Nanoparticle Coalescence

Computational Modeling of Nanoparticle Coalescence

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The coalescence of nanoclusters fabricated in the gas phase is a fundamental growth mechanism determining cluster shapes, sizes, compositions, and structures, with resultant effects on practically all of their physical and chemical properties. Furthermore, coalescence can affect properties of larger structures that consist of nanoparticles as their elementary building blocks, such as the fractal dimension of cluster aggregates and the porosity and conductance of thin films. Therefore, it comes as no surprise that a great body of research, both experimental and theoretical, has focused on nanoparticle coalescence over the course of the past few decades. This review attempts to summarize the most important recent results from computational studies on nanoparticle coalescence and draw parallels between theoretical and experimental findings. The approach used here aspires to explain nanoparticle coalescence within the framework of a single intuitive narrative by integrating previous results obtained using various methods by the authors and others. Simultaneously, it is discussed where understanding and controlling (i.e., enhancing or inhibiting) nanoparticle coalescence can have great technological interest.

1. Introduction

1.1. Invitation to a Game of Nano-Billiards...

Before we embark on our discussion on the computational modeling of nanoparticle coalescence, let us deviate slightly for a short while and start with a rather liberal thought experiment: supposing it was practically possible, what would a game of nano-billiards be like? Would it make any difference from the regular, macroscopic-scale game we have experience in, if the balls were, for instance, 1 nm in diameter? And, if yes, in what ways?

First, let us imagine a player shooting to break the object nanoball rack apart. He would soon find out, however, that this is hardly possible, as the cue nanoball would stick to the blue apex ball (i.e., the one closest to it during the initial setup), leaving the rest totally unaffected. In fact, they, too, would have already been stuck to each other since being placed in the rack. In a second attempt the player would hit much harder with his cue stick, hoping to be more successful in breaking. Instead, much to his surprise, he would witness the cue ball wrinkle, heat up, soften, and even melt. To make things worse, the blue ball would seem to have disappeared; in fact, so would the cue ball. In their place would now exist a new, larger ball; but this one would be red!

Of course, one should take this hypothetical scenario with a grain of salt. Its purpose is merely to demonstrate how dramatically different from the macroscopic matter of our everyday experience nanomatter may be. Unlike regular billiards balls, nanoballs have a major fraction of their atoms at the surface (commonly referred to as a very high surface-volume ratio). These atoms possess a significant amount of unsaturated dangling bonds, which, upon touching each other, can bind the balls together. Especially if assisted by additional energy (such as, e.g., by the hard strike on the cue, or high temperature), the balls may fuse together completely. The grave effect this can have on their physical properties is exemplified by the color change, as it is a well-established fact that nanoparticle color can be modulated by their size due to surface plasmon resonance effects.[1]

1.2. The Importance of Nanoparticle Coalescence in Nanotechnology

We hope that by now it is clear to the reader that all these effects are directly related to the phenomenon of coalescence, formally defined as the “formation of homogeneous particles through the collision of smaller particles and subsequent merging or mixing of constituent material.”[2] This fundamental process is among the most straightforward examples of differentiation between bulk and nano matter, and, as such, its understanding is vital for explaining numerous phenomena in the nano-regime; hence the great number of studies, both theoretical and experimental, focusing on it.[3-6]

From a thermodynamics point of view, when two or more nanoparticles collide, they should eventually coalesce fully regardless of the collision energy, driven by the requirement for...
potential energy minimization. However, thermodynamics does not specify the kinetics of this process.[7] Various experiments have shown that the degree of coalescence between interacting nanoparticles can vary to great extent, from fully fused spherical nanoparticles to dumbbells of practically tangential nanoclusters, as nanostructures fabricated by gas-phase synthesis are mostly metastable.[8,9] As Richard Feynman famously put it, “equilibrium occurs when all the fast things have happened but the slow things have not”,[10] and gas-phase synthesis is quite well-known to comprise very fast, out-of-equilibrium processes.[11]

The challenge, from a technological point of view, is to take advantage of this metastability and design nanostructures with bespoke properties for targeted applications. In various cases, when using nanoparticles as building blocks for thin films it is to our interest to regard them as “superatoms” whose individual properties should be maintained.[11] a common example of such application is in gas sensing, where sensitivity and response time depends on the small size and uniformity of individual clusters.[12,13] In other cases, on the other hand, nanoparticle coalescence is welcome, as it enhances functionality such as mechanical stability[13] or electrical conductivity.[14] In fact, there are cases where coalescence can be either advantageous or detrimental depending on its degree or on specific conditions. For instance, whereas full fusion of small nanoclusters can seriously degrade the performance of a nanoparticulated catalyst,[15] partial coalescence can also be beneficial,[16–18] providing additional active sites for catalysis (also known as 3-phase points) via necking.[19]

1.3. Nomenclature

In this review, we will be using the term cluster (or nanocluster) and particle (or nanoparticle) rather loosely. However, the term cluster will always imply smaller size than particle; therefore, two clusters may coalesce to produce a nanoparticle, but the opposite convention will never be used. Also, by coagulation (or collision) we will describe the initial translational motion of the clusters leading to their contact, regardless of kinetic energy value. Coalescence (or sintering) will always imply hard aggregation of clusters (i.e., the formation of chemical bonds between them), whereas by agglomeration we will refer to soft aggregation of clusters (e.g., by weak bonding such as van der Waals forces, or simple physical entanglement). Fusion will always imply full coalescence.[2,22]

2. Methodologies on Nanoparticle Coalescence

2.1. Phenomenological Methods for the Study of Nanoparticle Coalescence

Modeling of the coalescence process typically utilizes some phenomenological approach. Initially, the models were directly based on continuum schemes, where nanoparticle properties were extrapolated from bulk spheres.[23] The sintering itself was also considered as a thermally activated, capillary driven (i.e., reducing surface-energy), continuous process, which started with the formation of a neck connecting the sintering clusters.[24] In order to dissect the phenomenon into elementary mechanisms, a distinction was deemed expedient between crystalline and amorphous
clusters. For the former, coalescence proceeded by atomic surface and grain boundary diffusion;\cite{25,26} the driving force for this diffusion was the stress gradient between the center and the surface of the neck, due to its curvature.\cite{27} For the latter, coalescence was facilitated by viscous flow of material from each cluster toward the neck binding them.\cite{21} In the so-called tangent-sphere model, atoms diffused from high-curvature surfaces (where they were bonded with only a few atoms) toward lower-curvature surfaces (where they were bonded with many more atoms) in order to increase their coordination number and thus minimized the overall potential energy of the system.\cite{25,28,29} It would be interesting to note that the same approach was also used for the fabrication of amorphous thin films by island growth via regular atomic vapor deposition.\cite{30,31} In either case, practically constant rates of coalescence were predicted throughout the whole process, once more indicating the continuous character of nanocluster coalescence.

However, treating clusters of nanoscale dimensions in a manner similar to bulk spheres has its obvious limitations. For example, the smaller a crystalline cluster’s diameter, the more its shape deviates from that of a perfect sphere. Clearly, for nonspherical clusters the uniform curvature argument does not hold true as a stimulus for atomic diffusion. For flat faceted clusters no such tendency for diffusion should be present in the first place, but, even if atoms did diffuse, edges between facets would create natural barriers for this diffusion;\cite{31} additional anisotropy would be introduced by numerous steps that typically form along these edges.\cite{32,33} Further, the implicit assumption of isotropic surfaces in the continuous phenomenological models would also prove wrong, as faceted clusters might be terminated by different surfaces with big differences in their surface diffusion coefficients.\cite{34–36} Finally, utilizing values obtained experimentally from bulk materials for properties at the nanoscale might incur problems related to the measurement methodologies, as these values were usually apparent values that were determined by numerous defects often present in bulk structures.\cite{37}

With the advancement of characterization techniques which enabled the experimental observation of nanoparticle coalescence, it became evident that the constant rates that continuum modeling predicted for the sintering process was also a very rough approximation. For example, in situ high-resolution transmission electron microscopy (HR-TEM) observations of Co nanoparticles sintering during annealing revealed a three-stage process, where very fast preliminary coalescence was followed by a much slower stage and a subsequent very slow saturation period.\cite{18} It soon became clear that another approach with fewer implicit assumptions and higher resolution was necessary to model an inherently atomistic process such as that of nanoparticle coalescence; enter the atomistic simulations.

2.2. Atomistic Simulations of Nanoparticle Coalescence

2.2.1. Initial Comments on Atomistic Simulations

There has been a lot of debate over the past decades regarding the role of computer simulation in scientific research. Today it is generally accepted that computer simulation bridges the gap between theory and experiment, being neither the one nor the other. On the one hand, in theoretical models (such as those described above) the description of phenomena was always limited to “special circumstances” due to the unavoidable approximations they entail. Experimental measurements, on the other hand, were not always possible (or cheap, for that matter), and might lack the resolution capability (either spatial or temporal) to capture the subtle mechanisms governing atomic-scale processes. With the advent of high performance computing (HPC) and the development of optimized, sophisticated algorithms, experiments in silico have managed to push the boundaries in the nano-regime and shed light to phenomena that both other methods often fail to reach.

A fortuitous advantage is that the length and timescales associated with phenomena related to nanoparticles are within the range of not only experimental characterization methods such as transmission electron microscopy (TEM), atomic force microscopy (AFM), or X-ray diffraction (XRD), but also of atomistic computer simulation techniques such as molecular dynamics (MD) or Monte Carlo (MC). This enables the a priori theoretical study of nanoparticle-related phenomena; once optimal structures and properties are determined, simulation predictions can be confirmed experimentally a posteriori, thus considerably reducing time and cost. Naturally, the communication between theory and experiment is bi-directional: computer studies can also be fine-tuned based on carefully elaborated experimental feedback, leading to more sophisticated simulations in an iterative fashion. Specifically with respect to nanoparticle coalescence studies, which are of interest in this review, atomistic computer simulation methods proved to be ideal candidates, since the temporal and spatial scales involved are well within their resolution capabilities.

In this section a very brief reference will be made to the methods used by the authors and others in order to simulate nanoparticle coalescence at the atomic scale, but no attempt will be made to delve deeply into technical issues. The interested reader can refer to a plethora of dedicated textbooks on the methodology of each technique,\cite{39–41} or to the cited papers for specifics on individual simulations presented in Section 3. The goal is to unravel some technical details of the simulation methods here, prior to the discussion of Section 3, where a single, method-independent narrative is formulated that describes the physical mechanism of nanoparticle coalescence in a coherent manner.

