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Molecular dynamics study of nanoparticle evolution in a background gas under laser ablation conditions

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ABSTRACT

Long-time evolution of nanoparticles produced by short laser interactions is investigated for different materials. To better understand the mechanisms of the nanoparticle formation at a microscopic level, we use molecular dynamics (MD) simulations to analyse the evolution of a cluster in the presence of a background gas with different parameters (density and temperature). In particular, we compare the simulation results obtained for materials with different interaction potentials (Morse, Lennard-Jones, and Embedded Atom Model). Attention is focused on the evaporation and condensation processes of a cluster with different size and initial temperature. As a result of the MD calculations, we determinate the influence of both cluster properties and background gas parameters on the nanoparticle evolution. The role of the interaction potential is discussed based on the results of the simulations.

1. Introduction

The development of nanotechnology has attracted a great interest both to the properties of nanoparticles and their synthesis. Recently, laser ablation of different materials has been suggested to be a new technique of nanoparticle manufacturing [1–3]. This method provides the chemically clean synthesis and the control over the cluster size distribution by carefully choosing the laser irradiation parameters and properties of the background gas. The need to understand the mechanisms of clusters formation and the physical and chemical processes that affect the time-evolution of the nanoclusters in a plasma environment is extremely important for further development of this technique.

Current analytical approaches based on classical nucleation theory (CNT) [4,5] and Rice, Ramsperger and Kassel (RRK) theory [6,7] are used to explain the evaporation–condensation process. Molecular dynamics (MD) method [4,5,8,9] directly simulates molecular movement and interactions and can be used to investigate the evaporation process or to study the formation and evolution processes of clusters of many materials [6,9–12].

In the present paper, we investigate the evolution of clusters of different materials (molecular, argon and nickel) in presence of the same background gas with different properties by using the molecular dynamics method and corresponding potential model (Morse [9], and Embedded Atom Model [13] and Lennard-Jones [14]). The main objective is to study the influence of background gas and cluster parameters on the evolution of molecular nanoclusters, to investigate the interaction potential influence on the evolution of the cluster with MD.

2. Modeling details

The evolution of a cluster in a gas plume is investigated using molecular dynamics simulations. Cubic unit cell with a cluster placed in its centre was chosen for the simulations. Periodic boundary conditions are used in all directions. In order to use molecular dynamics, we have to define the rules that are governing interaction of atoms in the system. In classical and semi-classical simulations these rules are expressed in terms of potential functions. In order to describe the interactions between nickel atoms, argon atoms and molecular bonds, Embedded Atoms Model (EAM) [13], Lennard-Jones (LJ) [14] and Morse [9] type potential models are respectively applied.

Each spherical cluster is built from a crystal with FCC lattice structure for argon and nickel and simple cubic for molecular material. After quenching, the cluster is slowly heated in order to obtain a liquid sphere at the initial temperature T_0, such as each component cluster particle velocity in each direction correspond to the Maxwell–Boltzmann distribution.

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Next, the background gas associated with the plume is randomly generated based on the gas density and temperature. The volume of the computational cell and the gas density determine the number of gas particle in our simulation. The cell volume is constant and equal to 100 nm × 100 nm × 100 nm. To heat the gas, each particle of gas is given a velocity (Maxwell–Boltzmann distribution) according to the initial temperature.

One of the objectives of the present study is to provide the reaction rates/probabilities for a much larger-scale direct simulation Monte Carlo calculations of the expansion of a laser plume [7]. Therefore, we perform a series of NTV simulations with gas parameters corresponding to the instantaneous parameters found under typical laser ablation conditions. In addition, the performed simulations provide information on cluster evolution in typical plasma environment corresponding to a background gas with different properties (density and temperature), for three kinds of material (molecular material, LJ material and a metal).

