

Condensation and Evaporation of a Nano-sized Particle Moving in a Fluid Environment

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ABSTRACT

Condensation and evaporation of a low temperature nano-sized argon particle moving in a gas/vapor environment was analyzed using the molecular dynamics simulation. First evaporation temperature for various heating rates was found and successfully compared with the analytic result. Condensation and evaporation rates observed through simulation depended on particle velocity and thermodynamic properties of the gas, and the radial distribution of particle temperature was found to be a good indicator to characterize the process. Characteristics of condensation and evaporation for two different particle velocities and various environmental conditions were discussed in detail. In low gas density environments all the gas atoms got condensed on the particle, and in high gas density environment condensation / evaporation characteristics became much different depending on particle velocity.

Keywords: molecular dynamics, nanoparticle, condensation, evaporation

1 INTRODUCTION

Studies of nano-sized particles are usually concerned with the generation of nanoparticles, the physical properties of nanoparticles, and the synthesis to produce nanostructured materials. Nanoparticles studied are mainly clusters of metal, metal alloy or ceramic materials, and experiments or molecular simulations are performed to reveal the phase change behaviors and thermodynamics properties. Since the size of the clusters is very small, molecular simulations, like molecular dynamics (MD), are known very useful to explore the properties of clusters.

The primary concern of this study is to see the thermo-mechanical behavior of a nano-sized volatile solid particle moving in a vapor environment, and that in the presence of a temperature gradient. Depending on the pressure and temperature of the particle and the surrounding vapor, particle size may increase due to condensation of the surrounding vapor onto the particle or decrease due to evaporation of the molecules of the particle. The changes in particle size, temperature and velocity will vary depending on the particle velocity and ambient fluid conditions.

This kind of system can be found in the so-called aerosol cleaning system, where contaminant particles on a substrate are removed by bombardments with energetic bullet particles. The bullet particles are made of volatile molecules such as Argon through a cryogenic expansion process, so are at cryogenic temperatures and moving at a high speed [1]. The aerosol cleaning system is known to be very successful in cleaning nano-sized contaminant particles, but detailed mechanisms are not well known yet. One proposed mechanism is the removal by the force generated with evaporation or sublimation of aerosols through heat exchange with the substrate. This study can provide some clues to the understanding of this kind of systems.

The system consists of a nano-sized solid argon particle at a temperature much lower than the triple point and ambient argon atoms (vapor) at various conditions close to the saturated vapor line. The particle is either stationary or shot into the surrounding vapor with a high enough initial velocity V_0 . The characteristics of condensation on and evaporation from this particle in an ambient vapor at a higher temperature will be investigated using the MD simulation techniques, for a variety of surrounding conditions and the temperature distributions.

2 SYSTEM CONFIGURATION AND SIMULATION METHODS

The computational domain is a cube where a nano-sized solid argon particle is located at the center of the domain. Initially, the argon particle is made of 2093 atoms arranged in the FCC (face centered cubic) structure. Its shape is made nearly spherical, with the outermost diameter of 5.4nm, and the initial temperature was set at 36K. The computation domain is a cube with a side of 16.2 nm, which is three times the particle diameter.

In the MD simulation, interactions between argon atoms are modeled using a pair-wise Lennard-Jones potential,

$$V_{LJ}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + r\delta V \quad (1)$$

, where r is the distance between atoms, ϵ the characteristic energy, and σ the length scale. V_{LJ} was truncated at $r_c = 2.5\sigma$, and the additional correction term $r\delta V$ is included so

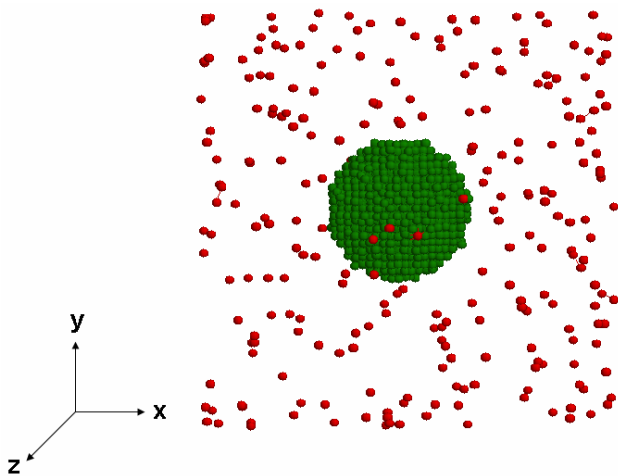


Figure 1 : Typical system configuration: green ball is the particle located at the center of the computation domain, and red balls the ambient vapor atoms

