

## Influence of the carrier gas molar mass on the particle formation in a vapor phase

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The influence of the molar mass of a carrier gas on the formation of nanoparticles in the vapor phase is investigated. The function of the carrier gas atmosphere is the regulation of the particle temperature by collisions with the cluster surface. The aim of this work is to optimize the carrier gas in a simulation in order to mimic a large amount of carrier gas atoms by few gas atoms with effective parameters. In this context the efficiency of the heat exchange with the carrier gas depending on its molar mass is analyzed. As a result one finds for varying molar masses and unchanged interaction parameters a competition between the efficiency and the number of the collisions. For too small molar masses the energy exchange per collision is too small while for too high masses the carrier gas atoms become very slow, decreasing the number of collisions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3204780]

### I. INTRODUCTION

The vapor phase synthesis of nanoparticles usually takes place in an atmosphere of an inert gas. This inert gas is also called carrier gas and is not involved in the particle formation except that it removes the latent heat set free during nucleation and growth. These early stages of particle formation are very difficult to access experimentally. Here molecular dynamics simulation can contribute to the understanding of nucleation, growth, and structure formation of nanoparticles. Zinc particles are of interest in a process for solar hydrogen formation.<sup>1,2</sup> It is possible to suppress reoxidation of zinc to a large extent at certain conditions yielding pure zinc clusters from a supersaturated vapor. This is for example the case when a large excess of carrier gas is present.<sup>3</sup> For a reliable mapping of such systems by molecular simulation, an explicit carrier gas has to be used, which removes the heat from the forming clusters. This is because thermostats that are directly applied to the condensing substance can cause artificial effects. A problem of a carrier gas thermostat is the additional computing time required for the simulation of the carrier gas atoms. In experiments the amount of the carrier gas is often much higher than the amount of metal atoms. Consequently most of the simulation time would be used for the simulation of the carrier gas if the same carrier gas to metal atoms ratio is used as in the experiment. In this context it is desirable to increase the efficiency of the carrier gas for the heat exchange with the clusters.

During nucleation latent heat is set free, which heats up the forming clusters above the temperature of the vapor phase. Intuitively one expects that this reduces the nucleation rate compared to a perfectly isothermal nucleation, i.e., heat is removed instantaneously. The effect of the amount of carrier gas on the nucleation and particle formation has been analyzed in several investigations on metal particle

formation.<sup>4,5</sup> Instead of increasing the amount of carrier gas, one can also increase the efficiency of the heat exchange by varying the molar mass of the carrier gas atoms. The effect of the carrier gas on the nucleation rate has been discussed by Feder *et al.*<sup>6</sup> in a review on nucleation theory. In their treatment the carrier gas is not an ensemble of molecules or atoms, it is rather effectively included by its properties such as heat capacity or impingement rate. The resulting expressions for the nonisothermal nucleation rates of Feder *et al.* is<sup>6</sup> given by

$$J_{\text{noniso}} = J_{\text{iso}} \frac{b^2}{b^2 + q^2}, \quad (1)$$

The impingement of molecules of the nucleating substance and of the carrier gas leads to the addition of energy and to the addition of energy fluctuation. The energy  $q$  is released during the addition of a monomer to the cluster and  $b^2$  is the mean square energy fluctuation of the impingement

$$q = h - \frac{k_B T}{2} - \sigma \frac{\partial A(n)}{\partial n}, \quad (2)$$

$$b^2 = \left( c_V + \frac{k_B}{2} \right) k_B T^2 + \frac{\beta_c}{\beta} \left( c_{V,c} + \frac{k_B}{2} \right) k_B T^2. \quad (3)$$

Here  $\beta$  and  $\beta_c$  are the impingement rates of the nucleating substance and the carrier gas, respectively,  $c_V$  and  $c_{V,c}$  their molecular heat capacities,  $h$  is the molecular latent heat of the nucleating substance, and  $\sigma \partial A(n)/\partial n$  is the work required to increase the surface by adding a monomer. Feder *et al.* estimated values for the nonisothermal factor value in Eq. (1) ranging from 0.2 to 0.01 in case of small carrier gas concentration.

