A molecular dynamics simulation of platinum nanoparticle formation during vapour deposition

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Abstract. As modern concerns about carbon emissions increase the desire for platinum nanoparticles to be used as a catalyst in the catalytic converters of cars also increases. Therefore it is important to understand how platinum nanoparticles form in order to manufacture the desired nanoparticles with the correct size and shape. A unique insight regarding the different parameters and process can be gained by using Molecular Dynamics (MD) to simulate the formation of the platinum nanoparticles. For the simulations in this study, the Sutton-Chen potential was used since it is well suited for simulating FCC metals such as Pt. This study focused on the growth of Pt nanoparticles during physical vapour deposition. In the model used, Pt atoms are projected from random locations above a surface towards the surface. This simulation was done for different evaporation rates and temperatures in order to investigate their effect on the growth of the nanoparticles. When varying the surface temperatures it was found that the structures at higher temperatures are more closely packed compared to that at lower temperatures. By lowering the evaporation rate the atoms have more time for movement at lower temperatures to form closed structures. It was also noticed that the structures tend to be layered structures on the surface. This can be explained by looking at the energies required to move the atoms between different positions on the structures and the minimisation of the energies at those positions.

1. Introduction

Platinum is an important catalyst for applications such as catalytic converters in the exhaust systems of automobiles. By using nanoparticles of platinum, a smaller amount can be used while increasing the surface area. This will lead to a more effective catalyst that is more affordable. Looking at the structures that form during physical vapour deposition can help in the manufacture of catalysts.

One method in which nanoparticles can be manufactured is that of physical vapour deposition. In this study molecular dynamics simulations was done in order to investigate the structures that form when platinum is deposited on graphite substrates by means of physical vapour deposition. The effects of temperature and evaporation rate on the growth of the structures were investigated.

In molecular dynamics simulations atoms are moved classically according to forces calculated from a potential field. The potential field is described by a potential function that takes effects like metallic

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bonds into account. In this study, the Sutton-Chen potential was used because it is well suited to FCC metals like platinum.

2. Sutton-Chen potential

The Sutton-Chen potential, $U_{\text{Sutton-Chen}}$, for atom *i* is given by

$$U_{\text{Sutton-Chen}} = \varepsilon\left[\frac{1}{2}\sum_{j\neq i}\left(\frac{a}{r_{ij}}\right)^{n} - c\sqrt{\rho_i}\right] \tag{1}$$

where

$$\rho_i = \sum_{j\neq i}\left(\frac{a}{r_{ij}}\right)^{m}. \tag{2}$$

The Sutton-Chen potential is composed of two terms. The first term represents the repulsive part between the atomic nuclei. The second term represents the attractive part between the electron cloud in the metal and the nuclei. The electron cloud is modelled by using the density of the atoms in the region. The parameters *m*, *n* and *c* are obtained from fitting to experimental characteristics of the material [1]. The lattice parameter is given by *a* and the energy scale is given by ε. For platinum their values are $m = 8$, $n=10$, $c = 34.408$, $a = 3.92$ Å and $\varepsilon = 1.9833 \times 10^{-2}$ eV.

It can be seen that in order to calculate the potential for a single atom it is necessary to consider all the atoms. The contribution of an atom is inversely related to its distance to a high power. For this reason, it is only necessary to consider the neighbours below a cut-off radius when calculating the potential. This speeds up the simulation significantly. Even with this optimisation, it is still too computationally expensive to do the deposition simulation for periods much longer than 20 ns. For this investigation, it is required to look at a relatively large system of about 100 Å by 100 Å for a relatively long period of about 100 ns.

3. Steele potential

One option for the deposition onto a surface is to represent the surface with a few atom layers. Less than one atom layer will be deposited onto this surface. The simulation will be sped up greatly if a faster method to represent the surface was used instead. The Steele potential is an analytical expression that provides the potential between an atom and a regular surface.

The potential of an atom close to a regular crystal surface can be taken as the sum of the Lennard-Jones potentials between the atom and the atoms in the crystal. When looking at the crystal in Fourier space an analytical expression can be found because the crystal is regular. This was done in order to obtain the Steele potential [2].

