

Atomistic and quantum simulations of materials: Classical Molecular Dynamics of Platinum

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1 Introduction

Molecular Dynamics (MD) is a numerical technique to follow the time evolution of a system, the trajectory of N atoms is determined from the initial set of positions and velocities by numerically integrating the equations of motion. However, one can also use MD as a statistical mechanics method, and it is in that sense that MD will be used in this work. Every simulation will be run using LAMMPS, a powerful software to compute large system evolving in time [1]. We will not be interested in the trajectory, but as a set of configurations distributed according to a statistical ensemble. The following work focuses on a bulk platinum and its phase transitions. First the convergence for important variables of the system will be studied. Then we will be interested at looking at the temperature of the phase transition between solid to liquid, and the properties changes of the system.

2 Molecular Dynamics

2.1 microcanonical (N, V, E) and canonical (N, V, T) phase space

We place N atoms in a box with constant volume V and we keep their total energy E constant during the simulation. It follows automatically that each time step of the system trajectory will be a point in the microcanonical phase space (N, V, E) at those constant N, V, E values. But one can also choose to keep the canonical ensemble (N, V, T) to make the calculation, where this time the temperature T is kept fixed.

For the following of this work, we will consider the convergence of some property A as :

$$\bar{A} = \lim_{\tau \rightarrow \infty} \frac{1}{T} \int_0^\tau A(\vec{r}(t)\vec{p}(t))dt \rightarrow \langle A \rangle, \quad (1)$$

and when applying the discretization to the problem:

$$\langle A \rangle = \frac{1}{N_{ts}} \sum_{n=0}^{N_{ts}} A(t_0 + n\Delta t) \quad (2)$$

3 Convergence

3.1 Convergence of the time step

The first variable needed to be converge is of course the timestep Δt . A good time step need to be big enough in order to save computational time but small enough in order to avoid

integration error in the system, and thus losing any physical meaning or at least reducing the precision (the constant of total energy $E_{tot} = K + E_p$ must be conserved at every time t). Thus a threshold for the standard variation of 10^{-3} eV will be imposed. The convergence for Δt will be computed for the highest simulated temperature ($T = 3000$ K), in order to ensure good time step for all temperatures, as the system is likely to be more energetic and then have higher fluctuations.

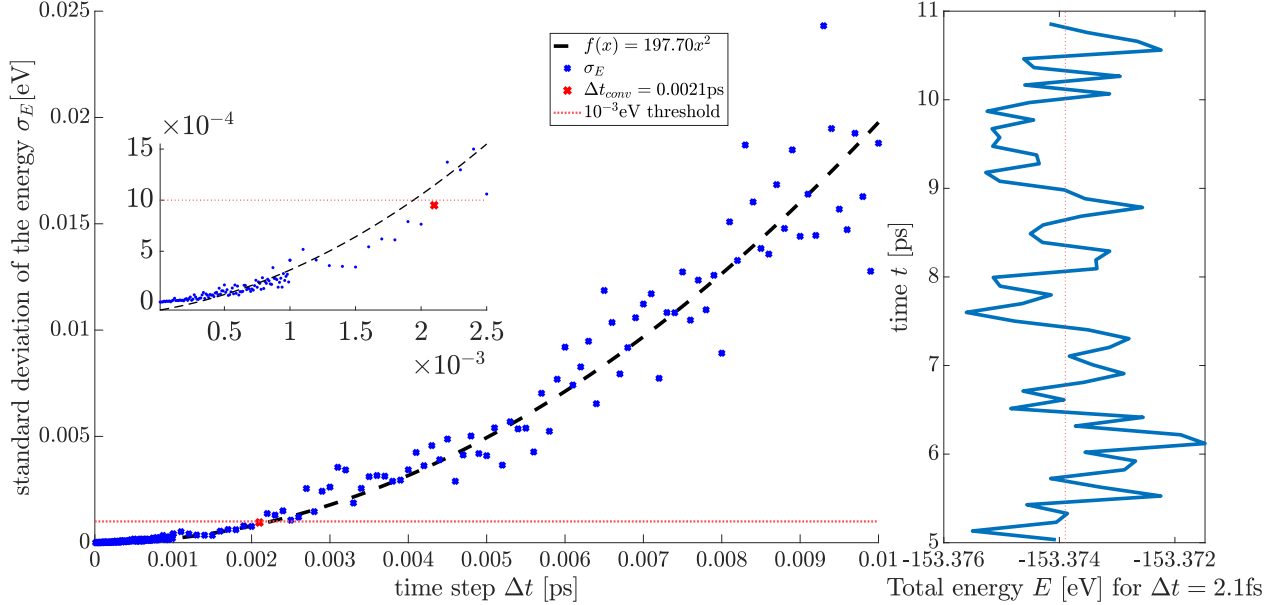


Figure 1: Standard deviation of the total energy σ_E [eV] as a function of timesteps Δt [ps] of bulk platinum. The total energy E is shown as a function of time t [ps] for the ideal time step $\Delta t = 0.021$ ps.