Later Barret *et al.*<sup>7</sup> developed a model describing the effect of a carrier gas on the nucleation rate based on changes in the energy distribution of clusters due to collisions with a carrier gas. They obtained an expression, which

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is somewhat similar to the expression of Feder *et al.* and includes the masses of the nucleating molecules and that of the carrier gas. If only the molar mass of the carrier gas is varied and the interactions are kept constant, one can simplify the equation of Barrett *et al.* to

$$J_{\text{noniso}} = J_{\text{iso}}(c + dm_g^{-0.5}). \quad (4)$$

Within this expression one finds that for a small molar mass of the carrier gas  $m_g$  the nucleation rate should become higher. This is because the system cools down faster with a light gas and the lower the temperature the higher the nucleation rate.

Tang and Ford<sup>8</sup> investigated by molecular dynamics simulation the influence of a helium carrier gas on the evaporation of small argon clusters and found that the carrier gas has little influence on the evaporation rate. Via the potential of mean force they also found that a carrier gas stabilizes a cluster. In a recent work Yasuoka and Zeng<sup>9</sup> investigated the influence of the carrier gas on the vapor phase nucleation of Lennard-Jones systems by molecular dynamics simulation. They found that the nucleation rate actually increases with the amount of carrier gas, which is explained by an excluded volume effect. The molecules of the nucleating substance have less free volume and hence a higher density. Probably this is an effect taking place at high densities where the addition of a carrier gas has a stronger influence on the free volume than in dilute gases. Yasuoka and Zeng<sup>9</sup> found that the attraction parameter between the nucleating substance and the carrier gas influences nucleation. However they observed the adsorption of carrier gas molecules at the cluster surface, which influences the results in so far as the adsorbed carrier gas atoms are coupled to a thermostat and the cluster of the nucleating substance is coupled to the adsorbed carrier gas atoms. In this way the thermostat influences the cluster indirectly. In the investigation here the temperature is always high enough that no carrier gas atoms adsorb at the zinc cluster surface to exclude such possible effects.

Wedekind *et al.*<sup>10</sup> investigated the influence of the amount of the carrier gas helium on the argon nucleation rate and found a factor of 1.7 between the Ar:He ratio 1:1 and 1:3. In case of zinc nucleation even a smaller effect of the carrier gas argon has been found for Ar:Zn ratios ranging from 0.5:1 to 8:1.<sup>4</sup> This is probably because the latent heat is very high for zinc and it requires much more carrier gas to remove this heat. Therefore one needs a much larger variation of carrier gas concentrations to see a significant effect in case of metals. Furthermore, Wedekind *et al.* found that a direct thermostat such as velocity scaling or Nose–Hoover thermostat does not affect the nucleation rate significantly.<sup>10</sup> However, they also wrote that this conclusion may not be valid in case of nucleating systems with a very high latent heat such as metal vapor nucleation discussed here and in earlier papers.<sup>4,11,12</sup> If one employs a velocity scaling thermostat for metal vapor nucleation, one obtains a “frozen” vapor phase, i.e., due to the strong heating up of the forming clusters the monomers are strongly cooled down that they do not move anymore.<sup>13</sup> In that work Erhart and Albe<sup>13</sup> investigated the Berendsen thermostat, the Nose–Hoover thermostat, and the stochastic Andersen thermostat. All these ho-

mogenous thermostats turned out to be not useful for the nucleation of strongly interacting systems. Nose–Hoover and Berendsen lead to freezing monomers while Andersen significantly overestimates the monomer consumption. The cluster has no chance to heat up as in a carrier gas and therefore the shape of the resulting particles is far from being realistic. In such strongly interacting systems, the isothermal approximation, as represented by homogenous thermostats, is just not reasonable. Wedekind *et al.* also discussed the influence of the molar mass of the carrier gas in the nucleation rate using the theory of Feder *et al.*<sup>6</sup> and found that a light gas should be more efficient for thermalization than a heavy one. They speculated that the number of collisions, which is higher for a light gas, is responsible for this counterintuitive effect. In a work by Westergren *et al.*<sup>14</sup> the effect of the Lennard-Jones parameters and the molar mass on the energy exchange during a collision has been analyzed in detail. It has been found that the efficiency of the energy exchange increases with the molar mass. This seems to contradict the result of nonisothermal nucleation theory or at least suggest that the present versions of nonisothermal nucleation theory do not include all effects.

In order to investigate the influence of the molar mass of the carrier gas separately, i.e., independent of the interaction parameters, we here vary only the molar mass but maintain the Lennard-Jones interaction parameters of argon. The molar mass of such pseudoargon carrier gas is varied from 0.1 to 160 u. In addition we use other noble gases from helium to xenon with their unique molar masses and Lennard-Jones parameters as carrier gases for comparison.

