Size dependence of the melting temperature and mechanisms of the coalescence/sintering on the nanoscale

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Abstract. We have proposed to use the nanoparticle (NP) melting temperature \( T_m \) to distinguish between the coalescence and sintering processes on the nanoscale. According to our molecular dynamics results, obtained on Au NPs, the coalescence of nanoproplets may be interpreted as a hydrodynamic phenomenon on the nanoscale, and the characteristic coalescence time \( \tau \) is a linear function of the initial particle radius \( r_0 \). In turn, the sintering of two crystalline NPs \( (T < T_m) \) relates to a grain boundary formation as a result of an alignment of the crystallographic orientations of the sintering NPs, and in this case a dependence of \( \tau \) on \( r_0 \) has not been revealed.

1. Introduction
Coalescence is usually defined as a process during which two or more droplets merge, i.e. form a larger single daughter droplet. In turn, until the 1930s sintering was interpreted rather as a technological process of producing a sintered material from a powder than as a physical phenomenon. Obviously F. Sauervald [1] for the first time considered sintering from a scientific point of view as a contact formation between two or several particles. The coalescence/sintering on the macroscopic scale was intensively enough studied experimentally and theoretically in the former Soviet Union by J.I. Frenkel [2] Ya. E. Geguzin, B. Ya. Pines, M. Yu. Balshin et al. However, most of their results were published in Russian and, respectively, those papers and monographs are hardly available for scientific community. A strict differentiation between the coalescence and sintering processes seems to be absent, especially on the nanoscale. For example, phrase “sintering or coalescence” figures even in the title of paper [3] devoted to molecular dynamics (MD) of sintering of Au nanoparticles (NPs). The term “coalescence” is attributed to solid particles as well when the complete, to a greater or lesser extent, merging takes place, i.e. a globular compound particle forms. Nevertheless, the term “coalescence” is usually attributed to liquid droplets whereas the term “sintering” to solid particles. However, interpretation of NPs in terms of the solid (crystalline) and liquid states is disputable and worth to be separately discussed.

Till late 90s experimental investigations of scientific aspects of coalescence and sintering of NPs were practically impossible in view of many principal difficulties. For this reason computer (MD) experiment only could be used to elucidate laws and mechanisms of the coalescence and sintering phenomena. Presumably, the first serious MD study of the coalescence phenomenon was performed by L. Lewis et al. [4] on Au NPs. Two years later an interesting MD investigation of the gas-phase Si NP sintering was performed in [5]. However, metal and, especially, Au NPs seem to have been the main pattern when studying coalescence/sintering mechanisms in MD experiments [3, 6, 7].
Experimental studies of the NP coalescence/sintering have been mainly performed by using the transmission electron microscopy (TEM) [8, 9]. No doubt, that laboratory experiments in this field of science have some advantages and disadvantages in comparison with MD investigations. One of such advantages is that some processes preceding the coalescence/sintering itself and occurring on the time scales of order of 1 s, 1 min or ever 1 h in principle cannot be studied in MD experiments. We mean processes of the NP migration and coagulation before establishing some contacts between them. Besides, MD cannot reproduce late stages of the solid NP sintering, including the grain boundary migration taking, according to [9], of order of 10 s for Au NPs with a diameter of 3-7 nm. However, MD makes it possible to observe the entire NP coalescence process and early states of sintering at the atomic size level and to study dynamics of the process in question.

Beginning with Lewis [3], when studying coalescence/sintering of NPs in MD experiments, the size dependence of the NP melting temperature $T_m$ has been also studied by most of authors [6, 7, 10]. First of all the $T_m(r_0)$ dependences ($r_0$ is the initial particle radius) were found to verify the chosen parametrizations of the involved many-body interatomic interaction potentials e.g. potentials corresponding to the embedded atom method (EAM) usually employed for metals. At the same time, it has been suggested that laws and mechanisms of the coalescence/sintering process should depend on the state of NPs proposed to be either solid (crystalline) or liquid. However, up to the present time the relationship between $T_m$ and the coalescence/sintering mechanisms seems not to be studied in detail. Therefore in the present paper a concept is put forward and justified that the cases when $T > T_m$ and $T < T_m$ should be distinguished. In other words, we propose to refer the case $T > T_m$ to as the nanodroplet coalescence and the case $T < T_m$ to as the NP sintering. In what follows this concept will be justified by using our MD results obtained on Au NPs.