The convergence of the time step is plotted in Fig.1, as well as the total energy for the converged time step $\Delta t_{conv} = 2.1$ fs, which shows the micro fluctuations around the mean of E . As mentioned, according to the convergence threshold explained above, a good value for the time step is $\Delta t_{conv} = 2.1$ fs. Nevertheless, the computational cost of the calculations using LAMMPS for this work is low enough to allow an even smaller time step, $\Delta t_{conv} = 1.0$ fs. Finally, a fit is also plotted to show the convergence rate of σ_E towards 0. This fit is given by $f = 197.70 \cdot \Delta t^2$, indicating a power of 2, and it will be justified with Fig.2 as to why it is the best choice for convergence.

Bonus: Four fits $f(x) = a \cdot x^n$ of order $n \in [1, 4]$ have been tried to determine a precise convergence order. These fits are shown in Fig.2. The expected convergence order for the Verlet algorithm is known to be $O(\Delta t^2)$ [2]. One can observe that this is indeed the case for the standard deviation of the total energy σ_E in Fig.1. It is worth noting that σ_E appears to decrease more slowly once it reaches a value around $5 \cdot 10^{-4}$ eV. It could be argued that for such small time steps and standard deviations, another type of error, such as round-off error, could slow the decrease[2].

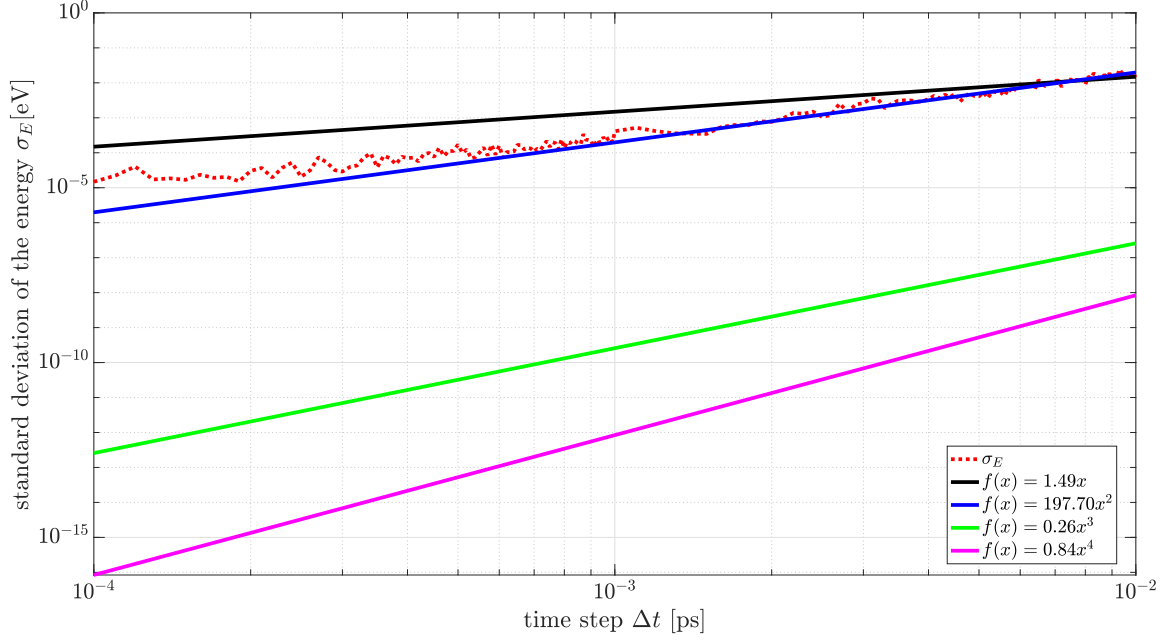


Figure 2: loglog plot convergence order of the total energy σ_E [eV] as a function of timesteps Δt [ps] of bulk platinum

3.2 Convergence of the supercell size

Next, it is essential to ensure the convergence of the supercell size, this will be achieved by looking at the standard deviation of the temperature, both the lowest temperature $T = 1000$ K and the highest temperature $T = 3000$ K. The convergence is supposed to be reached when the standard deviation turns to be below 5% of the input temperature for some supercell size.