3. Results

MD simulations are performed until a time delay of 3 ns for a cluster of different initial sizes and internal temperatures, in the presence of a gas containing the same species as the cluster. The time-evolution of cluster's size is shown in Fig. 1 for the three different interaction potentials, in presence of a background gas with density of 2.0×10^{19} part./cm^3. After a fast growth, the cluster size decreases, as rapidly as the initial cluster temperature is high. The simulation results show that the size of the hotter argon cluster (60 K) decreases more rapidly than that of the colder argon cluster (50 K), with initially the same size and in the same background gas conditions. Under the same gas conditions, e.g. temperature larger than the boiling temperature (∼100 K for LJ material and ∼500 K for molecular material), the colder argon cluster reveals the same behavior of the molecular cluster. Then, in the region of the plume with a high gas density (2.0×10^{19} part./cm^3), the cold clusters rapidly grow, before evaporating. The size of the hot metal cluster (nickel, T_0 = 4000 K) evolves similar to that of the hotter argon cluster (60 K). Interestingly, for all the initial temperatures used for clusters of different materials, the behavior of both cluster growth and decay are similar.

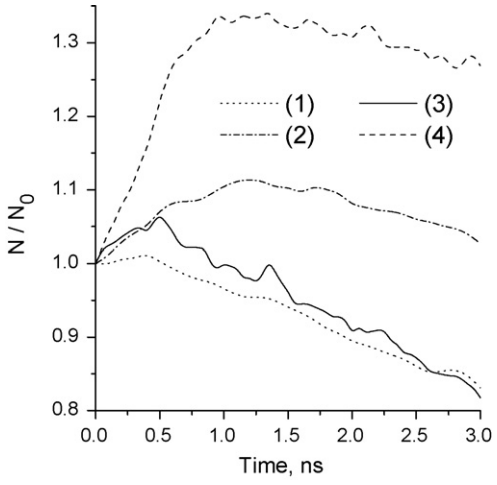

Fig. 1. Time-evolution of the cluster's size for two LJ clusters composed of 1088 particles: (1) initially at 60 K; (2) initially at 50 K in a background gas at 200 K; (3) a nickel cluster composed of 532 particles and initially heated to 4000 K in a background gas at 7113 K; (4) a molecular cluster of 1000 particles initially at 400 K in a background gas at 773 K. The background gas has a density of 2.0×10^{19} part./cm^3 for all clusters.

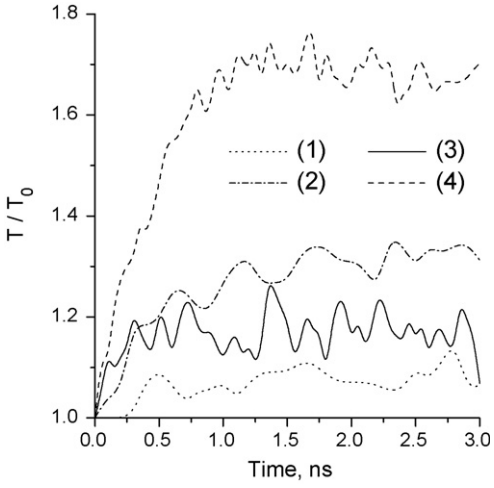

Fig. 2. Time-evolution of the cluster's temperature for two LJ clusters composed of 1088 particles: (1) initially at 60 K; (2) initially at 50 K in a background gas at 200 K; (3) a nickel cluster composed of 532 particles and initially heated to 4000 K in a background gas at 7113 K; (4) a molecular cluster of 1000 particles initially at 400 K in a background gas at 773 K. The background gas has a density of 2.0×10^{19} part./cm^3 for all clusters.

The cluster temperature T/T_0 is given in Fig. 2 for the three interaction potentials. For all values of the initial temperature used for several materials, the cluster temperature increases to a certain value (4400 K for Ni, 68 K for Ar, and 650 K for molecular material). When the cluster temperature reaches this value, the cluster begins its evaporation, and its size decreases. During the temperature rise, the cluster grows due to the collisions with the background gas. The calculation results show that the cluster has the same evolution for similar gas parameters (temperature and density).

During the evolution of the cluster in the presence of a background gas, two reactions are in competition: evaporation and condensation:

$$A_i + A \overset{\nu_e,\nu_c}{\longleftrightarrow} A_{i+1} \quad (1)$$

where ve and vc are the evaporation and condensation rates, respectively. The evaporation reaction is prevailing following the properties used to the background gas, such as temperature and density found in the ablation plume. The calculation results show that the condensation of monomers on the cluster do not interplay the evaporation in dense gas (larger than 2.0×10^{19} part./cm^3) with a temperature at least 1.5 times larger than the boiling temperature (Fig. 3). The cluster, however, grows in a gas with rather high density (larger than 2.0×10^{19} part./cm^3) for gas temperature at least 1.05 times larger than the boiling temperature of the material. The results show that the size of clusters decreases in a gas with density twice as less than 2.0×10^{19} part./cm^3 and with a temperature around the boiling temperature.