2.2.2. General Setup for Molecular Dynamics

Using the classical MD simulation technique, one could track the time evolution of a set of atoms (that follows a certain statistical ensemble) by integrating their Newtonian equations of motion.\cite{39} This allows for the direct observation of atomic diffusion (either on the surface or within the bodies of nanoparticles), defect formation and interaction (such as grain boundaries or misfit dislocations), and phase transitions (e.g., melting or crystallization). As such, MD enables direct comparison with either continuum-level theoretical modeling (often by setting $T = 0$), or experimental observations (at $T > 0$), provided the simulation model corresponds adequately to the conditions of the experimental setup, maintaining the physics of the simulated system without creating unnatural artifacts.\cite{19}
Figure 1. Schematic summary of common setup for the study of nanoparticle coalescence by MD. The process consists of four main steps: i) nanoparticle creation, ii) geometry optimization, iii) thermalization and equilibration at the desired temperature, and iv) interaction of two (or more) sintering clusters. Various determining factors are also indicated such as the integration algorithm of the MD code, the employed statistical ensemble and the interatomic potential, and input parameters such as the current temperature, the thermostat constant, and the overall production time.

The most common setup for the study of coalescence between nanoparticles fabricated in the gas phase via MD is by placing two nonmoving particles in vacuum in close vicinity with each other. Typically, particles are either cut from bulk structures and statically relaxed individually until they reach some low energy configuration\cite{33,42} or are created in shapes corresponding to global energy minima (e.g., Wulff constructions) such as Marks decahedra, Mackay icosahedra, etc.\cite{43,44} If the initial clusters are not at least close to equilibrium, they can contribute additional potential energy upon sintering, which may affect the final structure. After individual geometrical optimization, the particles are also normally equilibrated separately at the desired temperature. Only then are they positioned together in the same simulation box, and allowed to interact with each other. Since the distance between adjacent atoms from different particles is closer than the inter-atomic potential cutoff range, these atoms feel the presence of their counterparts in the other particle, and attract and adhere to each other. This constitutes the very first step in the sintering process, and the forces exerted between these atoms are the initial driving stimuli for the coalescence. This MD setup consists of four main steps, as schematically summarized in Figure 1: i) individual nanoparticle creation, ii) geometry optimization, and iii) thermalization and equilibration at the desired temperature take place, followed by iv) coalescence of two or more adjacent clusters. Various important factors are also indicated in the figure, such as the integration algorithm used by the MD code, and the employed statistical ensemble and interatomic potential, as well as exemplary important input parameters, such as the current temperature, the thermostat constant, and the overall production time.

Of course, it should be pointed out that there were two approximations implicit in this simulation setup. The first one was the assumption that particles merely touch each other with practically no initial translational kinetic energy. Since, however, experimental gas-phase aggregation was commonly reported to take place in the soft-landing regime (i.e., kinetic energy is less than 1 eV per atom),\cite{45} and also considering that clusters in inert-gas aggregation sources have a more-or-less parallel drift velocity,\cite{11} this approximation might be considered realistic enough. Nevertheless, collisions have sometimes been explicitly included in MD simulations; for example, by Yun et al., who provided their coalescing Au nanoparticles with collision energies equivalent to their internal temperatures so that thermal collisions were implied.\cite{44} Also, Mariscal et al. reported variations in the chemical ordering of bimetallic nanoparticles formed by energetic collisions between monometallic clusters based on differences in the initial kinetic energies.\cite{46}

The second implicit approximation was that of using vacuum environment for nanoparticles which were, in reality, either already deposited on a support, or located inside a gas-phase environment. This was routinely catered for by the appropriate choice of statistical ensemble for the simulation. Typically, for nanoparticles coalescing after landing on the support, the constant-temperature, canonical NVT ensemble was used.\cite{33,42,47-49} The rationale was that, due to its much larger dimensions than those of the particles, a noninteracting, thermally conductive support acts as a heat reservoir, dissipating all additional heat generated during the sintering and maintaining constant temperature. Instead, the adiabatic, micro-canonical NVE ensemble was commonly utilized for nanoparticles.
colliding while still in the gas-phase. This choice was justified considering that, during gas-phase aggregation, nascent clusters are often sporadically coupled with the inert gas surrounding them. Hendy and Brown quantified this argument, estimating the mean time, \( \tau_g \), between successive collisions of a cluster of radius \( R \) with an inert-gas atmosphere of atomic mass \( m_g \) as

\[
\tau_g \sim \frac{1}{PR} \left( \frac{m_g k T}{8\pi} \right)
\]  

where \( P \) and \( T \) are the pressure and temperature of the source, respectively. Assigning reasonable numerical values to the parameters (for a Pb cluster 4 nm in diameter, inside a He atmosphere at 5 mbar and 500 K) they estimated an approximate \( \tau_g \) of 1 ns. This time period is usually long enough for the coalescence phenomenon to reach a steady state and the simulation to finish, meaning that the constant-energy assumption is essentially valid (please note that an elaboration on what is meant by “steady state” will be done in Section 3). Of course, the NVT ensemble can also be utilized for gas-phase aggregation under high pressures and temperatures (e.g., for the fabrication of titania, silica, or silver aerosol particles).

However, the coalescence of nanoparticles on a support has actually been investigated by MD simulations. For example, Tsai & Jeng compared the sintering of Cu nanoparticles in vacuum with that on a graphene support, and found that the graphene-supported nanoparticles have a relatively higher onset temperature of coalescence than the isolated ones. Similarly, the coalescence of clusters within a gas-phase environment has also been explicitly studied by MD, typically taking place during the late stages of the inert-gas condensation process. These simulations enabled not only the collision of primary particles with nonzero velocities but also the utilization of mere inert-gas temperature control for the clusters (instead of demands for energy or temperature conservation). This means that no artificial thermostat was used for the clusters; their temperature varied a lot during the course of the simulation run, depending only on heating up via decoration by adatoms or other small clusters, and cooling down by dissociation of atoms and elastic collisions with cool inert-gas atoms. The temperature of the latter was, actually, controlled by a thermostat, but only after passing the periodic boundaries of the simulation box. This way, the elastic nature of their collisions with the clusters was guaranteed. Also, every time an inert-gas atom disappeared from the opposite side of the box, it represented a new atom, in full conceptual agreement with the experimental setup. Therefore, in such simulations the resultant configurations after primary particle collisions depended strongly on the timing of the collisions, since the timing was directly associated with the current temperature. Indeed, the decisive effect of current temperature on the product of nanoparticle coalescence will be a recurring theme in Section 3.

Finally, it should be mentioned that MD simulation results have been used for determining collective variables necessary for coalescence studies via methods such as well-tempered metadynamics (WTMD). The main idea behind this approach is that computational efficiency can be improved if visiting rare events in the trajectory space is accelerated by enhancing the sampling of the probability distribution along only a limited set of degrees of freedom (also known as collective variables). This leads to a reduction in the dimensionality of the problem by reconstructing a more simplified free-energy landscape. The enhanced configurational sampling is achieved by adding a repulsive, history-dependent potential along certain collective variables, thus biasing the system toward unexplored regions of the configuration space. For example, Farigliano et al. used WTMD to study the coalescence between small Au and Co clusters, choosing the center of mass distance and gyration radius as their collective variables. By constructing free-energy contour plots, they showed that coalescence most likely proceeds via deformation of the core material, as indicated by the system residing in regions with large gyration radii. The Cu-core/Au-shell structure was found to be the most visited conformation, corresponding to the most stable configuration. Unlike MD, WTMD cannot address kinetic effects; however, it can identify local minima in the free-energy contour plots where the system stays for prolonged periods, indicating either metastability or deceleration of the coalescence process.

### 2.2.3. Principles of Monte Carlo Simulations of Nanoparticle Coalescence

Kinetic Monte Carlo (KMC) is a computer simulation technique that enables to follow the time evolution of processes occurring with certain transition rates among states; indeed, it has been used extensively to study atomic diffusion and related processes. Therefore, following our discussion about the phenomenological continuum models above, it is only intuitive that it would be a method of choice for the study of nanoparticle coalescence.

The rates used as input to the KMC algorithm are typically calculated based on a bond-counting algorithm and event-selection scheme, the main idea is that atoms bonded with only a few neighbors have a higher probability to move (i.e., they have a higher mobility rate) than those bonded with many neighbors. Ramping of the temperature during a KMC simulation results in overcoming an increasing number of event activation barriers; this triggers the atomic jumps of a growing number of atoms, with the resultant enhancement of the degree of coalescence between particles. Once more, this underlines the pivotal role of current temperature in the coalescence process. The usage of statistical ensemble follows the same rationale as for MD. Using KMC, McCarthy and Brown found that the power law describing the radius of the neck that connects two coalescing nanoparticles decreases rather abruptly at a certain point along the course of the process. In principle, this indicates a two-stage mechanism, in direct contrast to classical theory which predicted an approximately constant rate.

However, KMC has various shortcomings, too. First of all, the method cannot predict the rates of the processes it simulates; they have to be obtained elsewhere (experimentally, theoretically, or by MD) and be fed to the simulation. This also means that if two or more processes are in some way correlated with each other, their rates may not correspond to the values used by the KMC simulation, since these are obtained in advance. Also, to acquire a finite number of parameters, one has to take a finite number of local environments into consideration; this translates
into KMC using regular lattices, and thus missing out on taking into account effects such as of stress or elastic relaxation.

Nevertheless, hybrid simulation methods have been used that exploit the advantages of the KMC method circumventing its limitations. For example, Theissmann et al. used a combination of KMC and rigid body dynamics (RBD) to simulate the coalescence of oxide nanoparticles. In this modeling scheme, common KMC steps described the atomic diffusion within the required regular lattices of the crystalline nanoparticles, but with the additional feature that the particles are allowed to rotate as rigid objects by integrating their equations of motion using RBD, as shown in Figure 2. Interestingly, Theissmann et al., too, predicted a two-step process for the coalescence, comprising an early reorientation of the particles followed by sintering through diffusion.

Finally, in closing this section it should also be mentioned that Monte Carlo techniques are also commonly used to simulate the mixing or demixing of alloy nanoparticles which can be the end product of the coalescence of clusters of different elements providing the thermodynamically favorable chemical ordering of the system. In this case, Monte Carlo-based atom swap following the Metropolis algorithm is usually combined with MD steps in the NVT ensemble; the MD temperature is also used for the Metropolis criterion about the swap probability. This hybrid method is equivalent to pure MD simulation, but is computationally much more efficient and, therefore, significantly faster (but at the expense of losing the actual temporal evolution of the system). It enables the adequate sampling of the potential energy landscape in a manner similar to global optimization techniques such as basin hopping with tailored exchange moves.