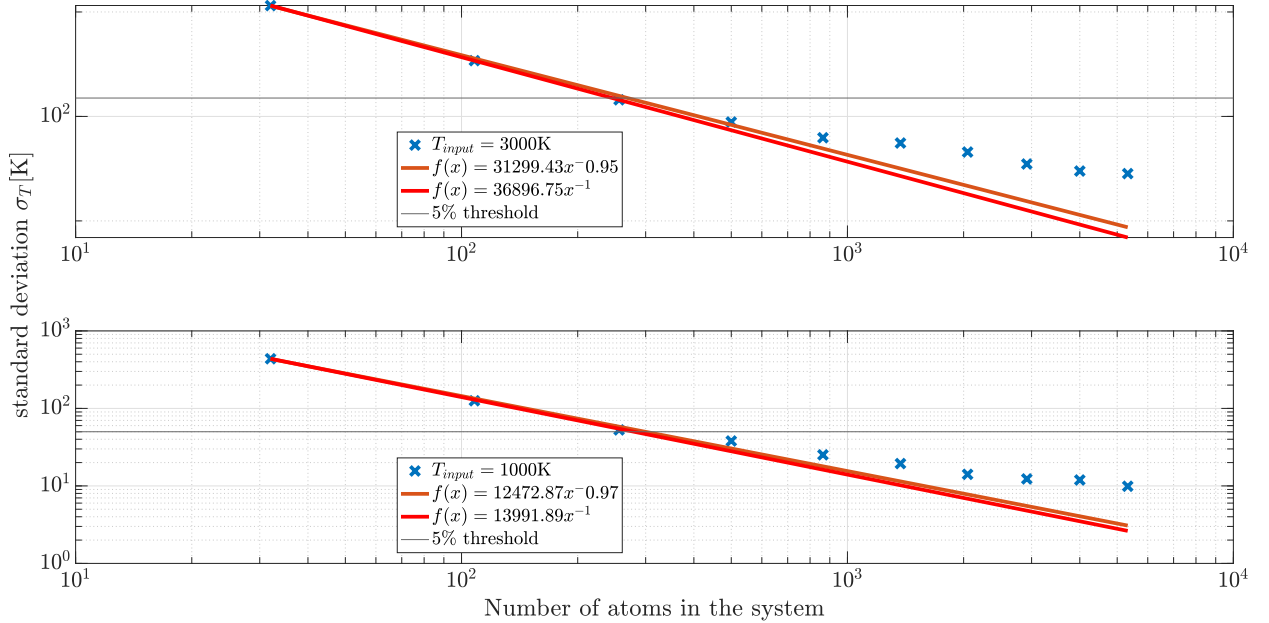


Figure 3: Standard deviation of the temperature σ_T [K] as a function of the number of atoms in the platinum bulk for 2 input temperatures: $T = 3000$ K (up) and $T = 1000$ K (down)

Two fits have been applied to both graphs in Fig.3 : one with the optimized parameter b such that $f = ax^b$, and the other with b rounded to the nearest integer. In both cases, the nearest integer is -1, implying that the standard deviation of the temperature is inversely proportional to the number of atoms in the system.

As written above, the convergence threshold accepted is 5% of the input temperature, this imply threshold of 150 K and 50 K for input temperature of $T = 3000\text{K}$ and $T = 1000\text{K}$ respectively. The first super cell size (eq. to the number of atoms in the system) that allows a σ_T bellow the threshold in both cases is 4 (or equivalently 500 atoms). Thus this value will be used for the following part of the work.

3.3 Convergence temps de run (VAF)

Finally, one last key parameter that needs to be converged as well is the production time. As it can be a very complex task, it is useful to instead look at the velocity auto-correlation function (VAF):

$$VAF(t) = \frac{1}{3N} \sum_i^N \sum_\alpha^3 \langle v_{i,\alpha}(0) \cdot v_{i,\alpha}(t) \rangle, \quad (3)$$

where $v_{i,\alpha}(t)$ is the velocity in the direction $i \in [x, y, z]$ of the particule α at the time t . After some decorrelation time t_c , the VAF will oscillate randomly around 0. Only simulation times above t_c give new information about the system. The simulations will be made for the smallest temperature studied ($T = 1000\text{K}$) as the system will have the lowest energies and velocities (particles will be less excited).