2. Method of atomistic simulation

We have used the well-known open program LAMMPS for our MD simulations of separate NPs and their pairs employing the embedded atom method (EAM) to reproduce the interatomic interactions in metal systems. For Au NPs we have employed a parametrizations recommended and justified in [11]. The temperature $T$ was controlled by employing the Nose-Hover thermostat. No doubt that the above EAM potential was verified by X. Zhou at al themselves. However, before simulating separate Au NPs and their pairs, the potential in question was additionally verified. First of all, the size dependence was investigated of the Au particle melting temperature $T_m$, that was fixed by observing a jump in the temperature dependence of the specific (per atom) particle cohesive energy $u$ ($-u > 0$ corresponds to the specific binding energy of NP). To determine $T_m$, a spherical NP configuration with the initial fcc structure, corresponding to the same bulk metal, was relaxed at a constant temperature $T$ for about 100 ns. The value of temperature $T$ was step-wise increased, and at a temperature $T = T_m$, interpreted as the particle melting temperature, an upward jump of $u$ was observed. A more detailed comments and discussions on determination of the NP melting temperature, are presented in our former papers [12, 13]. To simulate the coalescence/sintering process a relaxed NP was duplicated and put in a point contact with its copy.

3. Size dependence of the melting temperature of Au NPs

The dependences of $T_m$ on $r_0^{-1}$, obtained in our MD experiments on Au NPs, is presented in figure 1. The $r_0^{-1}$ quantity is chosen as an independent variable as the linear dependence of $T_m$ on $r_0^{-1}$ is predicted by the well-known Thomson formula, and such a dependence has been found, at least as a first approximation, in most of the available experimental studies, including experiments on Au NPs [14–16]. Our MD results, presented in figure 1, do also demonstrate the linear dependence of $T_m$ on $r_0^{-1}$ that makes it possible to evaluate the limiting value $T_m^{(\infty)}$ of $T_m$ corresponding to the linear extrapolation of $T_m$ to $r_0^{-1} \to 0$, i.e. to $r_0 \to \infty$. The value of $T_m^{(\infty)} = 1188$ K may be interpreted as an evaluation of the bulk melting point $T_0$ of Au. Its experimental value 1336 K [17] satisfactorily agrees with $T_m^{(\infty)}$. At the
same time, our MD results for Au NPs, i.e. for finite values of \( r_0 \), better agree with the available experimental \( T_m(r_0^{-1}) \) dependences, especially for small enough values of \( r_0 \) of order of 1 nm.

Figure 1. Size dependences of the melting temperature of Au NPs. The value of \( T_m(\infty) \), obtained by means of the linear extrapolation to \( r_0^{-1} \to 0 \), is equal to 1188 K. Dots ■ correspond to our MD results, open symbols present experimental data taken from [14] (□), [15] (○) and [16] (Δ).

4. Coalescence of Au nanodroplets \((T > T_m)\)

As it was noted in [4, 6] and other papers on the metal NP coalescence, it was traditionally assumed that the coalescence on the nanoscale proceeds in two stages: (i) the first rapid one corresponds to maximizing the contact surface; (ii) a much slower spherification stage. Then, under influence of the capillary induced surface diffusion (CICD) concept developed by Nichols and Mullins [18], most scientists believed that just the surface diffusion on the neck surface between two coalescing NPs should be treated as the basic mechanism of their coalescing. According to [18], the current coalescence time \( t \), relates to the neck radius \( x(t) \) and the initial particle radius \( r_0 \):

\[
t = \frac{(x/r_0)^4 r_0^{-4} RT}{C W D \sigma \Omega},
\]

