Bifurcation phenomenon in molecular dynamics model of coalescence/sintering on the nanoscale

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Abstract. Using the isothermal molecular dynamics, coalescence/sintering of Au nanoparticles (NPs) was simulated. We have found that the solid NP sintering scenario is switched to the coalescence scenario not at the NP melting temperature $T_m$ exactly but at a lower temperature $T_0 \approx 0.9T_m$ interpreted as the critical temperature corresponding to a coalescence/sintering bifurcation phenomenon: in the temperature range from $T_0 - 2 K$ to $T_0 + 2 K$ the resulting (daughter) NPs of the same size can have either liquid-like or crystalline structure after coalescence/sintering at the same fixed temperature.

1. Introduction
The term ‘coalescence’ is usually referred to merging of two droplets, i.e. formation of a larger daughter one whereas the term ‘sintering’ relates to agglomeration of solid particles without their complete merging. Since 90-s a great attention has been paid to coalescence and sintering processes on the nanoscale. On the one hand, sintering of nanoparticles (NPs) is used in powder metallurgy to produce some new nanostructured materials, in additive manufacturing and other directions of nanotechnology. On the other hand, the complete merging of NPs, i.e. coalescence, as well as the grain coarsening can be undesirable when a nanostructured material is manufactured with some controlled grain size or when metal powders are used as catalysts. Really, most of catalysts are used in high-temperature conditions when without any protective additives fine NPs tend to agglomerate. An analogous situation may occur in flexible cooling devices on the basis of metal NPs.

No doubt that regularities and mechanisms of the coalescence and sintering processes should depend on temperature and, in particular, on the NP melting temperature $T_m$ which, in turn, depends on the NP size, i.e. its radius $r_0$ or the number of atoms $N_0$ the NP consists of. So, in most papers, devoted to molecular dynamics (MD) simulation of the coalescence and sintering processes, the size dependence of $T_m$ is also often evaluated [1-6]. However, the relationship between the NP melting temperature and coalescence/sintering of NPs of the chosen size does not seem to be quite definitely formulated and discussed by other authors. Moreover, for NPs the terms coalescence and sintering are not strictly differentiated. In [7] it is noted that coalescence of metal NPs closely relates to the Tammann temperature $T_T = 0.5T_m^{(\infty)}$ where $T_m^{(\infty)}$ represents the bulk melting point. According to [7], when $T_T$ is reached, the atomic thermal motion results in the interparticle diffusion and, therefore, in the NP coalescence. However, the NP melting temperature $T_m < T_m^{(\infty)}$ seems to be a more adequate criterion of the coalescence/sintering scenario transformation as $T \geq T_m$ corresponds to the temperature region where NPs do not keep their crystalline structure, i.e. behave themselves as nanosized droplets. So, in our previous papers [8-10] we proposed to interprete the case when $T \geq T_m$
as the nanodroplet coalescence and the case when \( T < T_m \) as the solid NP sintering. Experimental results [11-13] and our MD results demonstrate different regularities and mechanisms of coalescence and sintering on the nanoscale. Coalescence may be interpreted as a hydrodynamic phenomenon on the nanoscale whereas sintering of two solid NPs reduced to the single or two-grain nanocrystal formation with possible following recrystallization of the last structure i.e. its transformation into a single crystal.

However, in our MD experiments [8-10] chosen temperatures were higher than \( T_m \) by at least 50 K or lower than \( T_m \) by at least 50 K, i.e. the region from \( T_m - 50 \) K to \( T_m + 50 \) K was not explored in detail. So, it remains unclear whether just \( T = T_m \) may be interpreted as a critical (characteristic) temperature of switching from scenario of the solid NP sintering to that of the liquid nanodroplet coalescence. The present paper is devoted to MD investigation of the coalescence/sintering regularities and mechanisms just in the vicinity of the NP melting temperature \( T_m \). We have found that the sintering scenario is switched to the coalescence one not at \( T = T_m \) exactly by at a lower characteristic (critical) temperature \( T_0 \approx 0.97T_m \). In turn, the sintering – coalescence transition at \( T = T_0 \) may be interpreted as a bifurcation phenomenon.

2. Approaches to atomistic simulation and processing simulation results
The isothermal MD simulations were performed by using open and well-verified program LAMMPS. This program makes it possible to involve parallel calculations on graphical processors that significantly extends both the size range of the simulated objects and the evolution time reproduced in MD experiments. The interatomic interactions were described by employing the embedded atom method (EAM) with parametrization recommended for Au in [14]. The size dependence of the NP melting temperature \( T_m \), obtained in our previous MD experiments [9] and compared to the available experimental data, will be used to interpret our new MD results on coalescence/sintering of Au NPs. At the same time, agreement between experimental and MD results for \( T_m \) confirms adequacy of parametrization [14] to Au NPs in a wide enough size range. To simulate the coalescence/sintering process, a spherical fragment of the bulk Au lattice was relaxed (annealed), duplicated and then put into a point contact with its copy providing an initial gap of order of the atomic size between NPs.

