Molecular Dynamics Simulation of Evaporative Deposition Process

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Abstract

Evaporative deposition process under different temperatures with different substrate materials were simulated with velocity-verlet molecular dynamics. Effects of temperature and substrate properties on deposition process and results were discussed.

1 Background

Evaporative deposition is the main subject of this project. Evaporative deposition is a kind of physical vaporize deposition. Source material is heated to evaporate in a vacuum chamber. Produced vapor then travel through vacuum and condense on substrate. The evaporate deposition process takes place in vacuum to allow vapor efficiently reach to substrate and minimize chemical reaction with atmosphere (e.g. metal vapor and oxygen, nitrogen). On substrate surface, vapor was cooled by substrate atoms and condense. Roughness on substrate can shadow vapor atoms from reaching some areas.

Molecular dynamics(MD) simulates physical motion of atoms and molecules. MD simulation was performed with time-steps. Within each time-step, force on atoms is assumed to be constant. The trajectories of atoms and molecules can thus determined with Newton's Law for this time-step. Then force under new positions are calculated and so forth. MD is widely utilized in physics, chemistry, biology, and materials science researches. [1]

There are multiple algorithms for molecular dynamics. In this project, Velocity-Verlet was used to simulate trajectories of atoms. Verlet algorithm was first utilized by Delambre in 1791.[3] Compared to traditional Verlet algorithm, Velocity-Verlet algorithm also calculates velocity of atoms, thus is more

applicable to this project. Velocity Verlet can be expressed as follow:

$$\vec{x}(t + \Delta t) = \vec{x}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2 \qquad (1)$$

$$\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\vec{a}(t) + \vec{a}(t + \Delta t)}{2}\Delta t \qquad (2)$$

Our implementation of Velocity-Verlet assume molecular potential is independent from velocity and includes three steps:

1. $\vec{x}(t + \Delta t) = \vec{x}(t) + \vec{v}(t)\Delta t + \frac{1}{2}\vec{a}(t)\Delta t^2$

2. $\vec{a}(t + \Delta t) = \vec{F}(t + \Delta t)/m = \frac{d}{dx}V_{LJ}(t + \Delta t)/m$

3. $\vec{v}(t + \Delta t) = \vec{v}(t) + \frac{\vec{a}(t) + \vec{a}(t + \Delta t)}{2}\Delta t$

Lennard-Jones potential (L-J potential) was used to model interactions between electrical neutral atoms. L-J potential is defined as follow: [2]

$$V_{LJ} = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6]] \qquad (3)$$

2 Method

Simulation was done with molecular dynamics simulator written during the course "Computational Methods for Materials Design"(MTLE 4500) in Spring semester 2016, at Rensselaer Polytechnic Institute(RPI). The code was modified for this project and can be found at `https://github.com/renyidong/MTLE4500/releases/tag/4500_final`.

Velocity Verlet algorithm on arbitrary dimensional space was implemented with C++. Number of dimension can be specified at compile time. Two dimensional spaces were simulated for this project, because three or more dimensional space requires significantly more computation power to simulate.

The simulated system was NV ensemble, which means volume and amount of substance were constant. The system is original designed to be NVE microcanonical ensemble. Code before modification was performing well without substrate atoms. However, to simulate substrate surfaces, either the whole substrate must be included in simulation system, or energy must leave the system. Since simulating the substrate will introduce massive amount to substance, which is far beyond of scope of molecular dynamics simulation, energy constant is thus sacrificed for efficiency. To verify energy conservation, we can calculate energy lost with cooling, and add it to total energy when output. However that requires more work to implement, and accuracy of repeated float summation is doubtful.

The simulation program was executed on Tardis server of materials science and engineering department of RPI. The server is equipped with two Intel(R) Xeon(R) E5-2690 v3 CPUs. To efficiently utilize the power of multi-CPU system, calculation of L-J potential and force on each atom was parallelized by multi-threading. MPI was also considered as parallel mechanism. MD simulation can share most data during calculation. MPI is based on multi-process parallelism. With isolated process memory space, all data must be passed between process by inter-process communication (IPC), which is considered extremely expensive for server local communication. Meanwhile, performance of Tardis server is quite sufficient for the simulation. Thus, MPI was not used in this project.

