Molecular Dynamics Study of Nanoparticle Evaporation and Condensation in a Gas

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Evaporation and condensation rates are investigated for small clusters and nanoparticles in the presence of a gas by using classical molecular dynamics. The effects of the initial cluster temperature and size, as well as of the gas temperature and density are analyzed. The surrounding gas characteristics are found to strongly affect the cluster evolution. The obtained simulation results are analyzed based on the collision rate and on the Rice, Ramsperger, and Kassel theory.

1. Introduction

The synthesis of nanoparticles with the desired properties represents one of the challenging issues for modern nanotechnology. The properties of nanoparticles are typically size-dependent, so that it is crucial to obtain nanoclusters with a desired mean size and/or cluster size distribution. In many techniques, nanoparticles are formed in a gas or a plasma environment (so-called “aggregation sources”, plasma source, or laser ablation source). A better understanding of the physical and chemical processes that affect the time-evolution of the nanoclusters in the presence of a gas is, thus, particularly important for further development of these techniques.

So far, only several theoretical models were proposed to explain the growth of nanoparticles. For instance, such models as the model of Rice, Ramsperger, and Kassel (RRK) and the Classical Nucleation Theory (CNT) were used in many studies. An alternative approach that can be successfully used for the investigation of the condensation-evaporation processes in small systems is based on the molecular dynamics (MD) method. In this method, molecular movement and interactions are simulated directly and one can easily study system dynamics. Therefore, MD was also used to study the formation and evolution processes of clusters of many materials, and the advantages of this approach were demonstrated.

Laser ablation was shown to be a possible technique for nanoparticle synthesis. To describe this process, combinations of the MD simulations with the Direct Simulation Monte Carlo (DSMC) calculations were developed. In these combined models, the MD part described the initial stage of laser ablation, including laser light absorption, energy relaxation, and laser-ablated plume formation through the ejection of molecules and clusters. Then, the longer time-scale DSMC method was used to model the expansion of the ejected plume. In these calculations, as in experiments, large clusters were observed in the region adjacent to the target surface, medium clusters were mostly present in the middle of the plume, and small clusters and monomers were found in front of the plume.

Herein, we study the evolution of clusters in the presence of the same gas species. The study focuses on the influence of the surrounding gas and cluster parameters on the time evolution of clusters and small molecules formed in typical laser ablation experiments. The cluster parameters, such as cluster temperature and size, are chosen based on the cluster properties found in the ablation calculations. In the same way, the corresponding characteristics of the surrounding environment, such as gas density and temperature, are set to represent the ablated plume. Calculations are performed for two different materials, molecular matrix and metal. The roles of both simulation parameters and material properties are investigated. The applicability of the RRK theory is verified.

2. Simulation Details

In the present calculations, classical molecular dynamics is used. In this technique, the system evolution is obtained by solving Lagrangian equations for a system of particles with forces calculated based on the interaction potential. Because the interaction potential differs for different material properties, we consider two different systems. The first system is a molecular cluster in the presence of a background molecular gas. This system represents typical target materials used in such techniques as matrix-assisted laser desorption–ionization (MALDI) and in matrix-assisted laser deposition of polymers and biological molecules. To describe the molecular material, we use the breathing sphere model that was previously developed. In this model, the parameters of the intermolecular potential are chosen to represent the van der Waals interactions in a molecular solid. The Morse potential is chosen to represent the intermolecular interaction as follows:
where $r_{ij} = |r_i - r_j| - R_i - R_j$ is the distance between edges of breaching spheres, $d_0 = 3 \, \AA$, $\varepsilon_0 = 0.1$ eV and $\alpha = 1 \, \AA^{-1}$. The interaction parameters are chosen to reproduce the properties of a molecular solid with a cohesive energy of 0.6 eV, an elastic interaction parameters are chosen to reproduce the properties of metals, we consider a second system by considering a nickel cluster surrounded by a gas of the same atoms. The effective Embedded Atom Model (EAM) potential is used in these calculations. This force field contains two terms: first, a delocalized electrons to the energy, which is modeled by an effective Embedded Atom Model (EAM) potential in nickel cluster surrounded by a gas of the same atoms. The nanoparticles are used in many applications based on their either optical (plasmonic) or chemical (sensing) properties. To compare the calculation results obtained for molecular material and for metals, we consider a second system by considering a nickel cluster surrounded by a gas of the same atoms. The effective Embedded Atom Model (EAM) potential is used in these calculations. This force field contains two terms: first, a pairwise additive interaction of the atomic cores shielded at short interatomic distances; and second, a contribution $F[\rho]$ of delocalized electrons to the energy, which is modeled by multibody term assuming a linear superposition $\rho_i$ of atomic electron densities $\rho_i$. The energy of an atom $i$ can be written as follows:

