MODELLING THE CONDENSATION OF NANOPARTICLES

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The condensation of Ni nanoparticles from the gas phase has been simulated with the help of molecular-dynamics simulations. By variation of the initial density of the metal vapor the formation mechanisms of clusters in different experimental synthesis methods were studied. In the case of a high initial density the formation of realistically shaped particles of several thousands of atoms was observed. In the case of a low initial density the simulations show the experimentally observed decrease of the dimer formation rate with increasing temperature. Moreover, the results indicate that this temperature dependence is caused by changes of the trimer formation rate.

1. INTRODUCTION

Nanoparticles — i.e. particles with diameters in the nanometer range — have interesting physical properties different from the corresponding bulk systems due to their unusual high surface to volume ratios. As these properties might be exploited in technical applications, there is currently a high technological interest to understand the processes governing the formation of nanoparticles. A general introduction into the physics of nanoparticles and nanomaterials can be found, e.g., in reference 1).

There are several established techniques for the synthesis of nanoparticles. Among these techniques gas-phase synthesis methods play an important role as they allow for the production of very small particles of uniform size and pure composition.[2] In order to achieve the gas-phase condensation of nanoparticles, a supersaturated vapor is expanded into an inert-gas atmosphere. Possible methods for the production of the supersaturated metal vapor are the thermal decomposition of a precursor gas in a shock tube,[3] thermal evaporation,[4] or DC sputtering.[5]

In this article we present results from two sets of computer simulations of the condensation of Ni nanoparticles in an Ar atmosphere. The parameters of these simulations were chosen in such a way that they reflect the conditions of different gas-phase synthesis methods.

2. COMPUTATIONAL METHODS

In our work we have performed molecular-dynamics simulations of systems containing a Ni–Ar gas mixture. For the calculation of the interatomic forces between the atoms we have made use of the empirical tight-binding second moment potential of Cleri and Rosato[6] with a hard cutoff radius. In this model the potential energy of the system is given by

$$E = \sum_i \left[-\left(\sum_{j \neq i} \xi_{\alpha\beta}^2 e^{-2q_{\alpha\beta}\left(r_{ij} / r_{\alpha\beta}^0 - 1 \right)} \right)^{1/2} + \frac{1}{2} \sum_{j \neq i} A_{\alpha\beta} e^{-p_{\alpha\beta}\left(r_{ij} / r_{\alpha\beta}^0 - 1 \right)} \right]$$

In this formula, r_{ij} denotes the distance between atoms i and j whereas α and β refer to the species of these atoms. The values of the element specific parameters $\xi_{\alpha\beta}$, $p_{\alpha\beta}$, $A_{\alpha\beta,}$ $q_{\alpha\beta}$, and $r^0{}_{\alpha\beta}$ used in this work are given in Table 1 together with the cutoff radii r_c. In the case of the Ni–Ni interaction these values were directly taken from reference 6). For the Ar–Ar and Ni–Ar interaction, however, we chose our own parameters. Clearly, the tight-binding second moment potential is in general not the best choice for the description of the interactions of inert gases and a Lennard-Jones potential, as used in a similar study by Lümmen und Kraska,[7] might be a better choice. However, the Ni atoms condensate at relatively high temperatures compared to the weak attractive interaction of the inert gas atoms. For this reason and in order to facilitate the calculations, we opted to use one and the same functional form for all interactions. By setting the prefactor $\xi_{\alpha\beta}$ to zero we eliminated the many-body part from the interactions of the Ar atoms. The remaining parameters $A_{\alpha\beta,} p_{\alpha\beta}$, and $r^0{}_{\alpha\beta}$ were then chosen in such a way that the remaining pairwise repulsive potential resembles the repulsive part of the Lennard-Jones interaction.

Table 1: Parameters of the interatomic potentials in atomic units. Values for the Ni–Ni interactions are taken from reference 6). Note that the value q = 1 for the Ni-Ar and Ar-Ar interaction is arbitrary since ξ = 0 in these cases.