(1)

where \( R \) is the molar gas constant, \( \Omega \) is the molar volume, \( D \) is the surface diffusion coefficient, \( W \) is a width of a diffusional zone, \( \sigma \) is the liquid-vapor or solid-vapor surface tension and \( C \) is a numerical constant. Assuming that \( x/r_0 = 1.26 \) (as it follows under assumption that the total volume of the system does not change under coalescence) or that \( x/r_0 = 0.84 \) (as it was recommended by Nichols and Mullins [18]), one can obtain the next power dependence between the characteristic coalescence time \( \tau \) and the initial particle radius.

\[
\tau \sim r_0^{-4}.
\]

(2)

Besides, according to (1), we find that

\[
\log_{10}(x/r_0) = (1/6) \log_{10} t + \text{const}.
\]

(3)

It is also noteworthy that according to [19], Eqs. (1) and (2) should be also valid for the grain boundary diffusion if \( D \) is attributed to the grain boundary.
Figure 2. Cross-sections of some successive configurations of the system of two Au NPs consisting each of $N_0 = 30000$ atoms and coalescing at $T = 1500$ K. Atoms primarily belonging to different NPs are colored differently (gray and dark).

In our MD experiments on Au NPs we have really observed the above rapid neck formation and slow spherification stages of coalescence (Figure 2). However, we have found that the law (2) corresponding to both surface and grain boundary diffusion models is not fulfilled, and our conclusion agrees with MD results [4]. At the same time, in [5] it is stated that MD experiments confirm the above diffusional mechanisms of coalescence of Au NPs. However, in MD experiments [20] on Si nanodroplets the characteristic time of coalescence $\tau$ followed to the linear dependence on the initial particle radius $r_0$:

$$\tau = K r_0,$$

where $K$ is a proportionality coefficient measured in s/m. Therefore, the authors of [20] made a conclusion that their results agree with Frenkel’s theory [2] predicting the linear dependence

$$\tau = \frac{8}{3} \eta \sigma r_0,$$

where $\eta$ is the shear viscosity coefficient.

So, the situation with the $\tau(r_0)$ dependence and the coalescence mechanisms on the nanoscale seems to be confused enough. Really, though Frenkel’s theory deals with the viscosity coefficient $\eta$ even the title of his paper [2] “Viscous flow of crystalline solids under the action of surface tension” demonstrates that the author believed that his theory should not be adequate to liquid droplets but to solid particles. In fact, this theory is based on a concept of diffusion of vacancies (vacancy pores) in a crystal. Besides Frenkel’s theory is entirely macroscopic and, therefore, its applicability to NPs is more than disputable.

Nevertheless in our MD experiments on Au NPs we have also observed a linear dependence of $\tau$ on $r_0$ (Figure 3). However, the value of the proportionality coefficient $K_{MD} = 0.05$ ns/nm found in our MD experiments turns out to be about 3 times higher than the value $K_{Fr} = 0.013$ ns/nm corresponding to Frenkel’s formula (5). Both evaluations were made for $T = 1500$ K. The values of $\sigma_m = 1.170$ N/m and $d\sigma/dT$ corresponding to the Au melting point were taken from review [22] to evaluate $\sigma(T) \approx \sigma_m(T_0) + (T - T_0)(d\sigma/dT)$. The value of the viscosity coefficient $\eta = 5.6 \cdot 10^{-3}$ Nm$^{-2}$s was taken from [23].

Figure 3. Our MD size dependence of the characteristic coalescing time $\tau$ for Au NPs ($T = 1500$ K).
So, a conclusion can be made that the linear dependence (5) observed in our MD experiments on Au nanodroplets and in MD experiments [5] on Si ones should not be interpreted in terms of Frenkel’s theory [2]. However, coalescence of nanodroplets really is rather a hydrodynamic phenomenon on the nanoscale, i.e. cannot be reduced to the surface or grain boundary diffusion mechanism.