2.3. Phenomenological Modeling Revisited: Input from Atomistic Simulations

Given the accumulated atomistic simulation results describing nanoparticle coalescence and taking into account the rapid advances in computational power, one would be inclined to presume that the problem can be tackled by a brute force tactic, that is, by running increasingly long and large atomistic simulations. Another approach, however, is to use the new information and insights provided by simulations to revisit rigorous, analytical modeling of the sintering process. This approach is inherently multiscale as, in doing so, data from simulations at different timescales define elementary processes into which the overall phenomenon can be decomposed.

As an example, Henz et al. formulated a phenomenological model for the coalescence of a Ni and an Al particle, based on continuum thermodynamic considerations. According to their model, the driving forces for the sintering of the particles are surface energy minimization, energy release due to reactions at the interface, and energy loss due to viscous dissipation. However, the values fed to their model were obtained from their MD simulations, instead of bulk properties, yielding, at least qualitatively, similar trends with MD results.

More recently, Grammatikopoulos et al. modified the cluster-heating model (CHM) originally developed by Meinander and Nordlund and Jarvi et al. for describing the deposition of nanoparticulated films, to develop an analytical model for nanoparticle coalescence based mainly on geometrical considerations. Inspired by their previous MD studies on the coalescence of Ta and Pd nanoparticles, they used the radius of the neck formed during the initial contact of monometallic clusters as the main variable to determine the degree of coalescence. The results from the so-called extended-CHM (e-CHM) emphasized the predominant dependence of coalescence on how close the current temperature is to the particles’ size-dependent melting points, in good agreement with their previous MD results. Figure 3 illustrates the four calculation steps necessary for the e-CHM, along with corresponding visualization snapshots of MD simulations of Ta nanoparticle coalescence at 1000 K. First, the free-surface area lost by the initial contact of the clusters is calculated, corresponding to the surface of a spherical cap determined by the range of the attractive forces between neighboring atoms (as indicated in Figure 3-top row). Heat is thus released and, consequently, some portions of the clusters melt temporarily (Figure 3-second row); an elaboration on what is meant by this will be done in the next section. Again, the shape of the molten regions can be approximated by spherical cups starting at the clusters’ touching point; however, this time their size depends on the proximity of the current temperature to the clusters’ melting points (Figure 3-third row). As a result, a neck is formed (Figure 3-bottom row), the radius of which depends on the previously molten portions of the clusters. The radius can be calculated using

\[ a = \sqrt[4]{\frac{C_1}{T_m - T_0} - \frac{C_2}{(T_m - T_0)^2}} \]  

(2)

where \( C_1 \) and \( C_2 \) are proportionality coefficients (approximately constant for any given material); notice the \((T_m - T_e)\) term in the denominators capturing the aforementioned dependence of the degree of coalescence on the proximity of the current temperature to the melting point of the clusters. To be discussed in Section 3, this model does not concern the final relaxation stage of
the process; however, it is still relevant since it describes adequately unrelaxed metastable nanoparticles obtained experimentally by cluster beam deposition.

3. Atomistic Simulation Studies on Nanoparticle Coalescence

3.1. Decomposition of the Coalescence Mechanism

Extrapolating the mechanism from coarse scale historical models, four mass transport modes were found responsible for nanoparticle coalescence: i) surface diffusion, ii) hydrodynamic flow, iii) evaporation versus condensation, and iv) volume diffusion. According to such models, the dominant transport mechanism for solid nanoparticles (such as those prepared by gas-phase condensation) is predicted to be the former, that is, surface diffusion. However, early MD simulations by Lewis et al. revealed the sometimes overrated role of surface diffusion, predicting a mechanism comprising two steps, an initial fast stage and a final slow one. A rather more detailed mechanism was later described by Lummen and Kraska, consisting of three steps: i) First, a neck is formed at the point of contact of the two interacting clusters, which transforms the two-cluster system into a dumbbell. This step is very fast. ii) Subsequently, the dumbbell turns into an ovoid (or a faceted rod, according to McCarthy and Brown). This step is slower than the initial one. iii) Eventually, the ovoid relaxes very slowly toward a spheroidal shape, driven by the minimization of surface energy associated with the two shapes.

Here, we will analyze the course of the coalescence process based on this scheme, but we will add more detail in each step, combining complementary findings from various studies, often obtained by different methods. According to our scheme,
nanoparticle coalescence can be decomposed into nine basic processes. However, we should emphasize that there exists no clear-cut temporal distinction or succession of these stages, some of which may occur simultaneously; our scheme is just an attempt to identify and evaluate the importance of each elementary component of the overall coalescence mechanism:

1) **Coagulation.** This stage describes the initial attraction (at $t = 0$) and contact between the primary particles. It can be due to either in-flight collisions during gas-phase condensation, or cluster diffusion on a support, after deposition; a phenomenon often referred to as Smoluchowski ripening.$^{[74]}$ In Section 2.2.2 we have referred to how MD addresses the issues of initial kinetic energies and the effect of local environment on the approach of the clusters.

2) **Rigid Body Reorientation.** Once the clusters have approached enough to feel the presence of each other, an interface is formed between them, as shown in the previously discussed hybrid KMC&RBD study by Theissmann et al.$^{[24,72]}$ Due to randomness in the coagulation geometry, this initial interface is usually misoriented, which leads to the shearing of a number of interface layers, as shown in Figure 4 depicting the initial twist misorientation after neck formation in coalescing Au nanoparticles.$^{[75]}$

Eventually, the particles rotate as rigid bodies, driven by mutual torques, in order to maximize their contact area. This results in the formation of a more coherent, larger-area interface between the two interacting clusters. The “tango” of monometallic Pd clusters striving to maximize their interfacial area was very clearly illustrated by MD simulation movies presented as electronic supplementary material in Grammatikopoulos et al.$^{[33]}$

3) **Defect Formation.** The reorientation stage is usually very fast (approximately few ps). It results in the formation of a dumbbell configuration, either with perfect alignment of the clusters, if their geometry allows it, or with the formation of a twin boundary, when the rotational motion is blocked by an excessive number of newly formed bonds; the latter case should be far more usual than the former, considering the expected randomness in the original relative orientation of the clusters. Simultaneously, twin boundary formation is commonly accompanied by the appearance of misfit dislocations, as shown in Figure 5.$^{[42,75,76]}$

4) **Heat Release Due to Free-Surface Annihilation.** Bond formation is accompanied by heat release. As the total surface area of the overall system decreases with the creation of the interface between the interacting clusters, surface energy annihilates and transforms into thermal energy.$^{[77]}$ In the case of
adiabatic, in-flight coalescence this energy remains trapped in the system, raising its temperature (at least within the timescales discussed here). To what degree the temperature rises depends on the area of the newly created interface, which in its own turn depends on the initial misorientation between the clusters and the current temperature and its proximity to the clusters’ size-dependent melting points. These dependencies will be further discussed, among others, in the next subsection. In the case of isothermal coalescence on a support this energy dissipates away from the system very fast.

5) **Temporary Melting of Interface.** This is a crucial step in defining the overall mechanism of the coalescence process, that was missing from previous continuous models which assumed reaction temperatures well below the clusters’ melting points (as, e.g., in Mayr et al.\cite{mayr2013}), or from KMC studies that required the conservation of crystallinity under the canonical ensemble.\cite{grammatikopoulos2017} However, Grammatikopoulos et al. observed clear signs of reorganization at the atomistic level near the interface practically concurrent with the interface formation,\cite{grammatikopoulos2017,grammatikopoulos2018} triggered by the release of additional thermal energy to the system, as described in the previous stage. This is easily identified in the case of amorphous Pd nanoclusters 3 nm in diameter coalescing at 1000 K, where the extra energy from the coalescence was sufficient to initiate a reorganization wave which originated at the interface and propagated along the full bodies of the clusters, resulting in their full crystallization. Snapshots from an MD visualization movie from this simulation are shown in Figure 6, where the so-called crystallization wave is evident, especially for the cluster on the left.

It should be emphasized that a unique, unambiguous definition of the onset of melting is lacking, especially for such small systems.\cite{grammatikopoulos2017} In the original CHM it is suggested that by melting point one should refer to the mechanical melting temperature (i.e., the limit of superheating, typically around 15–20% above the bulk thermodynamic melting point); it is also argued that the system melts practically immediately due to the disappearance of the local free-energy minimum.\cite{zhu2018} However, the term as used here describes an indubitable temporary disordering of the atoms at the interface and a “softening” of their bonds.

6) **Neck Growth.** A preliminary neck is, in principle, formed as soon as contact is established between the two clusters (i.e., at $t=0$), assisted by surface diffusion of atoms from the two clusters toward the interface, as prescribed by the phenomenological models discussed previously.\cite{zhu2018,grammatikopoulos2018} However, it only obtains substantial dimensions when supported by the temporary melting of the interface, which avails a much easier flow of atoms from the clusters toward the neck.

7) **Plastic Deformation.** Even after neck formation, the tendency for relative rotation of the two clusters persists, mostly within the elastic limit ($\approx 0.8$ nm, according to Zhu and Averback).\cite{zhu2018} The two-cluster system now behaves as a coupled-oscillator, where the thermal vibration of each cluster makes them pulsate around the initial touching point. However, assisted by the heat provided to the system, accumulated internal shear stresses help overcome this limit, and plastic deformation ensues via glide of the misfit dislocations and their annihilation at the surface. Often this is accompanied by the formation of protrusions or other anomalies at the surface. Displacement
maps of the atoms during this stage of coalescence capture the shearing of the cluster due to their vibration in a most emphatic way, as shown in Figure 7a for two single-crystal Pd nanoclusters 3 nm in diameter coalescing at 1000 K;[33] note the presence of protrusions evident at symmetrical positions on each cluster (top for the cluster on the left, bottom for the cluster on the right).

Simultaneously, temporary interface melting means that upon resolidification atoms at the neck region are repositioned, allowing the nanoclusters to reorient themselves as whole bodies. If perfect reorientation is achieved, the twin boundary disappears and the clusters align themselves epitaxially forming a single, oblong nanoparticle. It is, however, also possible that the clusters reorient themselves epitaxially only partially; in this case, the twin boundary may shift from its original position at the initial interface to some other, arbitrary location within the clusters’ bodies, as shown in Figure 7b–d and corroborated experimentally in Figure 7e. In Figure 7b, the same system is depicted as in Figure 7a, but from a different viewpoint, whereas in Figure 7c a one-atomic-plane width slab of \{111\} orientation is shown, cut along the blue-dash rectangle of Figure 7b, demonstrating practically perfect epitaxial alignment of atoms located both sides of the original interface (as indicated by the different hues of green color in which the atoms are depicted). In Figure 7d corresponding calculated diffraction patterns are shown, indicating a rotation of 70° between the clusters. The twin boundary has indeed shifted into the particle on the right, as indicated by the red lines in Figure 7b. A similar twinning of the same angle (i.e., 165°) between \{200\} and \{111\} planes was found for nanoparticles grown by gas-phase condensation, as shown in the TEM image of Figure 7e. For clusters consisting of atoms of the same element, this can be interpreted as a memory-loss effect: interface atoms lose memory of their origin (i.e., which cluster they originate from) during the temporary interface melting stage, and eventually solidify epitaxially to either of the clusters. If this happens to be their cluster of origin, the twin boundary remains intact; if this happens to be the other cluster, the twin boundary shifts.