	A	ξ	p	q	r^0	r_c
Ni–Ni	2.76349 10^{-3}	0.078641776	16.999	1.189	4.707569	11.095846
Ni–Ar	17.7233	0.0	9.90625	1.0	3.064249	7.22250
Ar–Ar	17.7233	0.0	9.90625	1.0	3.064249	7.22250

The simulations were carried out using standard methods as described, e.g., by Allen and Tildesley.[8] For the initial configurations the atoms were placed on sites of regular lattices inside a cubic simulation box with periodic boundary conditions. Such a regular arrangement could be used without problems since the distances of the atoms were beyond the range of the interactions and the velocities were chosen randomly according to the Maxwell-Boltzmann distribution at an initial temperature T_{i}. The equations of motion were then integrated with the help of the velocity form of the Verlet algorithm using a time step h = 2 fs. An important point for simulations of condensation phenomena is the coupling of the system to a heat bath. Since considerable amounts of binding energy are released as clusters are formed, such a coupling is necessary in order to avoid unphysical temperature increases. In the experimental situation this coupling is provided by the inert-gas atmosphere. In the simulations described in this work we have employed the stochastic Andersen-thermostat method[8,9] to cool the Ar atoms to a given heat-bath temperature. The energy released by the condensation of the Ni atoms is then transferred by atomic collisions to the Ar gas, from which it is removed by the thermostat.

3. RESULTS

3.1. Simulations with high initial densities

Our first set of simulations was designed in order to mimic the conditions in an inert-gas condensation (IGC) cluster source. In such a source the supersaturated metal vapor is produced by thermal evaporation or DC sputtering. This leads to an initially dense metal vapor that subsequently expands into a surrounding inert-gas atmosphere.

In an earlier work[10] we have described simulations of Ni nanoparticles from the gas phase where we have simulated a system of 8000 Ni atoms without any inert-gas atoms and with the Ni atoms directly coupled to an Andersen thermostat. The idea behind this procedure was that the virtual collisions of the Andersen-thermostat would have a similar effect as the atomic collisions between the metal vapor and the inert gas. Although the particles resulting from this simulation showed similar structural features as experimentally produced particles, several problems remained. First of all, the high cooling rate employed in the simulation of reference 10) resulted in the crystallization of relatively small primary particles (≈200 atoms). Moreover, the high cooling rate suppressed possible diffusion mechanism that could have altered the particles shape. Finally, the direct cooling of the Ni atoms by the Andersen-thermostat is somewhat

artificial since it cools all atoms uniformly whereas in the real system, only atoms at the cluster surfaces interact with the inert gas.

In order to overcome the shortcomings described in the previous paragraph, we have performed two simulations with 8000 Ni and 192 Ar atoms where only the Ar atoms were coupled to a heat bath as described in Sec. 2. In the first of these simulations the atoms were placed in a simulation box with a volume V = 4000 nm^3 as in reference 10). In the second simulation the linear size of the box was doubled, i.e. V = 32000 nm^3. As in reference 10) the initial temperature T_i = 700 K and a heat-bath temperature of the thermostat T_f = 77 K were used. The latter value gives partial pressures of the Ar gas of 500 and 63 mbar, respectively. The simulations were each carried out over a period of 5 million simulation steps corresponding to a simulation time of 10 ns.

Not surprisingly, the indirect cooling of the Ni gas by the dilute Ar gas slowed the cooling considerably. It now took simulation times of several nanoseconds in order to condensate and crystallize the primary particles, whereas these processes were completed after approximately 10 ps in the earlier work. Due to the longer time before the crystallization of the particles, more liquid droplets merged leading to strongly increased sizes of the crystallizing primary particles. In the case of the smaller volume only two particles with sizes of approximately 800 and 7200 atoms were left at the time of the crystallization. At the end of the simulation these particles had agglomerated into one single-crystalline particle shown in the left panel of Fig. 1. From this figure it is clear that the two particles have formed a perfect interface. Since the formation of such an interface would not be possible at low temperatures, this result emphasises the importance of a realistic cooling rate in simulations of this kind.

The lower density of the Ni atoms in the second simulation with the bigger simulation box partially counterbalanced the increase of the size of the primary particles caused by the slower cooling rate. For this reason, about ten particles with sizes from 50 to more than 1000 atoms crystallized in this system. At t = 10 ns these particles had agglomerated into three distinct particles with sizes of 147, 1704, and 6149 atoms. The most interesting of these is the largest particle shown in the right panel of Fig. 1. Although its shape is more rounded, this particle shows the same worm-like structure with flat facets along the segments that we have observed in our earlier simulation. As shown in reference 10), this structure compares well with TEM images of experimentally produced particles.