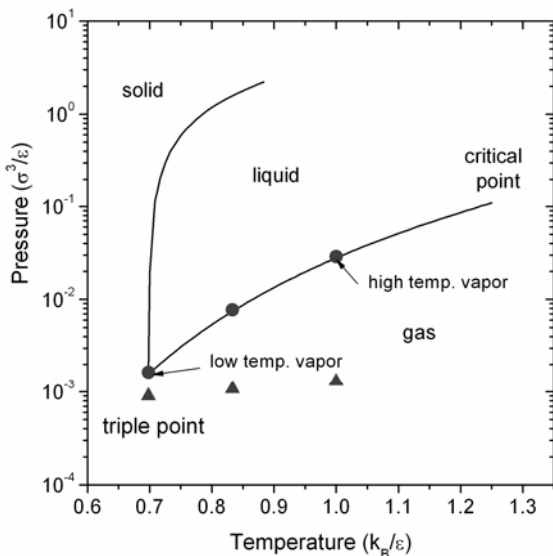


Figure 2 : Phase diagram of argon [2]. Solid circles represent saturated vapor states and triangles superheated or gas states, both used in the calculation

that the force vanishes at the cutoff distance. This interaction potential is known to successfully reproduce the properties of argon, when the parameters are chosen as $\sigma=3.405\text{\AA}$ and $\epsilon/k_B=120^\circ\text{K}$, along with a molecular mass $m = 40$ amu [3]. The natural time unit in the calculations is then, $\tau = (m\sigma^2/\epsilon)^{1/2} = 2.16 \times 10^{-12}$ sec.

Atoms corresponding to the solid argon particle and the ambient gas/vapor are all placed on a face-centered-cubic (FCC) lattice initially. Density of the solid argon is 1.0, and that of the ambient fluid is determined depending on the surrounding conditions used for simulation. Figure 2 is the phase diagram of argon [2], where solid circles represent the saturated vapor states and solid triangles represent ambient states used in this study.

The whole system is equilibrated for 10,000 time steps with constant temperature scaling. During equilibration, the interaction between fluid and solid atoms is set to zero, so there occurs no condensation or evaporation during equilibration. After equilibration, the Nosé-Hoover thermostat is applied to the particle or the fluid atoms depending on the condition of temperature control. For the cases of a particle in vacuum thermostat was imposed to the particle atoms, and for the cases of a particle in gas/vapor environment thermostat was imposed to fluid atoms to maintain the ambient temperature conditions. In the latter case, particle temperature changes only through contact with ambient atoms.

The equations of motion were integrated using the fifth-order Gear's predictor-corrector algorithm with a time step of 0.005τ .

3 RESULTS

3.1 First evaporation temperature

The temperature at which the first atom evaporates is an important parameter in the nano particle physics. Rytkönen *et al.* [4] obtained analytically the first evaporation temperature for a cluster heated at a constant heating rate. To find the first evaporation temperature for various conditions and to validate the current MD results, simulation results of this study are compared in Figure 3 with the analytical predictions of the aforementioned study. Open symbols are for a particle heated in vacuum at three different heating rates (2(\square), 4(\triangle) and 100(\circ) K/ns), and solid symbols for a particle in hot gas environments. Three curves are analytical predictions corresponding to the rates of heating in vacuum. Three different particle sizes are investigated for the vacuum condition and one particle size

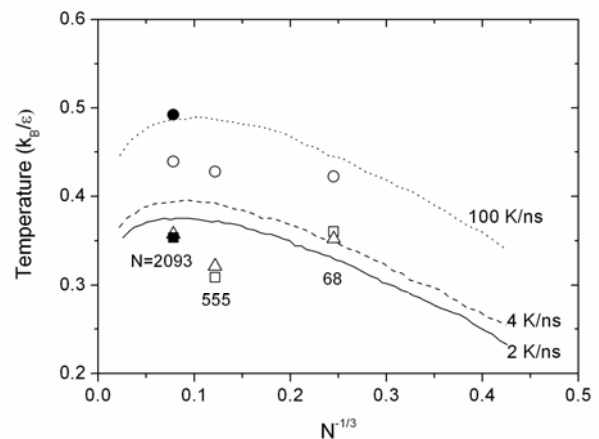


Figure 3 : Temperature of the first evaporation as a function of particle size N (number of atoms). Symbols represent different heating rates: square 2 K/ns, triangle 4 K/ns, and circle 100 K/ns. Filled symbols mean the particle in a gas, and open symbols particle in vacuum. Solid line, dashed line and dotted line are predictions by the analytic model for the corresponding rates of heating in vacuum.

is considered in the presence of hot gas. The simulation results are in good agreement with the analytic solutions.