$$ E_i = F[\rho_i] + \frac{1}{2} \sum_{\langle ij \rangle} \phi_{ij}(r_{ij}) $$

The subscripts $i$ and $j$ run over the number of atoms $N$ in the system. A cutoff radius of 0.53 nm is used for the electron density and the pair potential contribution to the $Ni-Ni$ interaction.

First, we build a cluster of $N$ particles with the initial temperature $T_0$. Then, a background gas is generated based on the gas number density and temperature. The volume of the cell is constant and equals to $100 \times 100 \times 100 \, \text{nm}^3$. Periodic boundary conditions in all directions are imposed. After generating the gas, each gas particle is given a velocity based on the Maxwell–Boltzmann distribution with a given gas temperature. Then the cluster is located in the center of the cell. Thus, we can vary four basic parameters: two for the cluster (initial temperature and size) and two for the gas (temperature and density).

In the calculations, we monitor the following processes (i) simple collision,

$$ A_i + A \xrightleftharpoons{v_{\text{coll}}} A_i + A $$

with the collision rate $v_{\text{coll}}$; and (ii) evaporation and condensation processes,

$$ A_i + A \xrightleftharpoons{v_e,v_v} A_{i+1} $$

with rates $v_e$ and $v_v$ respectively. The $v_e$ (or $v_v$) rate is calculated as the ratio of the number of evaporated cluster molecules (or condensated gas molecules on the cluster) with the time step $\delta t$. This time step is sufficiently larger than the MD calculation time step (1 fs for nickel and 5 fs for molecular material) and on the order of 50 ps. Calculations typically continue until about 3 ns. This time delay is long enough for the establishment of a dynamic equilibrium between the evaporation and condensation processes. This condition corresponds to $\sim 2$ ns in the present calculations.

To determine the number of cluster molecules, we use the neighbor list method. Before the simulation, cluster and gas molecules are marked in a different way. Then, the neighbor list data are updated every 25 fs, and the cluster molecule list is updated every 50 ps. If a molecule belongs to a cluster at the last step, but it is not in its new neighbor list, then the molecule is evaporated and the number of the evaporated molecules, $N_{\text{evap}}$ is increased (inversely for the recombination).

The cluster evaporation process can be described as unimolecular thermal decomposition process by using the RRK theory. In the RRK theory, the evaporation and the condensation of clusters are controlled by the sublimation energy $D_n = E_n - E_{n-1}$, where $E_n$ is the absolute binding energy of the cluster with $n$ molecules. The evaporation rate is defined as follows:

$$ v_e^{\text{RRK}} = v_0 g_n \left[ \frac{E_n - D_n}{E_n} \right]^{n-1} $$

where $v_0$ is the typical molecular vibrational frequency, $v_0$ is the number of vibrational degrees of freedom (1 for dimers and 3N − 6 for larger clusters), $g_n$ is the number of surface molecules and $D_n$ is the molecular evaporation energy. For clusters larger than 50 molecules in size, the evaporation rate can be approximated by,

$$ v_e^{\text{RRK}} = v_0 g_n \exp \left[ - \frac{D_n}{E_n} \right] $$

For large clusters, we use the following approximations:

$$ g_n = (36\pi)^{1/3}(N^{1/3} - 1)^2 $$

$$ D_n = 0.6 - 0.73(N^{2/3} - (N - 1)^{2/3}) $$

where Eq 6 is determined for the molecular material. In addition, we can approximate the condensation rate by the collision rate of monomers with the cluster,

$$ v_c = c\pi(r_0 + r_n)^3 \rho $$

The average thermal velocity of the monomers in the gas is $c = (8k_B T / \pi m)^{1/2}$, where $\rho$ is the monomer density, $k_B$ is Boltzmann’s constant, $T_g$ is the gas temperature, and $m$ the molecular mass, $r_0$ and $r_n$ are the hard sphere equivalent radius of a monomer and a cluster, respectively. In this expression for the condensation rate, we approximate the cross section by the surface area of a sphere of radius $r_n$ and assume unit sticking probability upon collision. The hard sphere equivalent radius is calculated based on the gyration radius of the cluster $r_{\text{gyr}}$.29
\[ r_n = \sqrt{\frac{5}{2} r_{gr}^3 + r_0} \]  