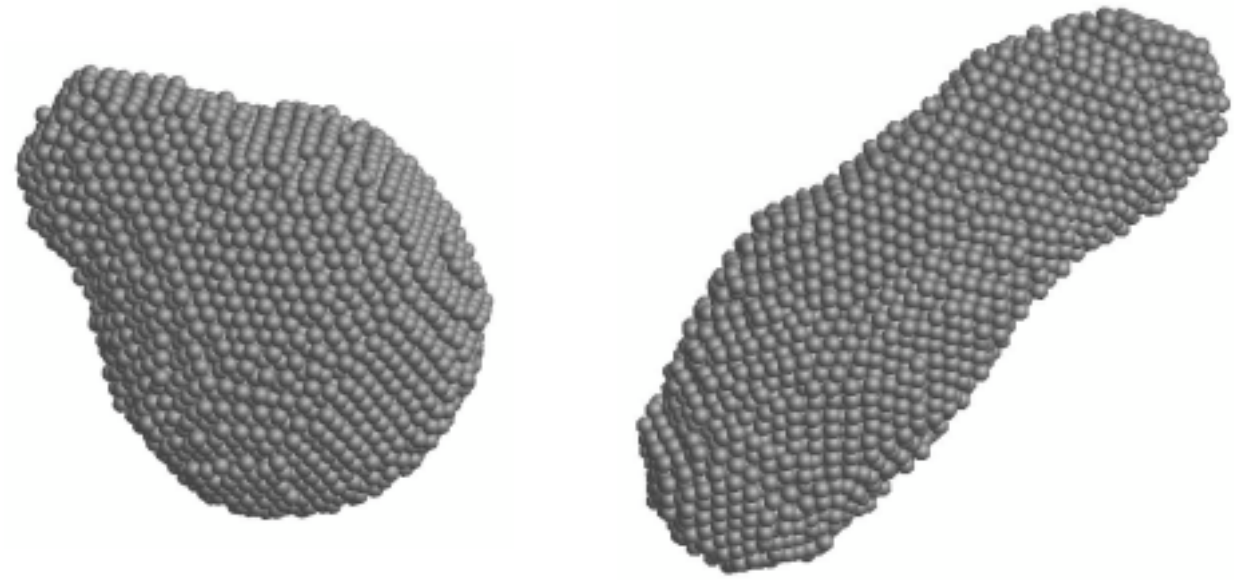

Fig. 1: Agglomerated Ni particles resulting from simulations at high initial Ni density

3.2. Simulations with low initial densities

The simulations described in the previous section are characterized by the fact that the initial density of the metal vapor is much higher than the density of the inert gas and drops during the simulation due to the condensation of the nanoparticles. In contrast to this, we recently began to perform a new set of simulations where the initial density of the metal vapor is much lower than the density of the inert gas. These simulations were inspired by the situation in a shock tube, where the precursor molecules are diluted in the inert-gas atmosphere before their decomposition.

The reduction of the initial density of the metal changes the role of the inert gas considerably. The reason for this is that in order to form bounded pairs of atoms a third collision partner is required that takes away the excess energy. In the case of a high metal density this third atom is in most cases another metal atom. In the low-density limit, however, this gets more and more improbable and collisions between two metal atoms and one inert-gas atom are becoming the dominating dimer formation mechanism.

In this study we simulated configurations of 250 Ni atoms in an atmosphere of 25000 Ar atoms at temperatures T = 500, 600, 800, and 1200 K. The volume of the simulation cells was adjusted in such a way that we obtained a partial pressure of 5 bar for the Ar gas. Clearly, the gas pressures in our simulations are considerably higher than typical experimental values. In Ref. 2), e.g., gas pressures of 0.3 – 0.45 bar containing 30 – 100

ppm Fe are reported. However, simulations at such low pressures are impossible since under these conditions the timescale for the formation of clusters is in the microsecond regime. The important point, on the other hand, is that in our simulations we are in the low-density regime where collisions of Ni atoms with Ar atoms are much more frequent than collisions between two Ni atoms. Therefore, the simulations should at least qualitatively show the most important processes of the cluster formation.

Under the conditions of our simulations the time interval between collisions of two Ni atoms is of the order of 10 ps and the formation of dimers takes place on a nanosecond timescale. For this reason, we did not try to simulate the formation of clusters of thousands of atoms as in Sec. 3.1, but contended ourselves with the observation of the formation of very small clusters of a few atoms during the first 25 ns of the simulation. Longer simulation times would not have been reasonable since at this time the density of free Ni atoms was reduced by 5 to 20 % due to the formation of clusters. Table 2 details the number of clusters produced at the different temperatures.