8) **Consolidation.** The neck radius becomes thicker as it starts growing with time, but its growth rate slows down because the difference in curvature between the neck and the
clusters (i.e., the driving force for atomic surface diffusion toward the neck) becomes smaller. The thicker the neck grows, the stiffer the two-cluster system becomes and its pulsation less pronounced. As a result, the distances between neighboring atoms at (or near) the neck become, more or less, fixed, reducing the probability for the formation of new bonds by the periodic approaching of different parts of the system. In other words, the system now starts behaving like a single particle (with an oblong, ovoid, or dumbbell shape). This is a longer, continuous process (≈100–200 ps),[33,42,76] by the end of which the effect of temporary heating via free-surface annihilation is infinitesimal. The system has now reached what was referred to in Section 2.2.2 as a “steady state,” in the sense that all dynamic processes have ceased. It should, however, be emphasized that this state does not necessarily correspond to the thermodynamic stable state. Oftentimes, experimentally grown nanoparticles are trapped in a metastable steady state due to quenching upon deposition, and commonly simulations describing nanoparticle coalescence stop at this point.

9) **Slow Aging.** However, an extremely slow “spherization” of the system, as Lewis et al. referred to it,[22] may continue, driven by surface diffusion,[79] and lasting for hundreds of ns up to a few μs or more. As discussed above, the already existing neck acts as a sink for diffusing atoms. However, aging is slower than predicted by the continuum phenomenological theories, especially at low temperatures, because of the energy barrier that needs to be overcome for shape changes to occur. McCarthy and Brown dissected the equilibration of a partially coalesced system of faceted clusters into three steps, namely the dissociation of atoms from existing atomic layers, their diffusion across and between facets, and the nucleation of new germs,[46] in agreement with previous studies that assumed that necking required (and its rate depended on) new germs grown on facets.[50,51] However, it was shown that germs are not necessary prerequisites, as steps on the preliminary neck can also act as nucleation sites for the accumulation of atoms flowing to the neck.[81,82] At any rate, all atomistic simulation results agree on the much lower rate of this diffusion-driven progression compared with the previous stage of plastic deformation; an example is shown in Figure 8, juxtaposing the evolution of the coalescence process obtained by atomistic simulations of Lewis et al. and the continuous numerical solution by Nichols.[72] Clearly, the atomistic simulations predict a clear transition from a fast, dynamic process (corresponding to plastic deformation due to heating by free-surface annihilation) to a very slow, constant-rate, prolonged aging process. It should be mentioned, however, that if full epitaxial reorientation was achieved during the plastic deformation stage, full fusion could occur within much shorter times.[24]

![Figure 8](image_url)

Figure 8. Temporal evolution of the ratio of the neck radius, x, over the overall cluster radius, R, as obtained by MD and numerical results from refs. [Lewis PRB 1997] and [Nichols 1966], respectively. Evidently, MD predicts a clear transition from fast to very slow rate process, unlike the numerical solution, which predicts a steady rate. Reproduced with permission.[19] Copyright 1999, The American Physical Society.

Even though the succession of these stages is not clearly defined, as stated above, a general correspondence between the proposed detailed scheme and that of Lumen and Kraska can be identified. Hence, stages 1 and 2 (coagulation and rigid-body reorientation) combined correspond to step i) of the Lumen and Kraska model (dumbbell formation). Stages 4–7 (describing plastic deformation as a result of additional heating due to free-surface annihilation) collectively correspond to step ii), during which the initial dumbbell turns into an ovoid. Both stage 9 of the current scheme and step iii) of the Lumen and Kraska scheme describe the slow relaxation toward the thermodynamically stable structure. Stages 3 (defect formation) and 8...
(consolidation) in principle designate the transitions between steps i) and ii), and ii) and iii), respectively.

3.2. Parameters Affecting the Coalescence Mechanism

Several parameters affect the coalescence mechanism, leading to a rather large variety of final configurations of the coalescing system after stages 1–8, as described above. Obviously, if one took stage 9 into account, too, a single, low-energy state would be reached, regardless of the intermediate states of the system. In fact, structural rearrangement of nanoparticles toward thermodynamically stable configurations is an important field in its own right; one which has been extensively studied, either by MD and MC or by some global optimization method, albeit not explicitly within a nanoparticle coalescence framework. For example, Rossi and Ferrando identified by MD a whole family of structures into which Au nanoparticles can crystallize as a result of different cooling rates following gas-phase synthesis. However, as already explained, oftentimes experimentally grown nanoparticles do not reach this thermodynamically stable state due to quenching upon deposition. Therefore, the “steady states” discussed here are more relevant in terms of their correspondence to experimentally observed nanoparticles.

A number of such parameters and their effects are summarized in Figure 9 showing exemplary snapshots of MD results of Ta nanoclusters coalescing under various conditions. Along the abscissa, the effect of temperature is shown, as the MD runs were performed for various temperatures in the range of 100–2300 K (the bulk melting point of Ta is 3290 K). In all cases it is evident that the effect of temperature is vital in determining the final structure; this is most intuitively demonstrated in cases where full fusion (i.e., spheroidal nanoparticles) is accomplished for high temperatures. It should be mentioned here that exaggerated temperatures often compensate for shorter MD run times, an approach which can be legitimate at temperatures significantly lower than the melting points of the individual clusters.

The effects of various other parameters are also visualized and compared in Figure 9. Starting from the bottom box and moving upwards the effects of a) relative orientation, b) degree of order/disorder, c) relative size, d) geometry of interaction among three clusters, and e) shape of the clusters are visually explored.

First, the relative initial orientation is investigated, for two perfectly crystalline Ta nanoclusters 3 nm in diameter approaching each other with different combinations of adjacent facets (Figure 9a). Clearly, the relative degree of coalescence at the end of stage 8 for the system, where the two clusters are facing each other with adjacent <100>- and <110>- facets, is the highest at all temperatures, even reaching full fusion at 2300 K. In contrast, the <100>-<100>- configuration exhibits the lowest degree of coalescence at all temperatures. The reason is that, due to the high symmetry of this initial configuration, the two clusters had no opportunity to rotate as rigid bodies on each other, and, thus, maximize their interfacial area, especially at low temperatures. As a result, less additional heating was provided to the system compared to the cases of the other initial relative orientations, minimizing the extent of interface melting due to heating from free-surface annihilation.

In the case of amorphous nanoclusters under the same conditions, it is clear that the degree of coalescence is more pronounced, even reaching full fusion at 2000 K, unlike any configuration consisting of crystalline clusters (see Figure 9b). The reason is that, in general, the coordination numbers of atoms in amorphous clusters are lower than in crystalline clusters, meaning that fewer bonds need to be broken for atoms to diffuse and coalescence to proceed. In the case of defective crystalline clusters (i.e., containing three vacancies each), the coalescence is more or less similar to that of the nondefective structures, since the vacancies can easily migrate to the surface and annihilate, due to the small sizes of the clusters.

McCarthy and Brown found that the effect of size itself is not very important, in the sense that there is no qualitative difference between the coalescence of smaller or larger clusters, at least for the size range they studied (roughly between 7 and 13 nm in diameter). Of course, they did point out that coalescence of larger clusters is slower, owing to the longer distances atoms need to diffuse in order for the system to reach thermodynamic equilibrium. Grammatikopoulos et al., however, with their e-CHM added an indirect yet crucial dependence of the coalescence on size, through the size-dependent melting points of clusters. In principle, this means that by correlating the melting points of clusters with their sizes, the effect of size translates into an effect of temperature, which, as stated above, is crucial. The main ansatz of the e-CHM is that it is not the absolute value of the current temperature which is of essence, but its proximity to the clusters’ melting points. This idea was first conceived by Yu and Duxbury, who observed the rapid coalescence of clusters containing less than 200 atoms when their temperature was close enough their melting point, but did not specify the process responsible for this phenomenon; the same notion is also pivotal in Hendy et al. As a result, a very interesting phenomenon occurs when two clusters of different sizes coalesce, especially at elevated temperatures. For example, take the case of a 3 and 5 nm Ta nanoparticle coalescing under different temperatures, as shown in Figure 9c. At low temperatures, their behavior is not qualitatively different than the equal-size cases discussed above. However, at 2000 K, the 3 nm nanoparticle (on the left) melts fully, wetting the surface of the 5 nm particle (on the right). This happens because the additional heat released to the system helps melt the small cluster but does not suffice to melt the larger one (the melting points for the 3 and 5 nm cluster were calculated using caloric curves as ≈2500 and 2900 K, respectively). In the case of clusters consisting of the same element (such as, e.g., Ta), wetting of one cluster onto the other does not have any real profound effect on the final structure. However, the situation is totally different when clusters composed of different elements are involved. In this case, which type of cluster wets the surface of the other completely changes the chemical ordering of the final particle after coalescence. This is a common situation during gas phase synthesis of bi-metallic nanoparticles; nevertheless, the inherent randomness of the process does not favor homogeneity among a batch of particles. However, provided one can harness the kinetics of the process, one can, in principle, take advantage of coalescence to design nanoparticles with specific elemental configurations. Of course, we need to underline that the situation is actually more complicated: first, if different elements are
Figure 9. Final configurations of two (or three) Ta nanoparticle coalescing at various temperatures after 100 ps MD runs. For ease of observation, different color combinations indicate different temperatures. In each box, the effect of a different parameter is investigated. 

a) Relative orientation between clusters approaching each other with different facets. 

b) Degree of disorder, as manifested by either amorphous structure or the presence of point defects. 

c) Relative size: both relatively large and small size differences are examined. 

d) Configurations consisting of three clusters, in two different geometries. 

e) Shape: coalescence between a spherical and a cubic cluster is examined for three temperatures. All panels adapted with permission.[42] Copyright 2014, Springer.
involved, the melting point of each cluster is not a uniquely defined function of size any more. Further, if the system has enough time or energy to relax to its thermodynamically favorable configuration, the chemical order of the bi-metallic nanoparticles depends on other parameters: namely, i) the enthalpy of mixing, that is, whether the atoms prefer to be surrounded by atoms of their own kind or different ones, ii) surface energy differences between the various elements, and iii) strain energy considerations.[43]

Different configurations (in tandem or triangular) of particle aggregates composed of three Ta clusters 3 nm in diameter are shown in Figure 9d, showing similar behavior as their two-nanocluster counterparts.

