag_{313}Au_{320} \qquad \text{(S47)}$$

Finally, these nanoclusters aggregate. Therefore, it seems that N^{*}_{Ag}=1000 system is more thermodynamically controlled because from 10 to 20 ns the clusters tried to be stabilized. This is in good agreement with the results of Figure 4. For N^{*}_{Ag}=1200 system the process from 5 to 7.5 ns includes:

$$Ag_{125}Au_{62} + Ag_{276}Au_{199} \rightarrow Ag_{401}Au_{261} \qquad \text{(S48)}$$

The surprising result is seen after 7.5 ns due to the fact that the process is too fast in such a way that from 7.5 to 10 ns some of the information of the system has been lost. Therefore, N^{*}_{Ag}=1200 system is basically probability-controlled. Finally for N^{*}_{Ag}=1600 system from 5 to 7.5 ns the reaction is:

$$Ag_{179}Au_{20} + Ag_{125}Au_{47} + Ag_{501}Au_{142} \rightarrow Ag_{805}Au_{209} \qquad \text{(S49)}$$

Also, for 7.5 to 10 ns the only reaction is:

$$Ag_{452}Au_{119} \rightarrow Ag_{449}Au_{119} + 3Ag_{(g)} \qquad \text{(S50)}$$

Now, the process from 10 to 15 ns is also fast and the information of 10 ns step has been lost. Please remember that a considerable fluctuation of $\langle x_{\mathrm{Ag}} \rangle$ was seen from 10 to 15 ns for this system in Figure 4. Therefore, the clustering process for N^{*}_{Ag}=1600 system is considerably probability-controlled. As an overall result, increase of Ag content leads to more probability-controlled clustering process.