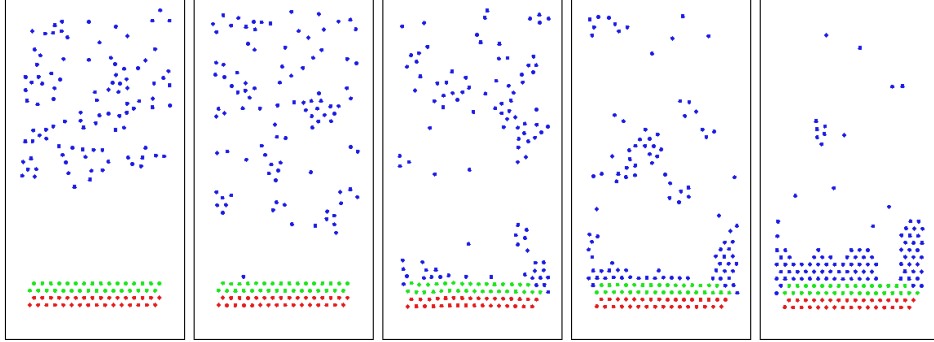# 3 Results & Discussion

3.1 Effect of Temperature

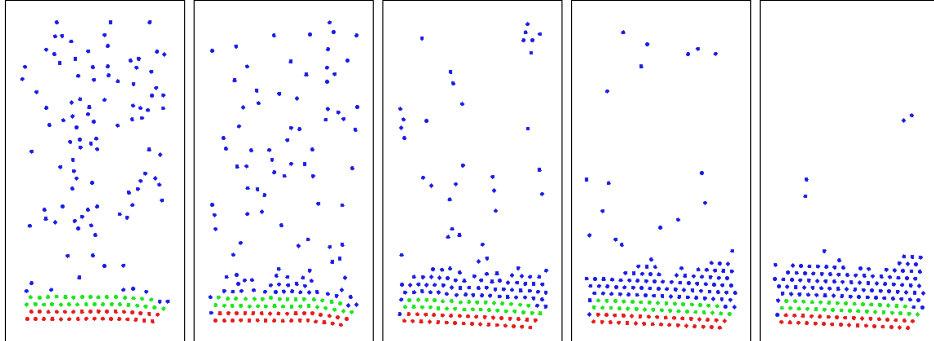Figure 1: σ=1.0; T=0.125; t=250, 500, 1000, 2000, 4000

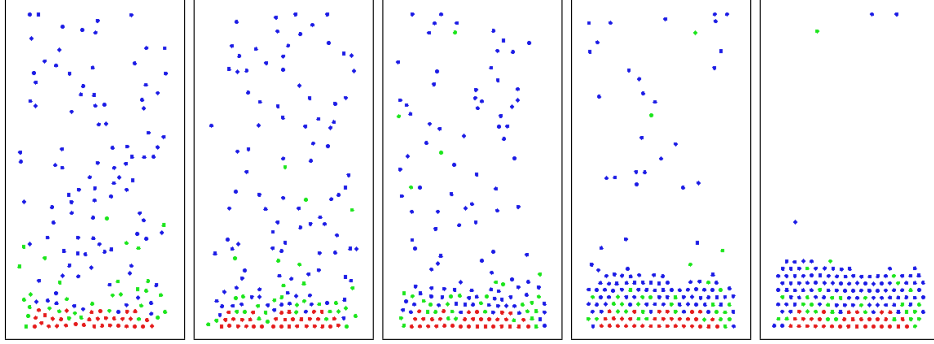Figure 2: σ=1.0; T=0.5; t=250, 500, 1000, 2000, 4000

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Figure 3: σ=1.0; T=2.0; t=250, 500, 1000, 2000, 4000

Figure 1-3 shows cases which temperatures are too low, suitable, and too high, respectively.