## II. METHOD

The molecular dynamic simulation method and software is described in detail earlier.<sup>4,15</sup> All simulations are performed with a leap frog algorithm with a time step of 2 fs, which is small enough to conserve the energy in runs up to at least 256 ns. In case of very light carrier gas masses, it was necessary to use smaller time steps (0.1–0.5 u: 0.5 fs, 5–20 u: 1 fs, >20 u: 2 fs) to conserve energy because of their high velocity. At the beginning of the simulation all zinc atoms are placed on a simple cubic lattice. The lattice constant is larger than the interaction range of the zinc atoms avoiding artificially formed clusters at the beginning of the simulation. No influence of different initial configurations on the course of the simulation is found because the system remains in a metastable vapor phase for sufficient time to lose any correlation with the initial state. Using a carrier gas thermostat corresponds to the NVT ensemble in the long time limit, but here rather the transient phenomena of particle formation are of interest. The zinc-zinc interaction is modeled by an embedded atom method (EAM) parametrization, which mimics the multibody effects in metals.<sup>4</sup> The interaction between the carrier gas atoms is modeled by the Lennard-Jones potential using the parameters of argon, namely,  $\epsilon_{\text{Ar}}/k_B = 120$  K and  $\sigma_{\text{Ar}} = 0.3405$  nm. Lorentz–Berthelot combining rules are employed for the binary interaction. This requires in addition Lennard-Jones parameters for zinc, but it should be noted clearly that these parameters