The obtained calculation results clearly demonstrate that in a laser plume, where monomers collide with cluster, the evaporation process depends both on cluster temperature and on gas density. Clusters would evaporate more rapidly in a low density part (less than 2.0×10^{19} part./cm^3) of the plume than in a dense part of the plume, due to smaller collision frequency between clusters and monomers of the plume.

To quantify the evaporation and condensation processes, we compute the evaporation $\nu_e = Ne/\Delta t$ and condensation $\nu_c = Nc/\Delta t$ rates as the number of the evaporated monomers N_e or condensated ones N_c, divided by a time step Δt. This time step is large to avoid counting simple collisions between the cluster and

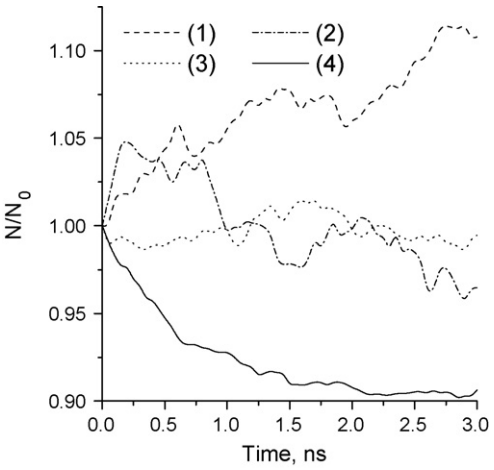

Fig. 3. Time-evolution of the cluster's temperature for molecular cluster composed of 1000 particles initially at 609 K in different background gas: (1) at 535 K and with a density of 2.0×10^{19} part./cm^3; (2) at 785 K and with a density of 2.0×10^{19} part./cm^3; (3) at 534 K and with a density of 1.0×10^{19} part./cm^3; (4) at 531 K and with a density of 2.0×10^{18} part./cm^3. The boiling temperature of this molecular material is around 500 K.

monomers. Simple collision allows a rearrangement of the cluster configuration and the change of cluster internal energy.

The reaction rates for the considered evaporation and condensation processes are shown in Fig. 4. The reaction rates depend on both the cluster and gas parameters (Fig. 4(a)–(c)). The reaction rates are compared for different materials (Fig. 4(b)–(d)), such as molecular material, LJ material and nickel. Under similar condition (both gas and cluster parameters), cluster evaporation and condensation rates behave similarly for all materials used in this study. When the initial cluster temperature is about 10% smaller than the boiling temperature, the evaporation begins at the beginning of the simulation, but it is negligible (Fig. 4(a)–(b)). The cluster, however, collides with gas species and grows. During this process, its temperature increases, and the evaporation process becomes significant, whereas the condensation process is present and significant from the beginning (Fig. 4(c)–(d)). When the temperature of the cluster reaches the mean value (650 K for molecular material, 68 K for argon and 4400 K for nickel), the evaporation of the cluster increases rapidly and the rates of condensation and evaporation reaches a mean value. This value depends on the cluster properties, such as its size and its initial temperature, and the gas properties (density and temperature). Under conditions used for the gas, the mean value of the evaporation rate is larger than the condensation rate mean value. Then, the evaporation process prevails under conditions used for the gas.

4. Summary

Molecular dynamics simulations have been used to investigate the evolution of nanoparticles in the presence of a background gas. In particular the evaporation and condensation processes have been considered. We have performed the MD calculations for molecular material, for argon and for nickel by varying the initial number of particles in the cluster, the initial cluster temperature and the parameters of the surrounding gas representing the typical conditions that correspond to a laser ablated plume.