In the present study we have found and analyzed kinetic dependences for two phenomenological parameters of the coalescence/sintering process. First of them is the reduced neck radius \( x^* = x/r_0 \) where \( x \) is the neck radius (see figure 1b) and \( r_0 \) is the initial NP radius. The second parameter is the shrinkage coefficient \( \xi = 1 - L/L_0 \), where \( L \) is the distance between the centers of mass of the coalescing/sintering NPs and \( L_0 \) is the initial value of \( L (L_0 \approx 2r_0) \). Evaluations of these parameters by other authors and previous investigations of their kinetic behavior were discussed in our papers [8-10]. To characterize the structure of coalescing/sintering NPs and of the resulting (daughter) NP, the degree of crystallinity \( \eta \) and the radial distribution function \( g(r) \) were calculated by employing the Ovito program. The \( x^* \) and \( \xi \) parameters were determined by employing our own program developed for the MD data processing.

3. Results and discussion
In order to determine the characteristic temperature \( T_0 \) for Au NPs, consisting each of 30000 atoms, we have performed three series of MD experiments. First of them corresponds to MD simulations of coalescence/sintering in the temperature range from 1050 K to 1100 K with the temperature increment \( \Delta T = 50 \) K. In other words, these MD experiments were performed at \( T = 1000 \), 1050 and 1100 K. The chosen temperature range contains the melting temperature \( T_m = 1090 \) K determined earlier just for NPs of the chosen size [9]. The second series of MD experiments corresponds to \( \Delta T = 10 \) K and the third to \( \Delta T = 2 \) K.

3.1. The first series of MD experiments (\( \Delta T = 50 \) K)
In figure 1a a snapshot is presented of a daughter nanodroplet formed after the coalescence time of 1.1 ns. One can see that for this very short time interval the daughter droplet acquires almost perfect
spherical shape. Here and in following figures we shadow differently atoms belonging to different NPs (light and dark colors) to better understand the structural rearrangements in the course of the coalescence and sintering processes. For the same time of 1.1 ns solid NPs (figure 1b) form a dumbbell bicrystal, i. e. a two-grain structure with a grain boundary between the grains in the neck region. The neck formation is typical for the droplet coalescence as well but at the initial very fast stage of the process. Contrary to the nanodroplet coalescence, configuration shown in figure 1b remains practically unchanged up to the MD evolution time of 100 ns.

![Figure 1](image1.png)

**Figure 1.** Snapshots of a MD daughter Au nanodroplet configuration consisting of \( N = 2N_0 = 60000 \) atoms (a) and of a daughter solid NP (b). Snapshot (a) corresponds to \( T = 1100 \) K, snapshot (b) to \( T = 1000 \) K. The melting temperature \( T_m \) of Au NPs, consisting of 30000 atoms is 1090 K [9].

According to figure 2, at \( T = 1100 \) K the reduced neck radius \( x^* \) very quickly (for about 0.1 ns) reaches its asymptotic value of 1.2 corresponding to the spherical shape of the daughter droplet of the twice greater volume in comparison of that of each of the initial droplets.

![Figure 2](image2.png)

**Figure 2.** Kinetic dependences for the reduced neck radius \( x^* \) corresponding to coalescence/sintering of Au NPs, consisting each of 30000 atoms. Temperatures are given in the figure.

### 3.2. The second series of MD experiments (\( \Delta T = 10 \) K)

Figure 3 demonstrates kinetic dependences of the \( x^* \) and \( \xi \) parameters corresponding to for the second series of MD experiments. The main conclusion drawn from these dependences is that they sharply change their behavior not at \( T = T_m \) but at a lower temperature of about 1050 K. Really, for higher temperatures parameter \( x^* \) reaches the asymptotic value of 1.2 corresponding to the spherical daughter NP shape.
3.3. The third series of MD experiments (ΔT = 2 K)
The results obtained involving the temperature increment ΔT = 2 K seem to be most interesting: behavior of the $x^*(t)$ and $\xi(t)$ dependences becomes irregular. For example, usually the shrinkage coefficient $\xi(t)$ grows under growing temperature. However, figure 4b demonstrates an alternative behavior of the $\xi(t)$ dependence when a higher value of this parameter (curve 1) corresponds to a lower temperature (1052 K) in comparison with dots ▲ corresponding to a higher temperature of 1054 K. To elucidate the nature of such an anomalous behavior, we investigated kinetic dependences if the degree of crystallinity $\eta$ using for this purpose the Ovito program.