The Steele potential in reduced units, U^{*}_{Steele}, is given by

$$U^{*}_{\text{Steele}} = E_0(z^{*}) + \sum_{n>0} E_n(z^{*})\, f_n(s_1, s_2) \tag{3}$$

where

$$E_0(z^{*}) = \frac{2\pi q A^6}{a_s^{*}}\sum_{p=0}^{\infty}\left(\frac{2A^6}{5(z^{*}+p\Delta z^{*})^{10}} - \frac{1}{(z^{*}+p\Delta z^{*})^{4}}\right), \tag{4}$$

$$E_n(z^{*}) = \frac{2\pi A^6}{a_s^{*}}\left[\frac{A^6}{30}\left(\frac{g_n^{*}}{2z^{*}}\right)^{5} K_5(g_n^{*} z_{*}) - 2\left(\frac{g_n^{*}}{2z^{*}}\right)^{2} K_2(g_n^{*} z_{*})\right] \tag{5}$$

and the first few values of g_s^* and f_n is given in table 1. For the graphite basal plane the number of atoms in the unit cell, q, is two, the length of one side of the unit cell, a_1, is 2.46 Å, the reduced surface area of the unit cell is given by $a_s^* = a_s / a_1^2 = 3^{1/2}/2$, the reduced distance of the atom from the surface is given by $z^* = z / a_1$ and the reduced distance between graphite layers is given by $\Delta z^* = 1.38$ Å. The gas solid (gs) interaction parameters are used to scale the potential to the energy and size scale applicable to the gas used and are given by the formulas $U^*_{\mathrm{Steele}} = U_{\mathrm{Steele}} / \varepsilon_{\mathrm{gs}}$ and $A = \sigma / a_1$ respectively.

Table 1: First five values for g_s^* and f_n as given in [2].

N	$g_n^* / 2\pi$	$f_n(s_1, s_2)/2$
1	$2/\sqrt{3}$	$-\left[\cos(2\pi s_1) + \cos(2\pi s_2) + \cos(2\pi(s_1 + s_2))\right]$
2	2	$2\left[\cos(2\pi(s_1 + 2s_2)) + \cos(2\pi(2s_1 + s_2)) + \cos(2\pi(s_1 - s_2))\right]$
3	$4/\sqrt{3}$	$-\left[\cos(4\pi s_1) + \cos(4\pi s_2) + \cos(4\pi(s_1 + s_2))\right]$
4	$2\sqrt{7/3}$	$-\begin{bmatrix}\cos(2\pi(3s_1 + s_2)) + \cos(2\pi(s_1 + 3s_2)) + \cos(2\pi(3s_1 + 2s_2)) + \\ \cos(2\pi(2s_1 + 3s_2)) + \cos(2\pi(s_1 - 2s_2)) + \cos(2\pi(2s_1 - s_2))\end{bmatrix}$
5	$6/\sqrt{3}$	$2\left[\cos(6\pi s_1) + \cos(6\pi s_2) + \cos(6\pi(s_1 + s_2))\right]$

The values for s_1 and s_2 are found from the projection of the (x, y) coordinate onto the graphite crystal structure so that the position of the atom on the surface, $\boldsymbol{\tau}$, is given by the formula $\boldsymbol{\tau} = s_1\boldsymbol{a}_1 + s_2\boldsymbol{a}_1$.

For the Platinum-Graphite system the distance between the Platinum and carbon atoms are given by $\sigma_{\mathrm{pc}} = 2.905$ Å and the interaction strength is given by $\varepsilon_{\mathrm{pc}} = 256$ K = 256 x 8.617 x 10^{-5} eV/K [3].

The E_0 term incorporates the uniform contribution from all the layers. Since the effect of each subsequent layer gets less, only the first few layers have to be used. Only the first 25 layers were used [3]. The E_n term gives the amplitude and the f_n term gives the shape of the nth term from the Fourier expansion. Only the first 5 terms are used because the effect of the others terms are negligible.

To further speed up the process simple functions was used in the place of E_0 and E_n. It was found that a sufficiently accurate fit was produce by fitting functions with the form $az + b(z + c)^d$ to E_n while a function with the form $az + b(z + c)^d + e(z + f)^g$ was required for E_0.

Using the Steele potential with simplified fits for the E terms results in much faster simulation times. For similarly sized systems for 8 million steps using the Sutton-Chen potential for the base takes 47 days while using the Steele potential takes only 16 hours which is a speedup of about 70 times. The speedup is similar for other number of steps.