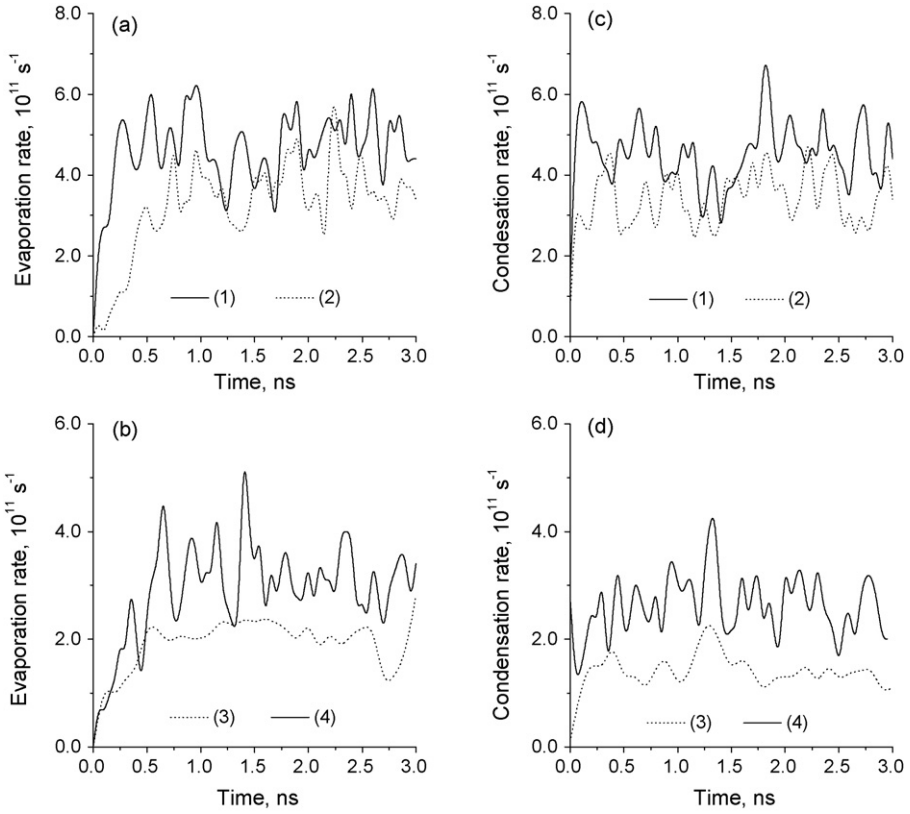

Fig. 4. Evaporation (a)–(b) and condensation (c)–(d) rates as a function of time, for (1) molecular cluster composed of 1000 particles, initially at 609 K in a background gas at 785 K; (2) molecular cluster composed of 500 particles, initially at 445 K in a background gas at 785 K; (3) argon cluster composed of 1088 particles initially at 50 K in a background gas at 200 K; (4) a nickel cluster composed of 532 particles and initially heated to 4000 K in a background gas at 7113. The background gas has a density of 2.0×10^{19} part./cm^3 for all clusters.

The simulation results show that the evaporation and condensation processes depend on the parameters of both cluster and gas. The evaporation of clusters is significant in a gas with density lesser than 2.0×10^{19} part./cm^3 and/or with a temperature at least 1.5 times larger than the boiling temperature of the material. For these gas parameters, the evaporation and condensation processes are not in interplay. However, the condensation process prevails in a dense gas (when density is larger than 2.0×10^{19} part./cm^3), and/or for the gas temperature around the boiling temperature (~10%) of the given material.

The calculation results show that the process of both evaporation and condensation are similar for all materials used in this study. Under the conditions of prevailed evaporation, the condensation process also takes place starting from the beginning of the simulation. For the initial cluster temperature at least ~10% smaller than the boiling temperature, the condensation rate is significant, leading to cluster growth. However, the evaporation process is negligible from the beginning of the simulation. Then the cluster evaporation becomes significant, when the temperature of the cluster increases. For the initial cluster temperature of at least ~20% larger than the boiling temperature, the evaporation is intense from the beginning of the simulation. Then, following the parameters of the background gas, the evaporation and the condensation can be in interplay, or one reaction can dominate.

In addition, it should be noted that we are currently developing a combined molecular dynamics and direct simulation Monte Carlo (DSMC) model (MD–DSMC) to simulate material ablation, plume formation and its long-term evolution. The results of the present calculations are required to properly parameterize the reactions probabilities in the DSMC part for the plume expansion. This work is underway and will allow a direct comparison of the obtained simulation results with the results of laser ablation experiments. The results of present calculations can be also useful for the explanation of cluster formation in other experiments (gas jet nozzles [14–18], fusion reactor [19,20], circulating fluidized bed [21]).

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