For larger molecular cluster, we use the following approximation:\(^2\)

\[ r_n = (3.28 \cdot N^{1/3} + 0.779) + r_0, [\text{Å}] \]  

To compare the calculation results with the RRK theory, we calculate the evaporation and condensation rates for a set of simulation parameters (cluster size and temperature and gas density and temperature and interatomic potentials) that corresponds to the typical laser applications, such as matrix-assisted desorption-ionization (MALDI) and laser ablation experiments.\(^30,31\)

### 3. Results and Discussion

A series of calculations are first performed for a molecular cluster with different initial size. Calculation results demonstrate that both evaporation and condensation rates increase with initial cluster size (Figure 1). The size dependencies are fitted by a polynomial function with the same order of the size function in theoretical rates. Theoretical fits agree with our results. The evaporation and condensation rates are larger than \(10^{11} \text{s}^{-1}\) for clusters of around 200 molecules and larger than 2.0 \(\text{10}^{11} \text{s}^{-1}\) for \(N > 1200\) molecules.

In addition, the Gibbs free energy is often used to describe transitions from the vapor state to the liquid state.\(^32\) This energy is associated with the creation of a new surface, and in the liquid drop approximation,\(^33\) the Gibbs free energy is as follows:

\[ \Delta G = 4 \pi r^2 \sigma - \frac{4}{3} \mu^2 R^3 \rho T \log S \]  

where \(r\) is the cluster size; \(\sigma\) is the surface tension (Laplace law\(^34\)); \(\mu\) is the molar mass; \(R\) is the gas constant; \(T\) is the cluster temperature; and \(S\) is the supersaturation degree (vapor pressure divided by the saturation pressure). Figure 1(c) shows the free energy for molecular cluster as a function of cluster size. In our simulations, gas temperature is larger than the boiling point (\(T_{\text{boil}} = 500 \text{K}\) at \(P = 0 \text{ Pa}\)). At this temperature, the Gibbs free energy linearly increases with the number of molecules in the cluster for clusters composed of more than 200 molecules.

Then, similar calculations are performed for the second system. The calculated results reveal rather similar trends for nickel clusters (Figure 2). Here the evaporation and condensation rates are larger than 1.2 \(10^{11} \text{s}^{-1}\) for cluster containing around 500 atoms and larger than 2.0 \(10^{11} \text{s}^{-1}\) for \(N > 1200\) atoms. The similarity observed for molecular and metallic materials can be explained by the role of collisions between the cluster and the surrounding gas.

Furthermore, we vary the initial cluster temperature, keeping other initial parameters equal to those in the previous series of calculations. Simulations results demonstrate that the evaporation rate of both molecular cluster (Figure 3) and metallic one [Figure 4(a)] decreases exponentially with the inverse of cluster temperature, while the cluster temperature dependency of the condensation rate is not significant [Figure 4(b)]. Again, we observe similar results for molecular and nickel materials. In addition, one can see that the calculated dependency of evaporation rate can be described by the RRK theory. In the RRK theory, the evaporation rate exponentially decreases with cluster temperature, and the coefficient in the exponential (sublimation energy) corresponds to the minimal kinetic energy required to obtain a significant evaporation. Our results show that we can determine the sublimation energy \(D_N\) for nickel and molecular clusters. For instance, a molecular cluster with 463 molecules, we found \(D_N = 0.363 \text{ eV}\), and for nickel cluster with 604 atoms, \(D_N = 1.725 \text{ eV}\).