4. Simulation Setup

The Steele potential was used to simulate a graphite surface and the Sutton-Chen potential was used to simulate the Platinum atoms. The Steele potential of the graphite surface is shown in figure 1. Periodic boundary conditions was used in the x and y directions. The sizes were chosen such that the cells from the graphite surface fits perfectly into the simulated area. The x direction had to be a multiple of 2.46 Å while the y direction had to be a multiple of 4.26 Å. An elastic wall was used in the z direction so that atoms that bounce of the surface can have another chance to stick to the surface. The Berendsen thermostat was used to control the temperature of the all the atoms in the system. The atoms were projected towards the surface from uniformly distributed random locations with a velocity of 3.6 Å/ps, which would correspond to a temperature of about 1000 K.

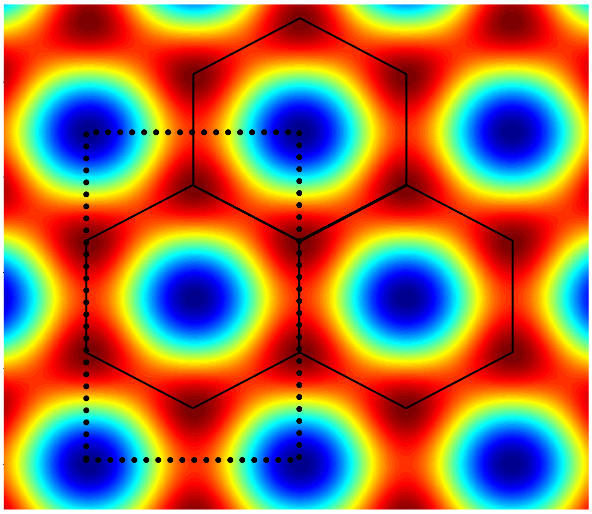

Figure 1. This figure shows the Steele potential for the graphite surface. The solid lines highlight the hexagonal structure of the graphite. The dotted rectangle is the minimum cell that must be repeated for smooth boundary conditions.

In the evaporation atoms are projected at the surface with certain intervals between projecting subsequent atoms. By varying this time the evaporation rate can be changed.

5. Results

The simulation was done for various temperatures and evaporation rates. The structures that form are shown in figure 2. At the fastest evaporation rates there were a few small particles. As the evaporation rate slowed the number of particles decreased and they became larger until there was only one particle. This took longer at lower temperatures. At 300 K the particles had shapes that are less clearly defined. At 900 K the particles tend to be hexagons or truncated triangles. When the evaporation rate becomes slower the shape of the particles becomes more clearly defined.

A single atom on the graphite surface is very mobile. When it bonds to another atom it becomes less mobile. As more atoms are joined to the cluster it tends to become more stationary. When atoms are added to the cluster sooner the atoms have less time to move to equilibrium positions. This explains why at very high evaporation rates there are smaller clusters while at low evaporation rates there is one large particle. When the temperature is higher the atoms move faster so they can form larger structures at higher evaporation rates.

When the platinum atoms are in a large cluster the individual atoms are bound in place so the cluster cannot change much to find the equilibrium structure. When the temperature is increased the atoms can move around more so it is more likely that the equilibrium structure will be found. The trend can be seen in figure 2 that the structures tend more to a clean structure when the evaporation rate is slower and the temperature is higher. The equilibrium structure that forms is a truncated triangle.

The attraction between the platinum is about an order of magnitude stronger than the attraction between the platinum and the carbon. The effect of this is that it will be more energetically favourable for the platinum to bond together than to just spread out on the graphite. This can be seen in that the platinum does not form a single layer on the graphite but rather a layered structure. The structure tends to grow layer by layer. The layers tend to cover the layers below them completely, except at low temperatures. At low temperatures the energy of the atoms are too low for them to easily jump down to the layer below.