McCarthy and Brown also argued that during the initial stages of coalescence the effect of shape is unimportant; by comparing simulations of sintering between spherical or truncated octahedral nanoclusters, they found the same, large exponent (~1/3) for the power–law relationship (r∝t) with which they fitted the plots describing the evolution of the neck radius during sintering.[49] However, this is a result of the two shapes not being very dissimilar to each other, with the surface atoms sharing approximately the same coordination numbers. In contrast, in Figure 9e a spherical Ta cluster is sintered with a cubic Ta cluster, 2 nm in edge length and {111} facets. The approach occurs between a <110> facet of the spherical cluster and a vertex of the cube. In this case, the high number of dangling bonds near the cube vertex facilitates the sintering of the clusters to a higher degree than between two spherical clusters. The difference between this case and that of two spherical nanoparticles, however, is marked only during the very initial steps of the sintering process; once the clusters have been deformed enough there is no clear distinction between the two cases.

Finally, as was mentioned above, the presence of a substrate supporting the nanoparticles during their coalescence can have a grave effect on the final structure, as the particles typically deform and wet the support at lower temperatures than they would if in vacuum.[93] This was further corroborated by Wang et al., both experimentally and by MD simulations, who investigated the effect of temperature in the flow of surface atoms between two Au clusters supported on a Si substrate.[84]

4. Calculated Properties

4.1. Calculated Properties of Nanoparticles

4.1.1. Coalescence between Same-Element Clusters

Descriptors: As expected from the discussion above, the coalescence of nanoclusters has a marked effect on the structure of the resultant nanoparticles. The most direct effect is, of course, on nanoparticle size and shape. Various criteria are used to describe the final structures based on the degree of coalescence achieved. The most typical examples are i) the neck radius, ii) the average distance between the particles’ centers of mass, iii) the radius of gyration, iv) the sphericity, and v) the aspect ratio of the final nanoparticle. We have already deliberated about the former in our discussion on the tangent-sphere model and the e-CHM, whereas the second is self-explanatory. The radius of gyration of a particle describes the radial distance from the particle’s rotation axis of a point which, if it contained the whole of the particle’s mass, the same moment of inertia would be maintained about the given axis as that of the real particle with its actual distribution of mass. An even more intuitive descriptor is sphericity, which, as the name implies, indicates how closely the shape of an object resembles that of a perfect sphere. Since the spherical shape is the most compact shape a body can assume for a given volume, sphericity also constitutes a measure of compactness of any given shape. The sphericity of a particle at any given stage during the coalescence process is defined as the ratio of the surface area of a sphere of the same volume as the particle over the surface area of the particle; clearly, during the sintering process its value approaches unity, justifying the term “sphericization” used by Lewis et al.[72] In a similar fashion, an equivalent measure of the degree of coalescence is the aspect ratio of the particle, that is, the ratio of the smallest to the largest principal moment of inertia of the particle. Just like sphericity, its value is always less than unity, but it approaches that value as the sintering proceeds.

Another set of properties relevant to single-element particles concerns the crystallographic structure, degree of crystallinity, and presence of structural defects. These can be analyzed using criteria such as the coordination number and radial distribution function. The former is used for the determination of the crystallographic system (or the deviations from it) the particle may adopt, whereas the latter indicates the degree of crystallinity, showing (or missing) peaks at pair-separation distances which correspond to neighboring atoms in a perfect crystal lattice.

Next, we will review essential literature on the coalescence of various same-element clusters, categorized by element.

Copper: In one of the most influential papers defining the field, Zhu and Averback used an embedded-atom method (EAM) type interatomic potential[85] to study the coalescence of small, single-crystal Cu nanoparticles at 700 K; they revealed the formation of dislocations at the neck and the rigid-body rotation of the particles, and interpreted plastic deformation by activation of their slip systems.[76] Kart et al. also studied the sintering of Cu nanoparticles of various sizes (but equal to each other),[86] whereas Tsai and Jeng found that the sintering and melting points of Cu nanoparticles are sensitive to the presence of a support (they used graphene support in their study).[33]

Gold: In another seminal study, Lewis et al. used the classic EAM-type potential developed by Foiles et al.[97] to simulate the overall sintering process (i.e., including step 9, as defined in our proposed scheme) of Au nanoparticles.[72] Through their atomistic simulation results they showed a distinct shift in the rate of coalescence, indicating a process comprising more than one mechanisms; thus, they could underline the limitations in reliability of macroscopic sintering theories which predicted a continuous one-step process. The comparison between their results and the continuous numerical solution by Nichols was shown in Figure 8 and discussed in Section 3.1.[72] as explained there, they attributed this transition to the nonspherical, faceted structures of the clusters. Interestingly, in the same paper Lewis et al. also determined the role of surface premelting in the melting of nanoparticles, which also has a profound effect on the necking stage and the coalescence process, in general.

By plotting the melting point as a function of cluster size, Lewis et al. could pick clusters of different sizes which, at a given
temperature, could be either liquid or solid. This way, they could also investigate the interactions between liquid–liquid or liquid–solid clusters. For the former case, they found that, despite being in the liquid phase, atoms from the two clusters counterintuitively do not mix, at least during the initial stages of coalescence. The system just minimizes its potential energy by optimizing the contact surface between the two clusters in a very fast initial step (≈50 ps). Of course, later on atoms diffuse all over the newly formed particle. A similar behavior was found for the latter case, that of solid-liquid cluster interaction, as demonstrated by the radius of gyration, $R_g$, and aspect ratio, $A$, of the system, shown in Figure 10. Again, the small, liquid cluster wetted the surface of the larger, solid one very fast (≈100 ps); however, the spherization stage in this case was much slower than in the liquid–liquid interaction, since the resultant nanoparticle was solid and atomic diffusion much slower due to the presence of surface facets.

In a similar setup, Goudeli and Pratsinis explored the crystallinity dynamics during coalescence between crystalline and amorphous Au clusters of different sizes.\[88\] In the case of a large crystalline cluster sintering with a smaller amorphous cluster, the small cluster wetted the surface of the larger one, eventually obtaining its crystalline order. In the opposite configuration, the initial sintered particle was amorphous; when it eventually crystallized, it became polycrystalline, due to the randomness of the positions of the crystallization nuclei.

Arcidiacono et al. also compared MD results on the coalescence of crystalline Au nanoparticles to validate their phenomenological macroscopic model.\[89\] Lange et al. focused on the dislocation mediated alignment of Au nanoparticles originally in various random misorientations (see Figures 4 and 5, above).\[75\] Yun et al. were able to capture the thermal arrest caused by the temporary melting of Au clusters sintering very near their melting point.\[44\] Finally, Wang et al. demonstrated the effect of temperature on the approach and coalescence of Au clusters supported on a Si substrate, which was facilitated by the flow between the clusters of loosely bound surface atoms.\[84\]

Silver: Zhao et al. investigated the role of surface premelting in the melting point depression of small nanoparticles, and, thus, in their coalescence.\[90\] They used a system of three Ag nanoclusters to prevent them from readily rotating on each other and from forming a low-energy boundary. The descriptor they used to define the degree of coalescence and spherization was the aspect ratio of their resultant three-cluster aggregates. Buesser and Pratsinis also studied the crystallinity of particles produced by the sintering of three or four Ag clusters of various initial configurations, and indicated coalescence as a potential underlying mechanism for the occurrence of polycrystallinity during particle synthesis.\[52\]

**Palladium:** Grammatikopoulos et al. emphasized the emergent structure and surface geometry owing to deformations of Pd crystalline nanoparticles as a result of their coalescence due to their significance for potential applications in catalysis and hydrogen storage.\[13\] The emergence of surface anomalies such as protrusions (see Figure 7), steps, and high-index facets are likely to enhance the catalytic activity and hydrogen adsorption efficiency, since they are believed to be chemically active sites.\[91,92\]

Simultaneously, starting from initially amorphous clusters, they showed that the energy released via free-surface annihilation was enough to crystallize the clusters via the propagation of a crystallization wave, originated at the primary neck, as corroborated experimentally by the high-resolution transmission electron microscopy (HR-TEM) study reported by José-Yacamán et al.\[93\] In Figure 11, the phase transition from amorphous to crystalline is indicated graphically both by means of the coordination numbers of all atoms in the system, which changed from a random assortment of values to mostly 12, the characteristic coordination number of the face-centered cubic (fcc) system of Pd, and through a narrowing of the average radial distribution function peaks around the value expected for crystalline Pd (i.e., 2.7 Å). Both descriptors are shown in Figure 11 for two temperatures, that is, 300 and 1000 K.

**Tantalum:** Grammatikopoulos et al. also used the well-established Finnis–Sinclair EAM-type interatomic potential\[90\] to simulate the coalescence of Ta nanoparticles ranging between 2.6 and 5 nm in diameter, as summarized in Figure 9, above.\[43\] Their focus was on qualitatively investigating as many parameters as possible that affect the degree of coalescence between the clusters and the shape of the combined nanoparticle.

**Iron:** Ding et al. used the gyration radius as the main descriptor for their study of the coalescence of Fe nanoclusters, once more with a focus on the difference between the current temperature and melting point of the clusters.\[95\]

**Silicon:** Atomistic simulation studies of nanoparticle coalescence are not limited to metallic systems. Blastein-Barojas and Zachariah investigated the sintering of Si nanoparticles using the classic Stillinger–Webber potential for Si, which was designed to describe explicitly interactions in both liquid and solid forms of
Si. They reported a similar result as that of Ding et al. for Fe by correlating the temperature increase during coalescence (and the resultant acceleration of the sintering process) with the surface area reduction (in accordance with the scheme described in Section 3.1). Further, echoing the work of Lewis et al., Hawa and Zachariah also studied the coalescence of Si clusters of different sizes at temperatures that would result in the small cluster being liquid and the large cluster being solid. Utilizing the reduced moment of inertia as their main coalescence descriptor, they concluded that sintering accelerates when the volume difference between the clusters is large, proceeding via convection and diffusion in the solid cluster and deformation (in principle, wetting) in the liquid cluster.