Finally, we investigate the cluster evaporation and condensation processes by running our MD simulations with the same cluster parameters (material, initial size, and temperature) but with different gas properties (density and temperature). Interestingly, the obtained calculation results show that the evaporation and condensation rates are proportional to the gas density (Figure 5 and 6) and the square of temperature (Figure 7 and 8). In particular, our simulations indicate a dramatic influence of both gas density and temperature on the evaporation process. For a molecular cluster containing initially 463 molecules (and for a nickel cluster with initially 604 atoms), calculations show that the evaporation rate is larger than 1.0 \(10^{11} \text{s}^{-1}\), if the initial gas temperature is larger than the boiling point (\(T_{\text{boil}} = 500 \text{K}\) at \(P = 0 \text{ Pa}\), for the molecular material, \(T_{\text{boil}} = 3190 \text{K}\) at \(P = 0 \text{ Pa}\).
for nickel) and its density is larger than \(1.0 \times 10^{19} \text{ cm}^{-3}\). Under these conditions, the evaporation process prevails over the condensation one. Similar effects are also observed for the nickel cluster (Figure 8). Interestingly, an intersection is obtained at 625 K for molecular material and at 4000 K for nickel. This effect can be explained by the interplay between the condensation and evaporation processes. At these temperatures, each process balances the other process, and the cluster size does not significantly change.

One can therefore expect that small clusters \((N < 50 \text{ molecules})\) evaporate rapidly in the ablated plume regions where the density and the temperature of monomers are large \((T > T_{\text{boil}} \text{ and } \rho > 1.0 \times 10^{19} \text{ cm}^{-3})\). These conditions typically correspond to the beginning of the laser plume formation and its expansion in MALDI experiments as well as in laser ablation.

Thus, the calculation results reveal the role of gas-cluster collisions in both evaporation and condensation processes. The performed MD simulations confirm that the RRK theory and the collision rate can be used to define the evaporation and condensation rates. Similar results for both studied materials are obtained. However, we can modify the RRK solution for the definition of evaporation and calculate the sticking probability for the condensation rate estimation based on our MD simulations. For this, we propose analytical expressions for the evaporation \(\nu_e\) and condensation \(\nu_c\) rates, for large clusters of nickel and molecular material, as follows:

\[
\nu_e = \nu_{e0} V e^{\frac{-D n_{\text{e}}}{k B T_n}} \tag{11}
\]

\[
\nu_c = \nu_{c0} c^2 \tag{12}
\]

where \(\nu_{e0} = 2.7441 \times 10^{-16}\) and \(\nu_{c0} = 3.607\) for molecular material and \(\nu_{e0} = 9.1272 \times 10^{-18}\) and \(\nu_{c0} = 5.4201\) for nickel. These constants are determinate by the MD simulations.

4. Conclusions

We have studied the evaporation and condensation processes of a molecular cluster in the presence of a background gas...
composed of the same molecules as the cluster for two different materials: (i) molecular material, which is modeled by the breathing sphere model; and (ii) metallic material (nickel), which is modeled by the embedded atom model. We have analyzed the calculated evaporation rate by comparing the MD calculation results with the rates given by the RRK theory. The condensation rate is analyzed by using collision rate. As a result, we have observed that both gas density and temperature have strong influence on the evaporation process. We have shown that, in the presence of a gas, evaporation is a collision-driven process, just like condensation is. Therefore, the evaporation rate depends on gas density and temperature. As a result, both evaporation and condensation rates depend on the gas parameters (Table 1).

Our results have shown that small clusters \((N < 50)\) evaporate rapidly in a gas if its temperature is larger than the boiling temperature, or if its density is larger than \(10^{19} \text{ cm}^{-3}\). Under these conditions, the evaporation process prevails over the condensation one. This effect is dominant for nickel ablation since plume temperature is typically much larger in metal ablation experiments than in molecular materials (due to the difference in cohesive energy, in melting temperature, and in ablation threshold).

The obtained MD results are in agreement with a slightly modified RRK collision rate expression. The corresponding modifications are proposed based on the MD calculation results. In particular, our calculation results have demonstrated that gas-cluster collisions affect cluster evaporation. The condensation rate has been also explained using the cluster-gas collision rate with a sticking probability determined by our MD simulations.

We note, finally, that the obtained calculation results can be used in a Monte Carlo (DSMC) model, which describes the expansion of the laser-ablation plume. Such simulations provide much longer expansion dynamics of the plume. The results of the present calculations can be also useful for the explanation of cluster formation in other experiments (pulsed-laser deposition, gas-jet nozzles, and plasma-aggregation sources).

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References and Notes

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