3.2 Evaporation of a moving solid argon

Now the effect of particle velocity is analyzed. The solid argon particle is made to move with an initial velocity V_0 in a gas/vapor environment. To move the argon particle, a constant external velocity component in the “- y” direction is applied to all particle atoms (Figure 1).

In the initial period ambient gas/vapor atoms may become condensed on the particle surface of a low temperature. But the particle temperature begins to rise through collisions with ambient gas/vapor atoms, and finally surface atoms begin to evaporate when the surface temperature becomes higher than the first evaporation temperature. The evaporation rate depends on the density and temperature of surrounding gas/vapor atoms, and particle velocity.

After the occurrence of the first evaporation, two distinct processes occur simultaneously on the particle surface - condensation of fluid atoms and evaporation of particle atoms. The two processes may occur simultaneously on different spots on the surface, and also intermittently with time. Three different conditions for the initial temperature and pressure of the surrounding gas/vapor are examined to see the effects of fluid conditions (Figure 2), and two different particle velocities, $V^*=0.1$ and 2.0 , are explored for each of the fluid conditions. Velocity V is nondimensionalized as $V^*=V/(m/\epsilon)^{1/2}$, so $V^*=1.0$ corresponds to 158m/s in real dimension.

When a particle moves in a gas/vapor environment, atomic flux onto the particle surface has a non-uniform distribution due to the particle velocity with a much higher collisions near the leading edge, which in turn results in a non-uniform condensation and evaporation. In order to check the degree of non-uniformity, the atoms in two different, leading and trailing, hemispherical sections are distinguished, and the shell-wise or radial temperature distribution for the two different hemispherical sections in a particle is plotted in Figure 4. For a slowly moving particle, vapor condensation on the particle surface is nearly uniform, so the temperature at the upper(trailing) and lower(leading) shells are nearly the same except at the surface layer. However, for a fast moving particle more vapor atoms condenses on the leading head, so the temperature of the lower shells are somewhat higher, which is most apparent at the surface layer. At $\tau=5$, the temperature of the outermost layer of the lower shell is highest due to the condensed vapor atoms, and the increased temperature induces the particle atoms to evaporate easily. Once the surface atoms of the particle begin to evaporate, the condensing atoms and evaporating atoms are nearly balanced, so no abrupt temperature change is observed at the surface.

Compared in Figure 5 are the variations of particle size and average temperature with time, for two different vapor

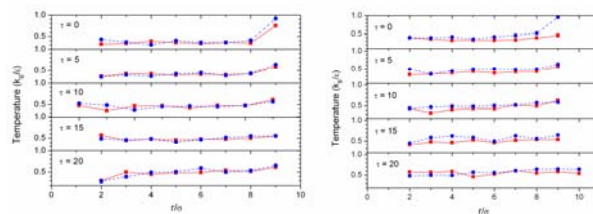


Figure 4 : Radial /shellwise Distribution of temperature and number of atoms in a particle moving in a high temperature vapor at two different velocities: (a) $V^*=0.1$ and (b) $V^*=2.0$. Red square solid line is for the upper(trailing) shells and green circle dotted line is for the lower(leading) shells. Time is counted after equilibration and onset of motion.

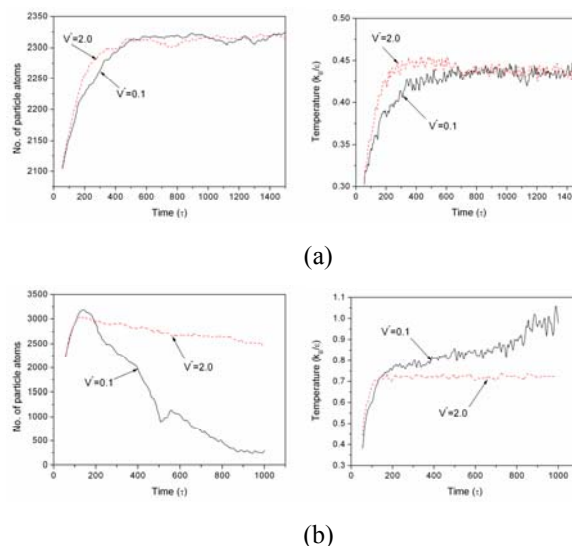


Figure 5 : Temporal variation of the size and temperature of the argon particle moving at two different velocities in (a) a low temperature vapor and (b) a high temperature vapor, defined in figure 2.

temperatures, $T^* = 0.698$ (low temperature vapor) and 1.0 (high temperature vapor), and two different particle velocities, $V^* = 0.1$ and 2.0 .