More interestingly, using the same descriptor, Hawa and Zachariah also compared the evolution of coalescence of hydrogen-terminated and bare Si clusters. They found that saturation of the dangling bonds of the surface Si atoms with H induces an additional step to the sintering process which is absent for bare clusters. This initial step involves the relocation of surface atoms near the adhesion region and, in itself, requires longer time than the time needed for full fusion of the bare clusters; this can be evident in Figure 12 that depicts the temporal evolution of the reduced moment of inertia of the system complemented with snapshots from the MD simulation.
at various points of interest during the process. It can also be observed in Figure 12 that, once this additional step is over, sintering of the surface-passivated clusters proceeds in the same way as for bare clusters. Interestingly, as the overall surface area of the newly formed Si particle decreases with advancing coalescence, the numbers of SiH3 and SiH4 species on its surface increases, due to the relevant excess of H atoms.

Ceramics: The study of ceramic nanoparticle coalescence is also of great interest, especially in the field of aerosols. Strictly speaking, ceramic nanoparticles such as of silica (SiO2) or titania (TiO2) are not single-element clusters, but we are examining studies on their sintering here, in the sense that the colliding primary particles are of the same composition.

Collins et al. decomposed the sintering of titania clusters into three stages, namely contact, locking, and fusion, which, in principle, coincide with the three steps in the Lumen and Kraska scheme.[100] Buesser et al. took this investigation one step further, by accelerated MD studies of the complete sintering of rutile titania clusters; from their simulation results they were able to derive an expression for the characteristic sintering time (defined as the time needed for the neck diameter to reach 83% of the primary particle diameter) that converges with phenomenological models for the sintering of large particles.[51] Alimohammadi and Fichthorn utilized the same interatomic potential (i.e., the Matsui–Akaogi potential, which was found to be the most suitable for the system),[101] to investigate the sintering of TiO2 particles of the anatase phase.[102] They observed a directional sintering of both Wulff-shaped and asymmetrical clusters, and determined a so-called “hinge” mechanism based on the electrostatic forces between under-coordinated titanium and oxygen atoms residing on the clusters’ edges and facets. Their results were corroborated by Raju et al. who, utilizing a reactive force field (ReaxFF potential), observed that the aggregation of anatase clusters in vacuo happens along their direction of approach, unlike that in water which results in oriented attachment of the clusters.[103]

Lehtinen and Zachariah focused on the energy accumulation and heat release during coalescence of titania clusters, showing that it can accelerate coalescence time even by a few orders of magnitude.[77] Based on their constructed temperature profiles during sintering, they suggested that low pressures and high volume loadings lead to full fusion (and, as a result, larger sizes) of primary particles. Along the same direction, hard aggregate versus soft agglomerate formation maps were produced for silica particles by Heine and Pratsinis and Tsantilis and Pratsinis, as a function of maximum temperature and cooling rate.[104,105] The distinction between fully fused primary particles of compact shapes, and hard aggregates or soft agglomerates of fractal-like structures will be further discussed in Section 4.2.

4.1.2. Coalescence between Different-Element Clusters

Additional Driving Force—Mixed Bond Formation: As with all spontaneous physical processes, nanoparticle coalescence is driven by the natural tendency for free energy minimization. This is achieved by a combination of decrease of surface area (with the resultant decrease of surface energy) and of the reactive synthesis that takes place first at the interface of the coalescing clusters, and later on throughout the whole newly formed particle. In the case of sintering of two clusters consisting of different elements A and B, the latter includes the possibility for an additional driving force: that of energy minimization due to the formation of energetically more stable mixed A-B bonds compared to A-A or B-B bonds. This is related to the enthalpy of mixing of each particular materials system, that is, whether the different atoms prefer to be surrounded by atoms of their own kind or different ones. This parameter is also crucial for the miscibility of bulk materials, determining their phase diagrams. However, as already discussed above, the phenomenon of metastability may occur for nanoparticles grown in the gas phase driving the system away from the expected structures according to the bulk phase diagrams. The development of nano-phase diagrams[105,106] may assist in predicting the chemical ordering of the nanoparticles, but only qualitatively, since the growth process is but a series of nonequilibrium states.

Due to this reason, the physical state of the coalescing clusters is key; elemental mixing is facilitated if one (or both) of the clusters are in the liquid phase. Of course, it is important that one should keep in mind that, depending on the conditions, initially solid clusters may melt due to heat released from surface annihilation.[44] The opposite phenomenon is also possible: imagine two clusters sintering at a temperature where both are liquid. The product nanoparticle, however, being larger, will have a higher melting point which may exceed the current temperature, and, therefore, re-solidify.[100]

Equilibrium Achieved—Demonstrating Bulk Phase Diagram Behavior: Mariscal et al. used MD to simulate the coalescence of small Au and Pd clusters, each containing 95 atoms (i.e., 1.3 nm in diameter) at room temperature.[66] They found a good degree of alloying, in full agreement with the bulk phase diagram for this bimetallic system,[107] as explained both by the negative cohesive energy for mixed bonds and negative alloy heat of solution for a single substitutional impurity (−0.02 and −0.12 to −0.15 eV, respectively). In contrast, the coalescence of Au and Pt clusters under the same conditions led to clear surface segregation of Au; once more, this result is in perfect agreement with the bulk phase diagram of the immiscible Au-Pt system.[108] In this case, the cohesive energy for mixed bonds and alloy heat of solution for a single substitutional impurity were both positive (+1.84 and +0.07 to +0.09 eV, respectively).

Similar demixing behavior was also exhibited by a system of coalescing Ag and Cu nanoclusters, whose bulk phase diagram is eutectic (with a eutectic temperature of 1053 K).[109] only, in this case, a three-shell, Ag-Cu-Ag quasi-onion-like structure was observed.[46] This structure was also the one predicted theoretically.[110] Of course, it should be noted that since all sintering systems Mariscal et al. investigated were small, they were able to reach equilibrium relatively fast.

Chandross, on the other hand, investigated the coalescence of larger, same-size Ag and Cu clusters (i.e., 5 nm in diameter) using a combination of MD and MC, and observed the partial dissolution of the Ag cluster and the heterogeneous diffusion of individual Ag atoms along the surface of the Cu particle, which remained more or less intact. This phenomenon is attributed to the much higher cohesive energy of the Cu-Cu bonds compared to the Ag-Ag bonds (−3.54 and −2.85 eV atom−1, respectively).[111,112] Most interestingly, he could identify the
preferable diffusion path of these Ag atoms along step edges on the \{111\} planes of the faceted Cu cluster, in agreement with previous calculations by Baletto et al.\cite{113}

Chandross also developed a model based on his MD and MC results, in which he calculated the energy gained by the system obtaining the energetically favorable core-shell structure, as a function of the radii of individual Cu and Ag clusters. For this calculation he assumed the formation of a core-shell structure, implicitly extrapolating the expected sintering behavior of a system of uneven sized clusters from same-size coalescence results. He found that the most stable core@shell structure utilizes relatively small Cu clusters as the core and large Ag clusters as the shell. However, even though this result indeed corresponds to the equilibrium structure, it does not necessarily reflect the final configuration after coalescence of clusters of different sizes, since this could be driven away from equilibrium due to variations in the clusters’ melting points as a function of their size. This effect was hinted at in Section 3.2; it will be further discussed next.

Equilibrium Avoided—Deviating from Bulk Phase Diagram Behavior: Recently, Grammatikopoulos et al. investigated the coalescence of Ag and Cu clusters of different sizes.\cite{116} Starting from random-alloy configurations, they reproduced the equilibrium Cu-core@Ag-shell structure of Cu-rich particles and Ag@Cu@Ag onion-type structures of Ag-rich particles using the MD\&MMC combined method. Having thus determined the equilibrium structures, they also identified various metastable configurations as products of coalescence of clusters of various size combinations, and correlated them with experimentally observed particles grown by magnetron-sputtering inert-gas condensation. With Ag and Cu crystals belonging to the fcc system, both cluster types exhibited near-truncated octahedron shapes displaying \{100\}, \{110\} and \{111\}-type facets.\cite{117,118} In Ag-rich samples (i.e., systems consisting of large Ag clusters sintering with smaller Cu clusters) the small Cu cluster wetted the surface of the larger Ag cluster as a single, cohesive object, maximizing the interfacial area thus reducing the overall potential energy of the system. In contrast, and in full agreement with Chandross’ results, in the Cu-rich sample individual Ag atoms adjacent to the interface diffused on the surface of the large Cu cluster. Therefore, both of these studies brought into the limelight the effect of a yet-unexplored parameter for nanoparticle coalescence, that of cluster cohesiveness.

Once more, heteroepitaxial diffusivity was explored, indicating preferential diffusion along, rather than across, step edges.\cite{113–115} Unlike Chandross, who examined only equal-size clusters, Grammatikopoulos et al. explicitly investigated the sintering behavior of clusters differing significantly in size. Figure 13 shows the time evolution of the sintering process at 800 K of systems comprising a 3 nm Ag cluster adjacent to a \{100\}, \{110\}, or \{111\} facet of a 9 nm Cu cluster \(a\)–\(c\), respectively, and a 3 nm Cu cluster adjacent to a \{100\} facet of a 9 nm Ag cluster \(d\). In all cases, \{111\} facets remain clear of any heteroatomic deposition, thus forming so-called “ukidama” structures, that is, core@partial-shell morphologies where the partial-shell atoms are aligned along specific directions and facets of the core cluster. Reproduced with permission.\cite{114} Copyright 2016, The Royal Society of Chemistry.

This specific core@partial shell structure, where atoms of species A form a cage around a core consisting of atoms of species B was termed by the authors “ukidama” structure, named after Japanese glass buoys surrounded by fishnet ropes. This structure had been presented earlier via high-angle annular dark-field (HAADF) Z-contrast imaging by Lu et al., describing an epitaxial Ag\{111\}/Cu\{111\} epitaxy.\cite{110} From an engineering point of view, the ukidama structure can be exploited for plasmonic applications since the length of the “ropes” (i.e., the sub-monolayers of the partial shell material) can, in principle, be adjusted by simply modifying the radius of the core cluster.

Similarly, Cu atoms in Figure 13d also avoid the \{111\} facets of the Ag cluster. In this case, however, the wetting is slower, due to the strong cohesion of the Cu bonds and the high diffusion barrier for Cu atoms on Ag surfaces (also note that in this case the whole structure is covered by a monolayer of Ag atoms, due to the lower surface energy of Ag compared to that of Cu).