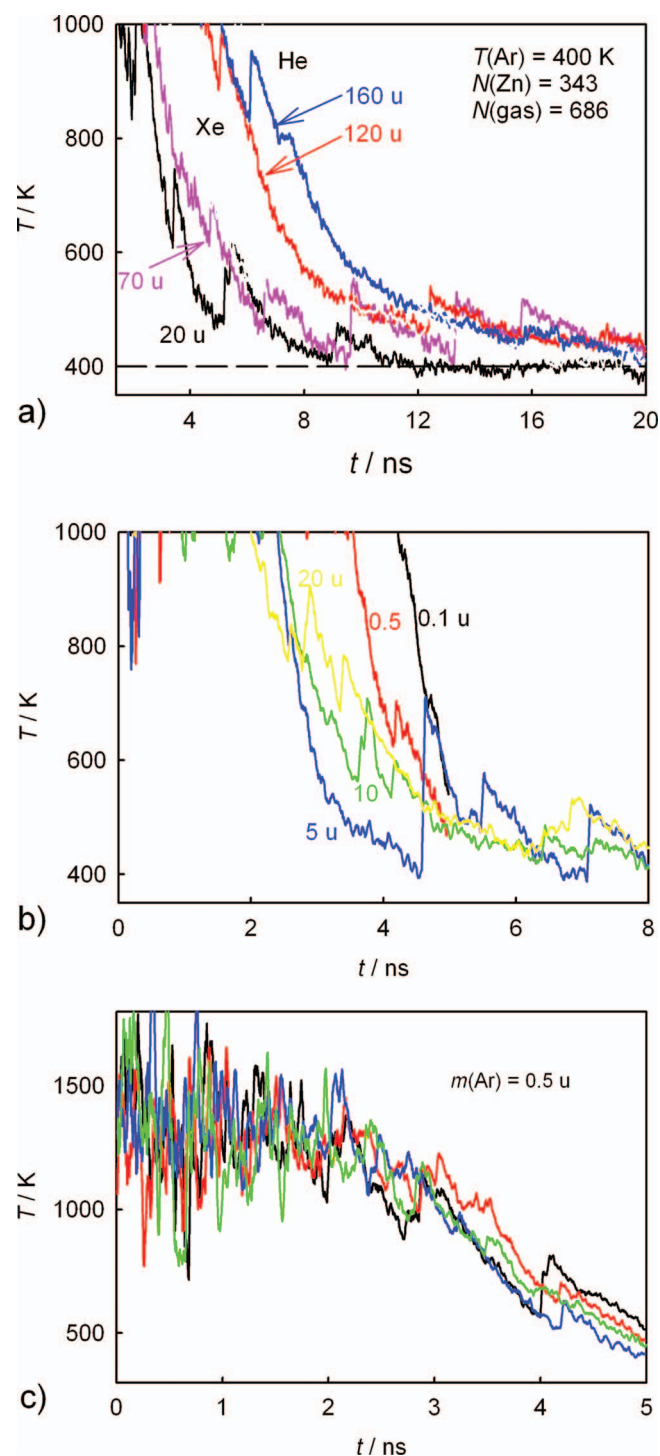


FIG. 1. (a) Temperature of the largest cluster plotted vs the simulation time for various pseudoargon carrier gases, xenon and helium for representative runs. All other noble gases give similar curves as for Xe. The molar mass is indicated by the number at the curves. (b) Representative runs for the comparison of various low weight pseudoargon carrier gases. (c) Check of reproducibility exemplary for four independent runs with the same carrier gas. Note that the time scale of the diagram is only 5 ns.

are only used for the metal-carrier gas interaction required for heat exchange. We therefore fitted the Lennard-Jones potential to the effective pair potential obtained from the EAM potential yielding  $\varepsilon_{\text{Zn}}/k_B = 2204.8\text{ K}$  and  $\sigma_{\text{Zn}} = 0.20\text{ nm}$ . Metal clusters are detected using the Stillinger criterion<sup>16</sup> with a small distance value of 0.205 nm corresponding to

$1.025\sigma_{\text{Zn}}$ . Atoms that are closer than this distance are counted to a cluster. This cluster definition is most reliable for strongly interacting metal systems as shown earlier.<sup>4</sup> The ratio of metal atoms and carrier gas atoms is 1:2 in all simulations.

### III. RESULTS

In a detailed investigation of the heat exchange between metal clusters and atomic carrier gases it has been found that the energy exchange in a collision of a single atom with a cluster increases with the molar mass of the carrier gas.<sup>14</sup> That would suggest that a carrier gas consisting of heavy atoms leads to a faster removal of heat and the nucleating system would cool down faster. However, the variation of the molar mass in particle formation simulations shows the opposite trend as one can see in Fig. 1(a) showing representative runs. The curves in Fig. 1(a) are growth curves by means of the temperature of the largest cluster in the system. During nucleation and growth latent heat is set free and the cluster heats up significantly due to the strong Zn–Zn interaction. As carrier gas pseudoargon is employed, i.e., argon with different molar masses but the same Lennard-Jones parameters. In the series shown in Fig. 1(a) the most efficient carrier gas turns out to be pseudoargon with the molar mass of 20 u. With increasing molar mass the largest cluster cools down significantly slower. For even lower molar masses ranging from 20 to 0.1 u, we found a change in this trend [Fig. 1(b)]. From 20 to 5 u the heat is removed faster but, for 0.5 and 0.1 u, it becomes slower again. In order to check the uncertainty of the simulation, we performed several independent simulations at the same conditions. In Fig. 1(c) a series of simulations with pseudoargon with 0.5 u are shown as an example. It should be noted that the time scale is only up to 5 ns in Fig. 1(c) but one can see that the variation of the curves obtained from these reproduction runs is significantly smaller than the changes due to the molar mass. Hence the overall most efficient carrier gas here is pseudoargon with a mass of the order of 5 u. It should be noted that this optimum value depends on the system and may be different for other metals. To cool down the largest cluster to, for example 600 K, it takes approximately 3 ns for 5 u, 6 ns for 70 u, and 9 ns for 160 u. Since there is a change in the effect of the molar mass on the heat removal, there must be opposing effects. In order to analyze these effects we calculate the number of collisions of the carrier gas atoms with the cluster. One can calculate the average time  $\tau_{\text{gas,cl}}$  between two collisions of inert gas atoms with the zinc cluster by<sup>17</sup>

$$\tau_{\text{gas,cl}} \approx \frac{1}{pR^2} \sqrt{\frac{mk_B T}{8\pi}}. \quad (5)$$

The pressure  $p$  can be approximated by the ideal gas law using the number  $N=686$  of inert gas atoms and the simulation box volume  $V=a^3$  with the edge length  $a=17.5\text{ nm}$ . This yields<sup>18</sup>