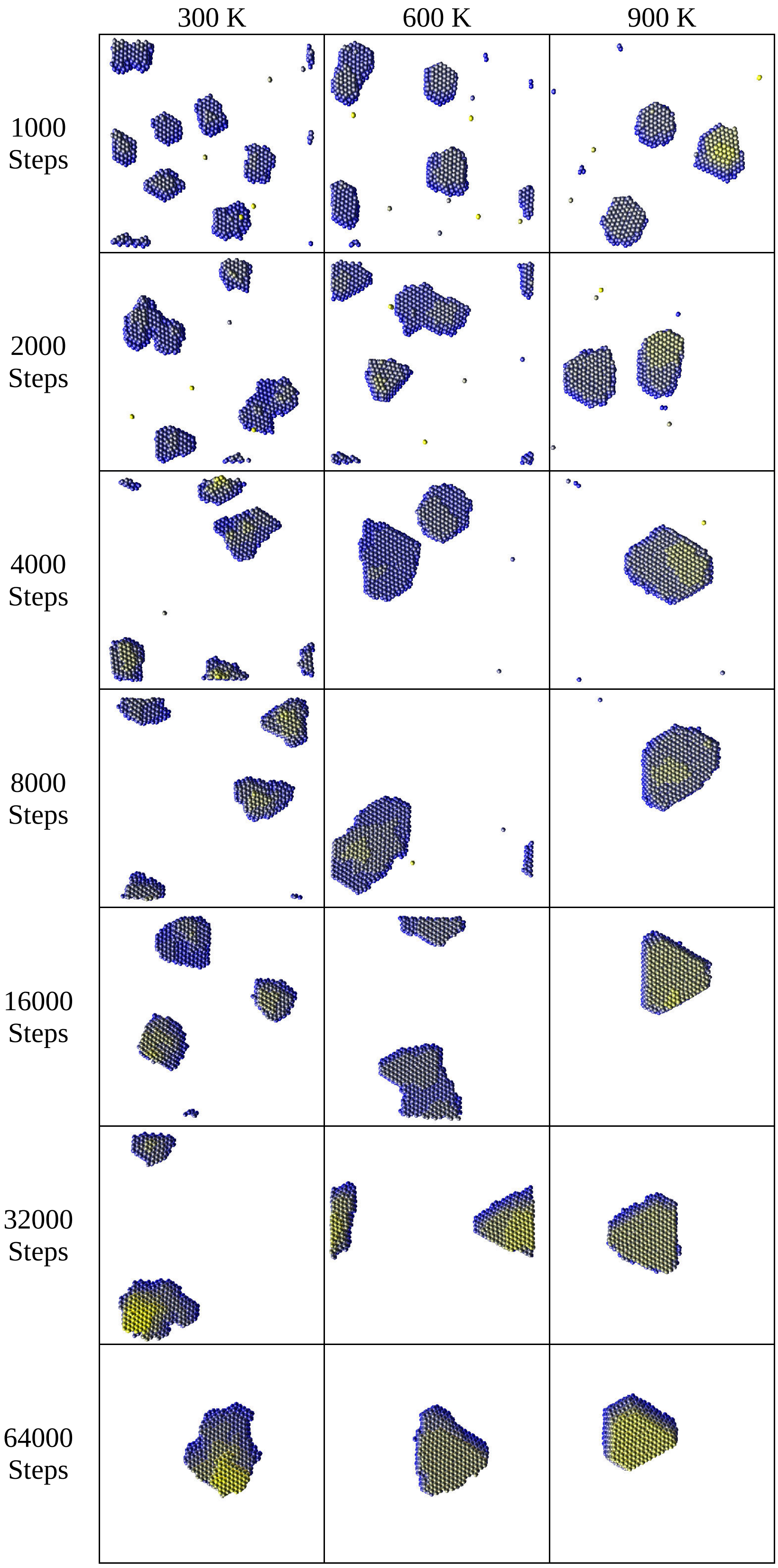

Figure 2. The structures that form at different temperatures and evaporation rates are shown. Each column contains the results from simulations at the given temperature. Each row contains the results from simulations at the given evaporation rate. Note that the steps between atom projections in subsequent rows doubles, which means that the evaporation rate halves for each row down. The first row corresponds to about 3 x 10^8 Å/s or 1.5 x 10^8 monolayers/s. In each of the simulations the same number of atoms was used.

6. Conclusion

Using the Steele potential instead of a few atom layers for the base provided a drastic speedup which enabled the simulation to be done for smaller evaporation rates.

Different structures form depending on the evaporation rate and temperature. Almost all the structures are composed of layers that completely cover the layers below. The structures tend to get larger as the evaporation rate slows. The structures tend to form truncated triangles at higher temperatures and slower evaporation rates. This agrees well with previous studies [4].

References

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