An analogous trend for forming partial shells was observed for the Au-Ag system by Goudeli and Pratsinis.\cite{117} Although
the system is miscible in the bulk, the lower surface energy of Ag led to preferential surface segregation of Ag atoms and the creation of a (partial) Ag shell upon coalescence of two single-element clusters. Interestingly, it was shown by simulated XRD analysis of the MD particles and comparison with experimental values that the chemical ordering of bimetallic clusters can be corroborated by XRD, since mixed clusters are likely to have different grain sizes than segregated ones. Like the aforementioned Ag-Cu system, the technological potential for designing bimetallic Au-Ag nanoparticles via coalescence is great: for example, Ag preferentially occupying the surface of its nanoalloys with Au can cure the cytotoxicity of nano-silver, while maintaining its plasmonic and, thus, facilitate its biomedical application (e.g., in theranostics).[64] Copyright 2009, American Institute of Physics.

Soon, however, the sintering rate slows down, as the sintering driving force attributed to surface energy minimization is counterbalanced by a resistance to flow in the Al cluster. Therefore, temperature increase during stage 2, lasting for about 450 ps, is related to the formation of Ni-Al bonds alone. At the first half of this stage, the Ni cluster remains in the solid phase and the formation of mixed-element bonds is only possible via Al atoms penetrating the Ni cluster, thus forming bonds with Ni atoms, or by Ni surface premelting and liberating atoms inside the liquid Al cluster. As the temperature increases, larger portions of the Ni cluster gradually melt; this results in further increase in the coalescence rate after an inflection point at around 300 ps. Mixing of Ni and Al atoms proceeds unimpeded afterwards, driven by the enthalpy of Ni-Al bond formation. Eventually the full Ni cluster is molten and the all Ni and Al atoms are interdiffused, forming a random solution. The sintering process has then approached completion, with very slow evolution toward more ordered mixing of the elements.

### 4.2. Calculated Properties of Cluster Aggregates

So far in this section we have focused on the effect of coalescence on the properties of nanoparticles which are the end product of consolidation of the primary particles. Next we will go one step further scale-wise and discuss the effect of coalescence on aggregates of clusters. This discussion is relevant mainly in the field of aerosol synthesis, as it is the structure of the aggregates that determines many of the aerosol properties of interest for industrial applications.

Aerosol-based materials are already used for various common products, even though this is not always obvious to the user. Typical examples are pharmaceutical products (e.g., drug tablets), cosmetics (e.g., make-up powders), pigments, car tires and filters, exhaust catalysts, battery electrodes, rubbers, etc.[22] A typical process cycle of aerosol manufacturing consists of i) the selection of appropriate precursors, ii) their introduction in a suitable reactor (various types exist, such as flame, hot-wall, plasma, microwave, or laser reactors), where the material turns into gas and the chemical reactions in materials synthesis take place, iii) cooling at a carefully selected pace, iv) collection, v) storage, and vi) gas treatment. Inert-gas condensation is an alternative approach for the synthesis step. Also, it is very common that the final cluster aggregates are further coated and functionalized to obtain specific properties for targeted applications.[23]

It should be clear from the process description above that during synthesis, either in a reactor or by inert-gas condensation, cluster sintering plays a decisive role in determining the structure of the final cluster aggregates. Depending on the application, hard agglomeration or soft agglomeration may be preferable; for example, the former is desirable for catalysts or sensors, where electron flow through cluster necks is necessary, whereas the latter is more useful for pigments, where dispersion in a liquid matrix is required. In either case, understanding and, potentially, controlling the degree of coalescence is key in designing aerosols for practical applications.

The main parameter determining the degree of coalescence of a number of coagulating primary particles is the competition...
between the rates of the two processes, that is, that of coagulation versus that of sintering.$^{[120]}$ This is schematically described in Figure 15, showing the temporal evolution of the average particle diameter during aerosol synthesis at non-isothermal conditions (the temperature profile is also indicated in the figure).$^{[22]}$ A schematic illustration of the produced structure at each individual stage of the synthesis process is also provided for intuitive comprehension of the process. At the beginning, while the temperature is still high and the primary particles are small, the characteristic time for sintering, $\tau_s$, is much shorter than that for coagulation, $\tau_c$. This means that full fusion can be achieved between two small coagulating primary particles, leading to a larger secondary particle long before a third primary particle collides with them. As a result, coalescence prevails during this stage leading to clusters of increasing diameters. At some point, the two characteristic times, $\tau_s$ and $\tau_c$, become comparable as the former becomes progressively longer due to the increasing size of the clusters. At this stage, only partial coalescence is possible between two coagulating clusters before a third one collides with them, leading to cluster aggregates. Simultaneously, the effective collision diameter of the aggregate, $d_c$, starts deviating from the diameter of the primary particles, $d_p$, thus manifesting the growth of fractal-like aggregates. Temperature is still high enough at this stage to guarantee strong chemical bonding between the clusters, in accordance to our scheme of Section 3.1. Eventually, the collision diameter of the aggregate, $d_c$, increases further, offsetting the balance between $\tau_s$ and $\tau_c$ even more.

Finally, at the last stage of the process, the temperature drops rapidly and the coagulation of individual clusters or aggregates of clusters leads to soft agglomerates, loosely bound by some form of weak interaction (such as, e.g., van der Waals forces).

As can be seen in the schematic illustrations of Figure 15, the agglomerates produced in this manner have dendritic structures which resemble mathematical fractals. Various descriptors of agglomerate sizes are used to indicate how compact they are; such descriptors are i) the projected aggregate surface area, $a_a$, ii) the mobility diameter, $d_m$, and iii) the radius of gyration, $r_g$. In the case of a cluster aggregate, the radius of gyration about a given axis is defined as the root mean square distance of the various clusters the aggregate consists of from the axis of rotation. The definitions and scaling laws of all three descriptors can be found in Eggersdorfer et al.$^{[21]}$ All three descriptors are correlated with the number of primary particles constituting the agglomerates, $n_p$, by a power law:

$$n_p = k_n \left( \frac{r_g}{r_p} \right)^{D_f} = k_m \left( \frac{d_m}{d_p} \right)^{D_m} = k_a \left( \frac{a_a}{a_p} \right)^{D_a}$$  \hspace{1cm} (3)$$

where $D_f$, $D_m$, and $D_a$ are corresponding fractal dimensions, $k_n$, $k_m$, and $k_a$ are corresponding pre-exponential factors, and $r_p$, $d_p$, and $a_p$ are the corresponding radius, diameter, and surface area of the primary particles. The effective fractal dimension of cluster agglomerates typically varies between 1.6 and 2.5. Values at the low end of this spectrum ($< 1.8$) are attributed to primary particle
polydispersity. $D_i$ values $\approx 1.8–1.9$ correspond to agglomerates of relatively open structures, such as those generated by diffusion-limited or ballistic cluster-cluster aggregation. If $D_i$ is larger (>1.9), aggregate sintering is implied; in the extreme case of $D_i = 3$, full fusion has been reached and the particles are compact 3D objects deprived of any fractal-like resemblance.

To determine the progress during agglomerate synthesis, fluid mechanics modeling is typically employed. However, even though the diffusivity and coagulation rate of spherical clusters have been well established for decades (using the Stokes–Einstein and Fuchs equations), those of fractal-shaped agglomerates are more challenging and rely on the development of specific mesoscale models. To this end, atomistic simulation methods have provided valuable input parameters for such models, determining equilibrium structures or sintering times for primary particles.

4.3. Calculated Properties of Nanoparticulated Films

Finally, moving our discussion to an even coarser scale, we will investigate the effect of coalescence on the physical properties of thin films that contain nanoparticles as their elementary building blocks. Nanoparticles have often been described as "superatoms," in the sense that they exhibit specific inherent structure and properties which may be maintained after their incorporation into thin films. However, this is not trivial since nanoparticle deposition is a complicated, random process, which is very sensitive to subtle changes in various parameters such as cluster size or deposition energy. Potential applications for nanoparticulated films include biomaterials, structural and electronic ceramics, catalysts, sensors, etc.

Various parameters can characterize these films, such as:

i) Morphology: for example, flat metallic scaffolds do not enable the adhesion and organization of living cells, but rough, bio-compatible implant scaffolds need to be designed instead.

ii) Porosity: in high surface-area applications such as catalysis, porosity is of utmost importance since it determines both catalytic activity and selectivity. iii) Percolation threshold: in sensors, electron flow is facilitated and electrical signal is amplified through necks formed between sintered clusters, thus minimizing contact resistance.

iv) Degree of epitaxial alignment (either among nanoparticles or between anchored particles and the substrate): catalytic properties depend on the transformation a nanoparticle may undergo as it becomes fully or partially epitaxially aligned to the support. This is most interestingly for our discussion in this review, all these parameters are directly or indirectly associated with nanoparticle coalescence upon deposition.

Historically, the first attempt to describe nanoparticulated thin film formation by cluster deposition utilized a rate theory approach. In general, rate equations compare in a mean-field manner the contributions of various processes that may be simultaneously at play during the evolution of a phenomenon, thus highlighting its sensitivity to kinetic effects. For example, Figure 16 shows the evolution of nanocluster island density as a function of film thickness. The effect of potential nanocluster coalescence is clearly very important. Clear distinction is indicated between static and dynamical coalescence, as represented by coalescencealand self mobile island (--) curves. Reproduced with permission.

More recently, the problem was tackled using atomistic computer simulations. In one of the two articles that proposed and described the CHM, Meinander and Nordlund used MD to study the density of Cu nanoparticle-assembled thin films as a function of particle size and deposition energy. They showed that, as the size of the deposited nanoparticles increased, the density of the produced film decreased (quite rapidly, in fact), due to the empty space left between or underneath them. However, this trend continued only up to a specific size threshold (of clusters containing roughly 1000 atoms); at this point, an upward jump in film density was observed. Meinander and Nordlund associated this jump with nanoparticle coalescence and the associated heating of the clusters (hence, cluster-heating model, CHM). As clusters grew in size, they could no longer readily stick to each other (as verified by the average relative angles between each other), but rather continued their deposition course onwards, filling the gaps in the lower parts of the film, thus reducing porosity and increasing film density. At sizes well above the threshold value, film density remained pretty much constant, near its minimum value, due to the decline of the degree of sintering associated with larger cluster sizes.