In Figure 1 gas was grouping before reaching substrate. Form the pattern of motion, we suspect it is in liquid state before deposit. As deposition proceed, we can observe gas phase is attacked by deposited atoms, so that thicker areas of coating are growing faster. The film formed at the end is very unbalanced. In graph, we can see that some substrate is not covered at all, while horns are formed at deposition rich areas.

Figure 2 shows case which gas temperature is suitable. Gas phase is remaining in gas state before reaching substrate. Once contact with surface, atoms are rapidly cooled to solidify. We can see deposited film growing evenly as proceed, finally forming a smooth surface.

Temperature for Figure 3 is apparently too high. Substrate can't cool down gas phase. Worse yet, upper layer of substrate (green atoms) is vaporized by heat from gas phase. Surface of substrate is heavily attacked. When the system finally cooled down, an alloy film is formed. Gas phase atoms are mixed with substrate. Please also notice at the end of simulation, an substrate atom remains in gas phase.

Overall, as temperature increase, more energy is brought to interface, the interface is more active, deposition is better spread and interfaced with substrate. However, in case where substrate is weakly bonded, temperature too high can ruin substrate surface by vaporizing etching. Oppositely, in case where substrate surface is not clean (e.g. oxide), or where an alloyed coating is desired, or where coating is immiscible with substance, higher gas temperature might be preferred. Lower temperature protects substrate, but also increases surface defect. Heats from latter atoms can warm-up former atoms and anneal the coating.
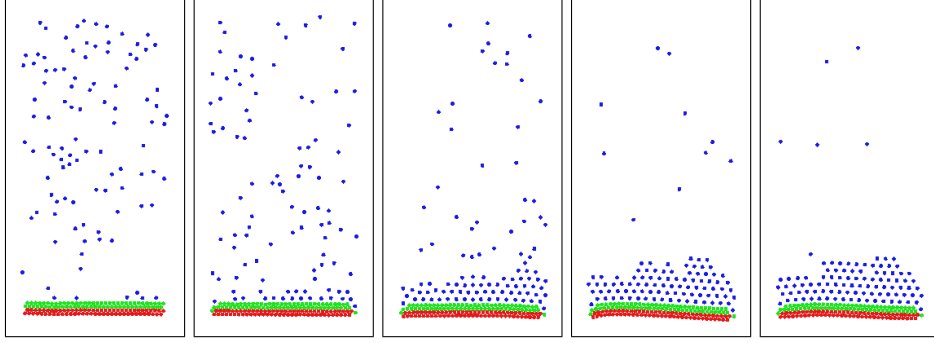
3.2   Effect of Substrate Materials

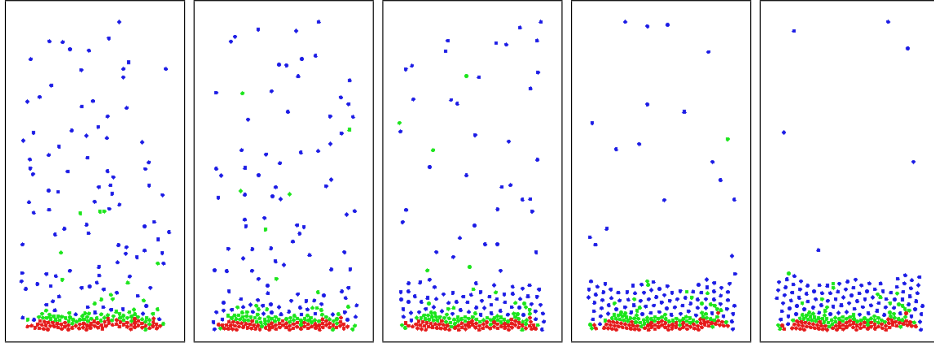Figure 4: σ=0.5; T=0.5; t=250, 500, 1000, 2000, 4000