When a fluid atom of low temperature collides on the particle surface, it gets condensed on the particle. Temperature or kinetic energy of the condensed atom decreases with time, and particle temperature increases, in turn. When particle velocity is low, condensation and heating occurs almost uniformly inside the particle, and the particle becomes melted when a sufficient number of ambient atoms are condensed. Once all the particle atoms are in the liquid state, particle temperature does not increase any more, and the particle size also remains almost constant. This implies that there occurs no more net condensation.

When the ambient gas temperature is much higher than the triple point, particle size and temperature change in a different manner from the case of low gas temperature. For a low temperature vapor shown in Figure 5(a), the total

number of ambient atoms is small compared with the particle, about 15%, almost all of the ambient atoms get condensed quickly on the cold particle surface, and the particle size and temperature change only a little. This result is similar to the case of gas environment of Figure 2. For a high temperature vapor shown in Figure 5(b), the number of ambient atoms is quite large, almost 1.4 times the number of particle atoms. For a particle moving in such an environment at a low speed, a lot of ambient atoms condense initially, but evaporation increases steadily with time, and the particle becomes completely melted after some 800τ . For a particle moving at a high speed ($V^*=2.0$), on the other hand, particle size (number of particle atoms) increases initially due to condensation, but begins to decrease after some time lapsed. The change of particle size and temperature is, however, much more gradual than for a slow-moving particle.

To elucidate the different condensation/evaporation behaviors between slow-moving particle and fast-moving particle in the high temperature gas atoms, the total flux of atoms on the particle surface is divided into the number of condensed atoms and that of evaporated atoms, and the temporal variation of the two different fluxes are shown in Figure 6. Shown in Figure 6(a) is the case of a slowly moving particle, where the number of condensed atoms equals the number of evaporated atoms at around 350τ , but the number of evaporated atoms increases and the number of condensed atoms decreases steadily thereafter, leading to a complete melting of the particle. For a fast moving particle as shown in Figure 6(b), on the other hand, the number of condensed atoms and evaporated atoms remain nearly the same over a long period of time, resulting in a very slow size change except for a short initial period.

4 CONCLUSIONS

MD simulation for an Argon particle in vacuum or gas environment of various temperatures and densities revealed the following characteristics of changes in particle size and temperature.

1. Heating a particle in vacuum using a thermostat increases the particle temperature nearly uniformly from the center to the surface. On the other hand, heating a particle by collisions with ambient gas molecules of a higher temperature increases the surface temperature of the particle first, which is conducted inside with time.
2. When the ambient gas/vapor density is low, condensation of the ambient atoms on the cold particle surface is dominant, and it is possible that all the ambient atoms get condensed before evaporation of particle atoms occurs.
3. Condensed atoms are uniformly distributed over the particle surface for a slowly moving particle, but are

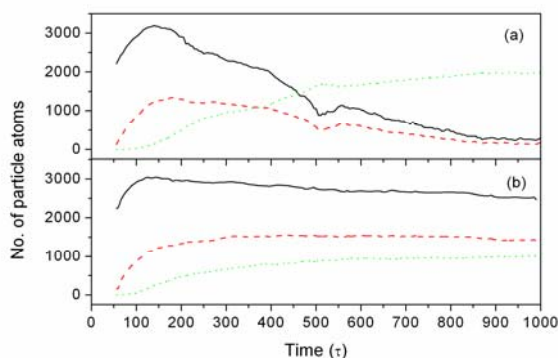


Figure 6 : Temporal variation of the number of particle atoms (solid line), condensed atoms (dashed red) and evaporated atoms (dotted green) in a high temperature vapor for two different particle velocities. $V^* = 0.1$ (a) and 2.0 (b)

concentrated near the leading head for a fast moving particle.

4. For a particle moving in a dense vapor environment, the rates of condensation and evaporation are nearly the same in the initial period, until some 350τ , irrespective of the velocity. For a slowly moving particle, evaporation begins to dominate condensation thereafter, which can lead to a complete evaporation of the particle. For a fast moving particle, on the other hand, the number of condensed atoms and evaporated atoms remains nearly the same for a very long time, keeping the particle size to stay almost the same.

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