Therefore, deposition of particles of substantial sizes can lead to films of varying porosity along the z-direction (i.e., thickness-wise). Singh et al. demonstrated an exemplary case of a porous film grown by cluster beam deposition and subsequent sintering of Ta nanoparticles. Ta particles are prone to oxidation; therefore, soon after deposition they turned into Ta-oxide particles. More interestingly, their degree of oxidation was found to be graded, and in direct correlation with their position in the film; with $Ta_2O_5$ at the top, where the pores were large, TaO near the middle, and pure, metallic Ta clusters near the bottom of the film, where the film was much denser. The variable porosity profile of
Ta nanoparticulated films was recently exploited by Haro et al. for the shadowing effect it caused during RF-sputtering of Si amorphous films, inducing porosity and mechanical heterogeneity in them, which was favorable for Li-ion battery applications.\cite{137}

Consolidation of ceramic nanoparticles towards materials of nanoparticulated morphologies leads to their reduced sintering temperature and improved mechanical properties compared to conventional polycrystalline materials. This is attributed to the high percentage of atoms in-between particles, as a result of their sintering.\cite{138,139} Campbell et al. investigated via MD the consolidation by sintering of nanometer-size amorphous silica clusters into a nanophase silica glass.\cite{140} Utilizing an isothermal-isobaric NPT statistical ensemble, they could vary the pressure thus generating nanophase solids with various densities, ranging between 76% and 93% of the bulk density of amorphous silica (i.e., 2.2 g cm\(^{-3}\)). They found that despite differences between pore sizes and distributions in glasses of different densities, the pores displayed remarkable self-similarity. Two exemplary MD visualization results can be seen in Figure 17a for density values of 1.67 and 2.05 g cc\(^{-1}\). The former structure contains many more pores, including a percolating one occupying 36% of the overall pore volume. The latter structure contains smaller, isolated pores. The average pore radius, \(R\), and pore interface width, \(W\), as a function of pore volume, \(V\), is shown in Figure 17b: it is found that both exhibit power-law behavior, which eventually translates into a common fractal dimension close to \(\approx 2\) and surface roughness exponent \(\approx 0.47\), regardless of density value. Interestingly, the short-range order of the nanophase glass was comparable to that of the bulk amorphous silica glass, but, at a longer scale, the intermediate-range order was quite different. Further, Chatterjee et al. demonstrated for nanophase SiC fabricated by consolidation via sintering of SiC nanoparticles that the elastic moduli of the material also scale with density according to a power law \((\approx \rho^{0.4 \pm 0.11})\).\cite{141}

When metallic nanoparticles are deposited on surfaces at low surface density, low coverage submonolayer films are formed, where little or no attachment is observed among the particles. If coverage is gradually increased (i.e., with extended deposition times), percolating paths may be eventually formed by adjacent particles, usually of irregular shape due to the inherent randomness of the deposition process, resulting in percolating films with remarkable electrical properties.\cite{142} Such films are ideally suited for high surface-to-volume ratio applications such as for sensing devices. In principle, an effective sensor comprises a nanostructured conductor characterized by low currents running through it. In a nanoparticle-based sensor, conductive nanoparticles are deposited onto a dielectric substrate attached to electrodes. If these nanoparticles assemble in a percolating cluster, they form a conductive path between the electrodes. Any detectable change in the overall resistance, as a result of majority carrier density variations due to interaction with specific molecules, produces a measurable signal that enables the detection of these molecules. Since different metallic nanoparticles can react with different molecule species, the detection procedure can be designed to be highly selective. With the selection of an appropriate support, superior sensitivity, selectivity, and response times can be achieved, which, coupled with other favorable properties of the support (e.g., mechanical flexibility or strength), can lead to tangible innovative technologies, that can be readily commercialized and incorporated with existing integrated-circuit technology. For example, Vernieres et al. have recently deposited percolating films of Fe nanocubes on CMOS-compatible microhotplate devices with exceedingly low detection limit (3 ppb) for NO\(_2\) gas.\cite{143} A schematic representation of a nanoparticle-based sensor is shown in Figure 18a, where the substrate surface appears discretized in order to simplify the discussion. Numerals on clusters indicate the chronological order of their deposition: once the 26th cluster is deposited, a percolating path is formed, indicated by the yellow arrow, enabling the flow of electric current between the two electrodes. Most interestingly, according to mathematical percolation theory, the phase transition of a discrete lattice (such as that of Figure 18) from a non-percolating to a percolating state occurs at a very specific critical percolation concentration, \(C_c \approx 0.59\), of occupied sites (in this case, of squares filled with a cluster). An implicit assumption so far in this model is that the effect of nanoparticle coalescence is negligible. If, however, coalescence is included, forcing adjacent clusters to consolidate at least partially, it is clear that the percolation threshold has to be shifted to a higher value, meaning that more clusters are necessary for a conductive path to form between the two electrodes (Figure 18b). Although the presented model is a very crude 2D approximation of a much more complicated 3D process, its message holds true for real systems: the amount of particles required to reach the..
Using variable-charge MD simulations, Ogata et al. studied the sintering of TiO₂ nanoparticles and showed two competing mechanisms owing to dynamic charge transfer: on the one hand, atomic diffusion at the interface was facilitated, especially at high temperatures, promoting the sintering of the particles. On the other hand, once charge was transferred between clusters, a double-charge surface layer was formed in each particle, leading to their repulsion and suppressing their coalescence.¹⁴³

Second, there are applications where being precisely at (or just below) the percolation threshold is key. For example, Fostner et al. investigated devices based on Sn clusters specifically grown so that they would be just below the percolation threshold, where quantum mechanical tunneling is dominant,¹⁴⁴ as also indicated by Ayesh.¹³¹ In particular, Sattar et al. demonstrated switching between well-defined, quantized conductance values, even at room temperature.¹⁴⁵ By application of well-controlled, pulsed voltage sequences, the devices exhibited neuromorphic properties, where groups of connected clusters can be likened to neurons, and tunnel gaps provide switching elements similar to those of brain synapses.¹⁴⁶ The inherent complexity of these nanoparticle networks, exhibiting power-law behavior near criticality, makes them promising candidates for on-chip neuromorphic computation and memristor applications.¹⁴⁷

Another trending field in nanotechnology is the cluster-support interaction of clusters fabricated by cluster beam deposition. It has been shown that when a nanoparticle lands on a specific substrate, a portion of it becomes epitaxially aligned with the substrate, that is, its crystal lattice follows that of the substrate instead of the nanoparticle’s original structure; this may happen even if the lattice-constant mismatch between the two is significant. Yeadon et al., who first reported MD studies on the phenomenon for Ag clusters deposited on a (001) Cu substrate, coined the phrase “contact epitaxy” to describe the final configuration of a partially molten cluster forming an epitaxial interface a few atomic layers thick with the support; an example can be seen in Figure 19.¹⁴⁸ This phenomenon induces strain to the crystal lattice of the nanoparticle changing its shape and electronic structure. In the latter of the two articles that proposed and described the CHM, Järvi et al. described the mechanism of this epitaxial alignment of Cu, Ag, Au, Pt, and Ni clusters on grounds of cluster heating and partial melting; they also defined the cluster size limitations for full epitaxy.⁶⁸ Therefore, even though at first sight this process seems irrelevant to particle coalescence, it can be, in principle, regarded as an extreme case of coalescence between two clusters, one of which (the support) is way larger than the other (the nanoparticle).

5. Disambiguation: A Case of Non-Coalescence

In closing this review on computational studies of nanoparticle coalescence, we consider it would be useful to include a case study where the consolidation of clusters does not constitute coalescence (i.e., hard aggregation) but soft agglomeration instead. We mentioned such an eventuality in Section 4.2 when we discussed about cluster aggregates and aerosols.

For example, subnanometer clusters consisting of a very small number of atoms are of great importance, especially for catalysis applications: on the one hand they have been found

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**Figure 18.** Schematic representation of a 2D lattice analog of a nanoparticle-based device. Nanoparticles are implied to be sequentially deposited (i.e., occupying individual boxes in the lattice), as indicated by the numerals. a) No coalescence included: a conductive path is formed between the two electrodes once the 26th particle is deposited, as indicated by the yellow arrow. b) Coalescence included: no conductive path is formed after the deposition of 26 particles (as indicated by the dashed yellow arrow), since neighboring pairs of clusters partially consolidated, reducing their overall areas and increasing the distances between them.
extremely active, due to all their atoms being on the surface. On the other hand, their containing a precise number of atoms means that their performance can be fine-tuned for their application. The latter also means, however, that the addition or subtraction of even a single atom can have detrimental effect on their catalytic efficiency.\textsuperscript{149} Considering the advantages of increasing the coverage of surfaces with catalytically active clusters without interfering with their structure (i.e., leaving their active sites intact), one immediately understands the threat cluster coalescence poses, leading to potential changes in the clusters’ structures and resultant properties.\textsuperscript{150}

Very recently, Halder et al. reported on the experimental growth of size-selected Cu nanoclusters containing precisely four Cu atoms with remarkable activity in carbon dioxide conversion to C1 fuels.\textsuperscript{17} They also found by in situ X-ray absorption near-edge structure (XANES) spectra analysis that, at high temperatures, the oxidized clusters self-assemble into 2D nanoassemblies, only to disintegrate upon eventually cooling down to room temperature. Clearly, the phenomenon could not be attributed to sintering, since disintegration upon cooling implies soft agglomeration. Using ab initio density functional theory calculations, the authors proposed another possibility for the weak binding of the clusters: hydrogen bonds, formed either directly between the highly polarized clusters, or, more likely, with water molecules acting as binding bridges by forming two hydrogen bonds between neighboring Cu$_4$O$_4$ clusters (see Figure 20). The latter theory could account for all experimentally observed phenomena, such as the counterintuitive dissociation of the cluster agglomerates upon cooling down: since the reaction rate and associated production of water is reduced at low temperatures, the cluster assemblies are depleted of their natural adhesive, which, eventually, leads to their disassembly.

6. Conclusion

With this review on computational studies on nanoparticle coalescence, we tried to cover all important past literature on the field, with a view to its future. We covered various simulation methods and their combinations, and compared theoretical predictions with experimental results. However, we avoided focusing on the methods during the description of the sintering mechanism, to create a single, intuitive narrative that emphasizes the physical procedures taking place. Atomistic simulation showed that the coalescence process is roughly divided into three main steps: i) very fast initial contact and interface formation, ii) fast plastic deformation assisted by the heating due to the free surface annihilation introduced at step (i), and, iii) very slow spherization, mainly by thermal diffusion of surface atoms after the additional heating is dissipated away from the sintering system. These findings are in contrast to previous continuum phenomenological models which predicted a steady-rate process. By discussing in detail the effects of nanoparticle coalescence on bigger structures (such as cluster aggregates or nanoparticulated films) or by including to our review seemingly-irrelevant cases (such as epitaxial alignment of nanoparticles on substrates, or soft-aggregation of subnanometer clusters by hydrogen bonds) we tried to pave the way for coalescence-inspired ideas and mechanisms to be used in a broader context. We aspire to shed new light to nanoparticle coalescence and advocate for its transition from fundamental science to applicable engineering.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

atomistic simulation, coalescence, molecular dynamics, nanoparticles, sintering