Figure 5: σ=0.5; T=2.0; t=250, 500, 1000, 2000, 4000
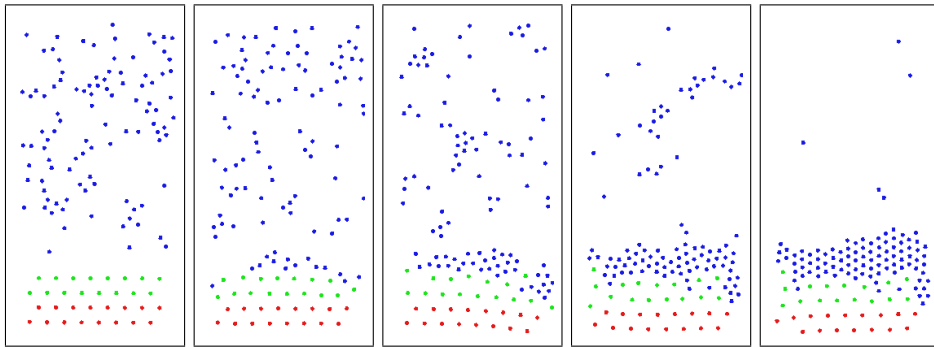

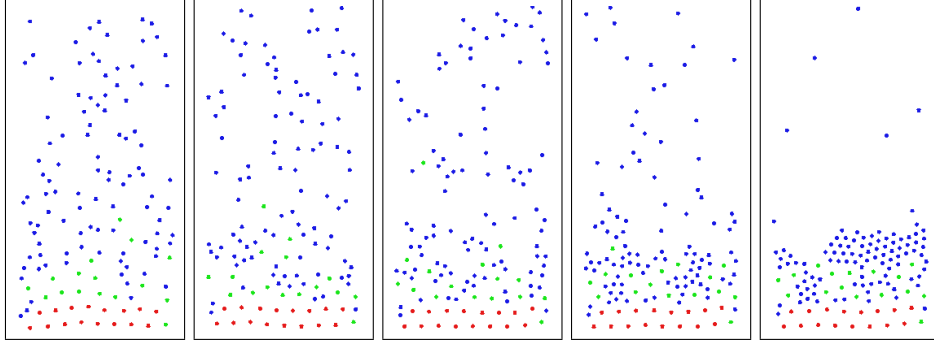Figure 6: σ=2.0; T=0.25; t=250, 500, 1000, 2000, 4000

Figure 7: σ=2.0; T=1.0; t=250, 500, 1000, 2000, 4000

Figure 4-7 shows results with different substrates.

In Figure 4 and 5, the substrate seems to be more resilient against etching by gas phase. With higher density, the substrate has, in theory, higher heat conductivity. Therefore, substrate can dissipate heat more efficiently, and the effective temperature on interface is lowered. Furthermore, there are more substrate atoms and bonds in unit volume. Then it is more difficult for substrate atoms to be knocked into gas phase. In Figure 4, we can also observe rough film and defect formed, similar to Figure 1.

Substrate in Figure 6-7 is less dense. T=0.25, which is found to be too low for Figure 1, seems just suitable. Film formed is evenly spread. T=1.0, which is found to be suitable for Figure 2, seems too high. Gas atoms penetrate into substrate, forming alloyed film.

As consequence, we can conclude that denser substrate should be processed with hotter gas.

4   Conclusion

From results of simultion we can conclude that at higher temperature, film formed is smoother, and bonding with substrate is better. Temperature too high can over etch substrate, causing excessive streess, and considered harmful. For denser substrates, higher gas temperature should be used. More research can be done with effects of ofter factors line ϵ in L-J potential and shape of susbtrate. Also, more work is nessesary to promoting to three dimensional space and correlate this model with deposition process in real-world.

References

[1] ALDER, B. J., AND WAINWRIGHT, T. Studies in molecular dynamics. i. general method. *The Journal of Chemical Physics 31*, 2 (1959), 459–466.

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[3] TRIBBEY, W. Numerical recipes: The art of scientific computing is written by william h. press, saul a. teukolsky, william t. vetterling, and brian p. flannery, and published by cambridge university press,© 2007, hardback, isbn 978-0-521-88068-8, 1235 pp. *ACM SIGSOFT Software Engineering Notes 35*, 6 (2010), 30–31.