Therefore, the \( \tau(r_0) \) dependence is worth to be newly investigated theoretically in the future not relating it to processes typical for the solid state of matter.

5. Sintering of crystalline Au NPs (\( T < T_m \))

The behavior of solid (crystalline) Au NPs in the course of their approaching each other with an initial misalignment angle (a difference in crystallographic orientations is meant) seems to be quite different in comparison with the liquid state coalescence. Really, NPs a little rotate to align their orientations. As a result a contact area, interpreted as a grain boundary is formed which connects two initial nanocrystals which, in turn, may be interpreted as some nanograins (figure 4). It is also noteworthy that our MD snapshots, including one presented in figure 4, are very similar to some TEM images of Au NPs on graphene [9] and on an amorphous carbon grid [24] for corresponding early stages of sintering. Graphene and the carbon grids may be interpreted as some low-energy supports, and their effect on mechanisms and kinetics of the NP sintering should not be noticeable.

After establishing a contact between two NPs (figure 4) and forming two nanograins with some different crystallographic orientations, the daughter (sintered) NP was quite stable in our MD experiments, and the characteristic sintering time \( \tau \) was of order of 0.05 ns. We have not revealed a correlation between \( \tau \) and the initial particle radius \( r_0 \). It is also noteworthy that for solid Au NPs we have observed surface diffusion of Au atoms to the contact area. However, the effect of the surface self-diffusion induced by the negative curvature of the compound NP neck surface at the grain boundary seems to be very small.

Of course, in our MD experiments we could not observe the grain boundary migration resulting, in accordance with experiment [9], in a single nanocrystal formation as the characteristic time of the migration phenomenon is of order of 10 s.

![Figure 4. Comparison of a central cross-section of a MD daughter Au NP configuration (a) with some available experimental TEM images (b, c). The MD configuration was obtained by sintering Au NPs consisting each of 3000 atoms (\( T = 700 \) K). TEM snapshot b was permitted us to be presented in our paper by Dr. J.Y. Lee and TEM snapshot c by Dr. B. Rellinghaus.](image)
6. Conclusion
So, the results of our MD experiments and their comparison with the available theoretical model and some experimental data have confirmed in general the adequacy of our initial assumption that the NP melting temperature found with respect to its size dependence really makes it possible to adequately distinguish between the coalescence ($T > T_m$) and sintering ($T < T_m$) processes. According to the above results, the coalescence mechanism relates rather to some hydrodynamic flows inside the daughter droplet than to the surface or grain boundary diffusion. The NP sintering ($T < T_m$) demonstrates some surface diffusion effect. However, first of all the NP sintering reduces to establishing a contact between two nanocrystals by means of an alignment of their crystallographic orientations and forming a daughter nanosized polycrystal consisting of two grains and a grain boundary between them.

It is also of interest that in our paper [25] the CISD mechanism of the solid state wetting phenomenon was confirmed on the nanoscale by both MD simulation results and some theoretical considerations. The solid state wetting corresponds to a limiting case of sintering when NP is put in contact with a flat solid surface. The last can be interpreted as the surface of a particle of the infinite radius.

Presumably, the adequacy of the CISD mechanism for the solid state wetting and its inadequacy for solid NP sintering may be explained as follows. The solid state wetting on the nanoscale [25] and the microscale [26] was observed in a vicinity of the particle melting temperature ($|T_m - T| \approx 30$ K). In the present paper coalescence has been studied for temperatures by 100 K and more higher than $T_m$ and sintering for temperatures by 100 K and more lower to strictly distinguish between mechanisms of these two processes. The case when, $T \approx T_m$ was beyond the frames of our paper.

Acknowledgements
The authors are grateful to Dr. J. Y. Lee and Dr. B. Rellinghaus for permissions to compare their TEM images with our MD configuration of sintering Au NPs.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation in the framework of the State Program in the Field of the Research Activity (no. 3.5506.2017/BP and no. 2019-0126) and in the framework of governmental program for ISMAN (topic no. 45.5).

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