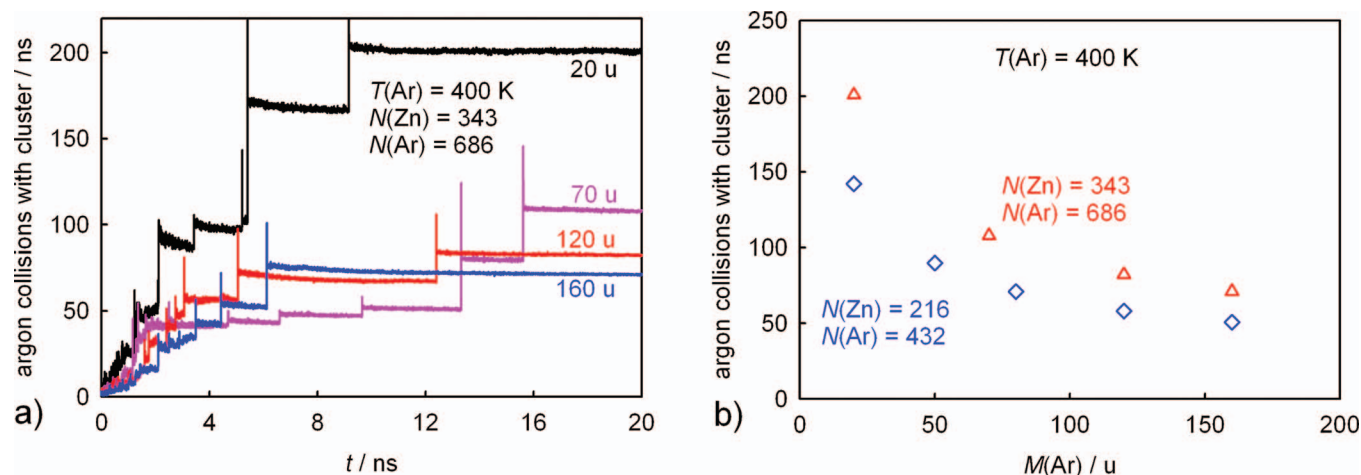


FIG. 2. (a) Number of collisions of argon atoms with the largest cluster during growth. (b) Number of collisions of argon atoms with the largest cluster after the cluster has reached his final size ( $t=20$  ns).

$$\tau_{\text{gas,cl}} \approx \frac{a^3}{NR^2} \sqrt{\frac{m}{8\pi k_B T}}, \quad (6)$$

where  $R$  is the cluster radius,  $T$  is the temperature of the carrier gas (400 K),  $m$  is the mass of the pseudoargon atoms, and  $k_B$  is the Boltzmann constant. Since the cluster radius increases during growth simulations, we have not a fixed value for  $R$  in Eq. (6). Instead we evaluate Eq. (6) using the cluster radius at each time step. The estimated number of collisions per nanosecond is plotted in Fig. 2(a) as function of the simulation time for some representative runs. Reproduction runs have been omitted in the figure for better visibility of the curves. The number of collisions increases with decreasing carrier gas mass. It appears that the slowing down of the carrier gas atoms with increasing mass dominates the overall heat exchange while the influence of the molar mass on the efficiency of the energy exchange of a single collision plays a minor role. The effect becomes larger with rising cluster size as one can see in Fig. 2(b) showing the results for two different cluster sizes. Since the carrier gas density in both systems is the same, the factor  $a^3/N$  is also the same. Therefore the difference in the number of carrier gas-cluster collisions is related to the cluster radius  $R$  only. Actually, the number of collisions per nanosecond is proportional to the square of the cluster radius  $10^{-9}/\tau_{\text{gas,cl}} \propto R^2$ . Hence, the low efficiency of a heavy pseudoargon carrier gas can be explained by the dependence of the argon atom velocity on the molar mass. The higher the mass, the slower the atoms and hence less collisions with the cluster happen in a given period of time. On the other hand, when the molar mass becomes too small, the inefficient energy exchange per single collision dominates and the overall efficiency decreases again. This leads to an intermediate, most efficient molar mass of pseudoargon, which is of the order of 5 u for the system investigated here.

The variation in the molar mass while keeping the interaction parameters of argon unchanged is a possibility to make the simulation more efficient. If one uses other gases having different molar masses such as helium or xenon, one finds a different behavior. This is because other gases have

not only other masses but also other Lennard-Jones interaction parameters. The resulting effective heat transfer is the result of the combination of all three parameters. We analyzed the gases helium, neon, argon, krypton, and xenon. For these gases, with the exception of helium, the temperature curves are very close. As an example the temperature curve for xenon is added in Fig. 1(a). The reason is that the effects of molar mass and interaction parameters appear to compensate for these noble cases. The only exception is helium, which removes the latent heat much slower than the other gases [Fig. 1(a)]. Hence the efficiency of the simulation method does not change much if one uses another carrier gas than argon except of helium. Another way, at least in simulation, is to reduce the molar mass while keeping the Lennard-Jones parameters at constant at the argon values.