Table 2: Number of cluster with size N after a simulation time of 25 ns

T (K)	$N = 2$	$N = 3$	$N = 4$	$N > 4$
500	6	2	2	2
600	7	2	0	2
800	5	1	0	0
1200	6	0	0	0

Although the total number of clusters produced in our simulations is rather small, a number of trends can be seen from Table 2. Clearly, the number of clusters produced as well as the number of atoms bound in clusters decrease with increasing temperature. This is in accordance with the experimental observations of reference 2). More interesting, however, is the fact that the number of dimers present in the systems at the end of the simulations is nearly the same for all four temperatures. Together with our observation that the first dimers did not appear significantly later at the higher temperatures, this means that changes of the trimer formation rate are the main reason for the differences in the number of bigger clusters. Finally, Table 2 shows that once trimers are formed in the systems bigger clusters also appear and grow rapidly.

4. CONCLUSIONS

We have performed molecular-dynamics simulations of the condensation of Ni nanoparticles in an Ar atmosphere. Variation of the density of the metal atoms in the initial vapor allowed us to study the formation of nanoparticles under the conditions of different synthesis methods.

By choosing a high initial metal density we investigated the condensation of nanoparticles under conditions similar to those in IGC cluster sources. In these simulations the explicit consideration of inert-gas atoms in the simulations resulted in much more realistic cooling rates and particle sizes than in our earlier work.[10] As in the former simulations the formation of a long worm-like particle was observed, whose shape compares well with TEM images of experimentally produced particles. The formation of a perfect interface between two agglomerated particles underlines the importance of realistic cooling rates in these simulations. For the future we plan to perform similar simulations on bigger systems in order to obtain more final particles.

Simulations with a low initial density of Ni atoms allowed us to study the elementary processes like the formation of dimers under the conditions of a shock tube. Clearly, the results of these simulations have to be regarded as preliminary since the number of observed cluster formations is too low to draw definite conclusions. Nevertheless, the results obtained from these simulations so far, reveal some interesting trends and show that it is worth to continue this work.

The number and sizes of the clusters formed during our simulations in the low density regime show in agreement with experimental observations of the synthesis of Fe particles[2] that the number of clusters as well as the number of atoms bound in clusters decreases with increasing temperature. Our results indicate further that it is the trimer formation rate that is mainly responsible for this trend, although the dimer formation rate is also reduced. A possible reason for this is the kinetic energy of the particles. In principle the formation of a trimer does not necessarily require a third collision partner since the released binding energy can be stored in vibrations of the bonds. With increasing temperature, however, this becomes more and more difficult as the amount of excess energy increases due to the higher kinetic energies of the collision partners. Therefore, at higher temperatures, the collision of a dimer with a Ni atom might more often result in a kick-out event where one of the atoms of the dimer is replaced by the monomer atom. The occurrence of such events could be verified by tracking the identity

of the particles in the clusters during the course of the simulations. This is work in progress.

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REFERENCES

1) A.S. Edelstein and R.C. Cammarata, Nanomaterials: Synthesis, Properties and Applications (Institute of Physics, Bristol).
2) A. Giesen, A. Kowalik, and P. Roth, Phase Transitions **77** (2004) 115.
3) H.J. Freund and S. H. Bauer, J. Phys. Chem., **81** (1977) 994.
4) R.W. Siegel, S. Ramasamy, H. Hahn, Li Zongquan, Lu Ting und R. Gransky, J. Mater. Res. **3** (1988) 1367.
5) S. Stappert, B. Rellinghaus, M. Acet and E.F. Wassermann, J. Cryst. Growth. **252** (2003) 440.
6) F. Cleri and V, Rosato, Phys. Rev. B **48** (1993) 22.
7) N. Lümmen and T. Kraska, Nanotechnology **15** (2004) 525.
8) M.P. Allen and D.J. Tildesley, Computer simulations of liquids (Clarendon, Oxford).
9) H.C. Andersen, J. Chem. Phys. **72** (1980) 2384.
10) R. Meyer, J. J. Gafner, S. L. Gafner, B. Rellinghaus, S. Stappert, and P. Entel, Phase Transitions (submitted).