According to figure 5, for the same temperature of 1054 K and the same NP size ($N_0 =$30000 atoms) coalescence/sintering of NPs may follow to two different scenarios. Really, according to
Figure 5, the first of these scenarios corresponds to $\eta \to 0$ i.e. $(1 - \eta) \to 1$ for $t > 0.7$ ns. The second scenarios (Figure 5b) corresponds to the asymptotic values of about 0.2 and 0.7, respectively.

**Figure 5.** Two different scenarios (a and b) of the kinetic behavior of the degree of crystallinity $\eta$ at 1054 K. Curve 1 corresponds to the term of the fcc local structure, curve 2 to the term of the bcc structure. Dashed lines correspond to $(1 - \eta)$ where $\eta = \eta_{fcc} + \eta_{bcc}$.

According to figure 6, for the first scenario the radial distribution function $g(r)$ has the shape typical for the liquid state.

**Figure 6.** Radial distribution function for the case corresponding to Figure 5a ($t \geq 0.7$ ns).

So, in some cases interaction between two solid NPs results in a melted daughter NP, i.e. the process under discussion looks like the droplet coalescence. However, for the same temperature and the same NP size the daughter NP can inherit, to a greater or lesser extent, the crystalline structure of the initial solid NPs. So, it may be assumed that $T_0 = (1055 \pm 1)$ K for Au NPs of the chosen size, i.e. $T_0 \approx 0.97 T_m$.

**4. Conclusion**
The above MD results confirm our hypothesis that the solid NP sintering scenario is transformed into the coalescence one corresponding to the complete merging of NPs and formation of a daughter nanodroplet occurs not at $T = T_m(N_0)$ exactly but at the characteristic (critical) temperature $T_0 <$
$T_m(N_0)$. For Au NPs, containing each $N_0 = 30000$ atoms, $T_0 = 1055$ K whereas $T_m(30000) = 1091$ K, i.e. the reduced critical temperature $T_0^* = T_0/T_m(N_0)$ is equal to 0.97. We have found that $T = T_0$ corresponds to a bifurcation point when coalescence/sintering can result in formation of both a dumbbell two-grain nanocrystal and a daughter spherical nanodroplet. The probabilities of these scenarios have not been exactly determined yet, but it seems that they are of order of 50%. As $T_m(2N_0) > T_m(N_0) > T_0$, the daughter nanodroplet should finally transfer into a nanocrystal. However, the characteristic time of such a crystallization should be long enough as $T_0 = 1055$ K is lower than $T_m(2N_0) = 1110$ K by 55 K only.

The above results have been obtained for coalescing/sintering of NPs consisting each of 30000 atoms. In the present paper we have not studied in detail the effect of size on the coalescence/sintering in the vicinity of the melting point. However, in general the same regularities were observed in the case when $N_0 = 10000$ atoms ($N = 20000$ atoms). In particular, we have found that the bifurcation point corresponds to $T_0 = 1047$ K $< T_m(10000) = 1076$ K. It is also noteworthy that the value $T_0^* = 0.97$ of the reduced critical temperature is not changed when $N_0$ becomes three times lower in comparison with $N_0 = 30000$.

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**References**

[1] Lewis J L, Jensen P and Barrat J-L 1997 *Phys. Rev. B* 56 2248

[2] Pan H, Ko S H and Grigoropoulos C P 2008 *Appl. Phys. A* 90 247

[3] Goudeli E and Prarsinis S E 2016 *Adv Mater: Thermod Molec-Scale Phen* 62 589

[4] Zachariah M R and Carrier M J 1999 *J. Aerosol Sci.* 30 1139

[5] Arcidiacono S, Bieri N R, Poulakakos D and Grigoropoulos C P 2004 *Int. J Multiphas Flow* 30 979

[6] Grammatikopoulos P, Sowwan M and Kioseoglou J 2019 *Adv Theory Simul* 2 (6) 1900013

[7] Sun J, Ma D, Zhang H, Liu X, Han X, Bao X, Weinberg G, Pfander N and Su D 2006 *J. Am. Chem. Soc.* 128 15756

[8] Samsonov V M, Talyzin I V, Vasilyev S A and Alymov M I 2020 *Colloid. J* 82 573

[9] Samsonov V M, Alymov M I, Talyzin I V and Vasilyev S A 2019 *Journal of Physics: Conf Series* 1352 012044

[10] Samsonov V M, Talyzin I V, Vasilyev S A and Alymov M I 2019 *Doklady Physics* 64 11

[11] Surrey A, Pohl D, Schultz L and Rellinghaus B 2012 *Nanoletters* 12 6071

[12] Yuk J M, Jeong M, Kim S Y, Seo H K, Kim J and Lee J Y 2013 *Chem Commun* 49 11479

[13] Alymov M I, Timofeev A A and Gnedovets A G 2013 *Nanotechnologies in Russia* 8 727

[14] Adams J B, Foiles S M and Wolfer W G 1989 *J. Mater. Res.* 4 102