So far we only focused on the temperature of the largest cluster; for further analysis we also need the temperature of the vapor phase monomers. It is plotted in Fig. 3(a) for various pseudoargon masses in the period of time in which nucleation takes place. The monomer phase heats up because prior to nucleation clusters are formed that partially evaporate again. The evaporated monomers heat up the monomer vapor phase. On the left side of Fig. 3(a) the highest monomer temperature is for 160 u followed by 120, 70, and 20 and 10 u, which almost coincide. The monomer temperature for 0.5 u starts later because the onset of nucleation is somewhat later. However, the temperature value is always the highest. One might argue that the lower efficiency is a result of the shifted onset of nucleation by 0.4 ns in case of 0.5 u. However, the shift between 5 and 0.5 u is of the order of 2 ns [Fig. 1(b)] and is therefore significantly larger. The fact, that for 0.5 u the onset of nucleation is later and is actually a result of the lower efficiency of the 0.5 u carrier gas. In conclusion the effect of the carrier gas on the cooling down and the onset of nucleation is correlated and the resulting efficiency of the complete process is of interest. So the trend described above can also be observed for the monomer temperature but after some time the monomer temperature curves cross and coincide more or less in a range from 450 to 550 K with the exception of 0.5 u. For comparison also the

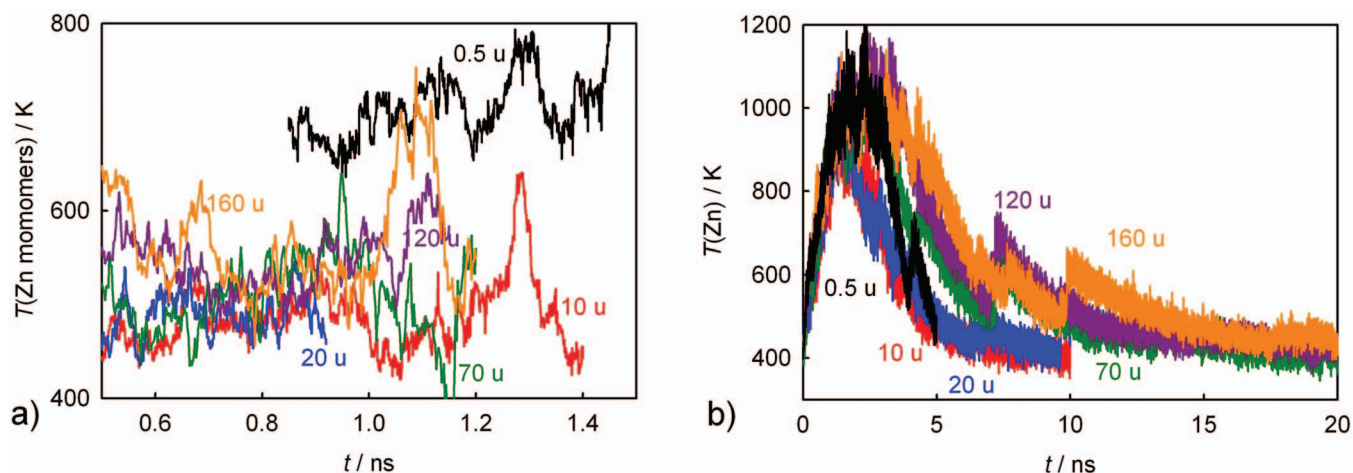


FIG. 3. (a) Temperature of the zinc monomers in the vapor phase plotted in the period of time of nucleation. (b) Temperature of the complete zinc subsystem (monomers and all clusters) as function of the simulation time. The temperature of the carrier gas is 400 K.

temperature of the complete zinc system including the monomers and all clusters is plotted in Fig. 3(b). These data are not smoothed because the total number of zinc atoms is high enough to get relatively small fluctuations of the temperature. The temperature rises at the beginning due to the formation of the first small and then growing clusters. The temperature decreases again when the heat removal dominates the latent heat of nucleation. Jumps in the curves such as for 160 u at 10 ns are cluster-cluster collisions leading to coalescence. The general trend of the influence of the molar mass of the pseudoargon carrier gas is hence also visible for the temperature of the complete zinc system.

In order to calculate the supersaturation the average temperature of the monomers in the period of nucleation is calculated. The zinc partial pressure is calculated from the ideal gas law using this averaged monomer temperature, the box size, and number of zinc atoms. The vapor pressure at the same temperature is calculated from a correlation equation.<sup>19</sup> The supersaturation is then given by  $S = p(T) / p_{\text{vap}}(T)$ . In Fig. 4(a) the nucleation rates obtained in several reproduction runs are plotted versus the mass of the pseudoargon carrier gas. The variation of the nucleation rate is about half order of

magnitude and within this variation no trend is visible. However, there are changes in the supersaturation as one can see in Fig. 4(b). While there is only a small change in  $\lg(J)$  we get a variation in the nucleation rate over several orders of magnitude. Starting from the highest mass the supersaturation rises with decreasing mass to 10 u. The supersaturation for 5 u jumps to much lower values again, which is related to the slow heat removal and hence high monomer temperature.

#### IV. CONCLUSION

We analyzed the effect of the molar mass of a carrier gas on the heat exchange in metal particle formation from the vapor phase based on a large number of simulation runs. To isolate the effect of the molar mass, pseudoargon was used. i.e., different molar masses but the same interaction parameters. As result we find a competing effect of the efficiency of the heat exchange of each single collision of a carrier gas atom with a cluster and the number of collisions. A high molar mass gives a high energy exchange but also a low number of collisions. Therefore there is an optimum molar mass of pseudoargon, namely, around 5 u for the system

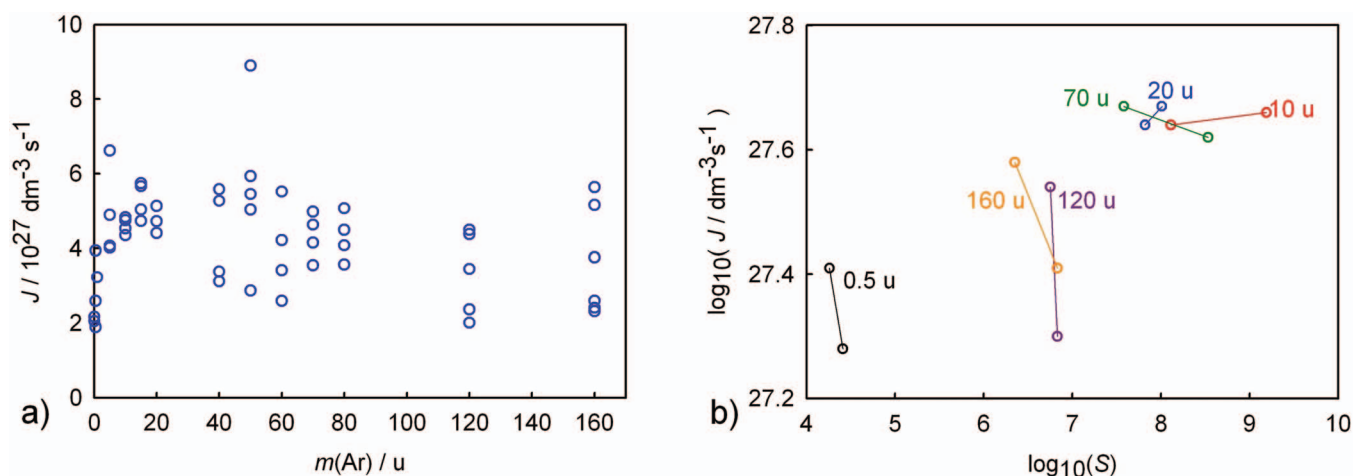


FIG. 4. (a) Nucleation rates for different mole masses of pseudoargon. For each mole mass several simulations have been done to show the uncertainty of the simulation results. (b) Double logarithmic plot of the nucleation rate vs the supersaturation. The temperature of the carrier gas is 400 K.

investigated here. For higher molar masses, the efficiency decreases due to the smaller number of collisions, while for lower masses the efficiency decreases due to the small efficiency of each single collision. Consequences of this investigation may be the improvement of nonisothermal nucleation theory to include both competing effects but also the speed up of molecular dynamics simulation using a carrier gas. Instead of using a larger amount of carrier gas requiring more computational power, one can use a light pseudoargon carrier gas.

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