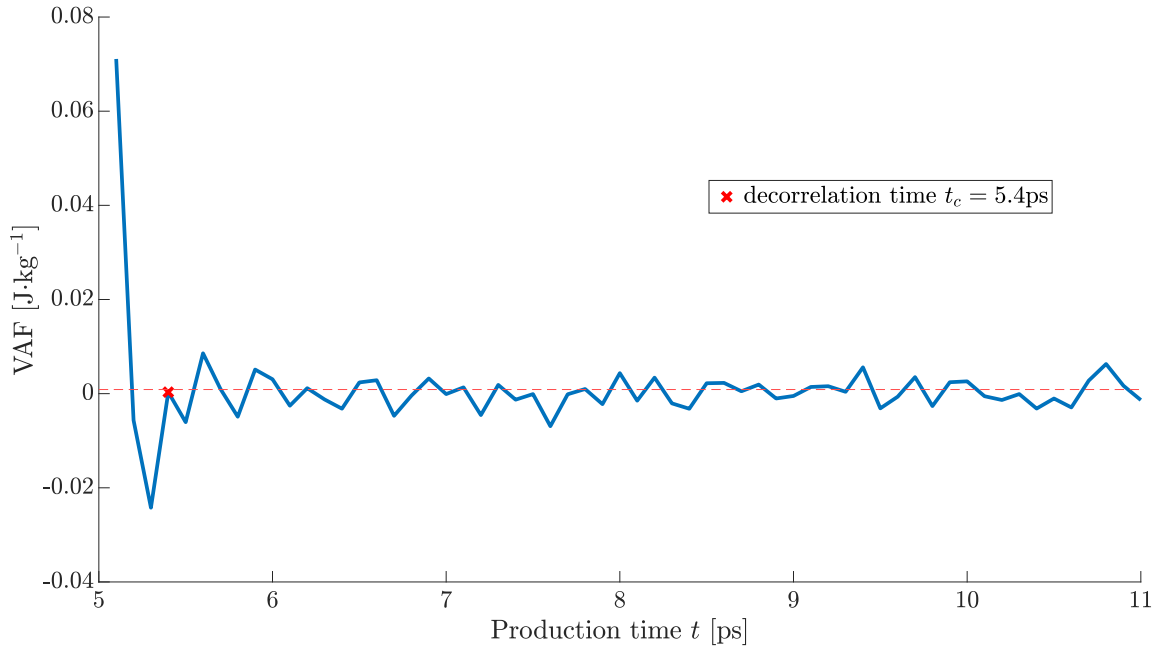


Figure 4: Velocity auto-correlation function [$\text{J}\cdot\text{kg}^{-1}$] as a function of time $t[\text{ps}]$

The critical time t_c is reach for a time $t_c = 5.4$ ps, but as the production start only at 5 ps, the critical time is reach 0.4 ps after the start of the production time.

We know that the kinetic energy can be written as $E_K = \sum_i \frac{1}{2} m_i v_i^2$. And the mean on the

time of this quantity is $\langle E_K \rangle = \frac{1}{N_{ts}} \sum_{n=0}^{N_{ts}} E_K(t_0 + n\Delta t) = \sum_i^N \langle \frac{M}{2} v_i^2 \rangle$, where we suppose every particle have the same mass $m = \frac{M}{N}$, which is equal for the platinum as: $m = 3.24 \cdot 10^{-25} \text{kg}$. Thus we can link this kinetic energy to the velocity auto-correlation function such as:

$$VAF(0) = \frac{1}{3N} \sum_i^N \sum_{\alpha}^3 \langle v_{i,\alpha}(0) \cdot v_{i,\alpha}(0) \rangle = \sum_i^N \langle \frac{1}{3N} v_i^2 \rangle = \frac{2}{3NM} \langle E_K \rangle \quad (4)$$

But if we try to compute this for one of the trajectories, we get: $VAF(0) = 4.1 \text{J} \cdot \text{kg}^{-1}$ and we got $\frac{2}{3NM} \langle E_K \rangle = 1.50 \cdot 10^2 \text{J} \cdot \text{kg}^{-1}$, so with a factor 10^2 of difference, something clearly does not work for these calculations.

4 Melting of bulk platinum

Once all the parameter have been fixed with good converged values, it is now possible to determine the melting point of the platinum using various methods. For these calculations, the temperature will be fixed as well as the volume (NVT).

4.1 Phase transition

One first way to find the melting point is to look at the caloric curve, so the potential energy per atom as a function of the temperature. Another way is to plot the total energy as a function of the temperature. The graph on Fig.5 shows both ways and is composed of 3 parts. First a part where the potential energy increases with the temperature linearly. Then after a temperature of approximately $T = 2180 \text{K}$, the Potential energy E_p increases faster until $T = 2340 \text{K}$ where a second linear part starts again. These three parts can be identified as the temperature bellow which the platinum is still solid (first part), the phase transition between solid and liquid and finally when the platinum is fully liquid. Thus the melting point happened in that second part and more precisely between $T_c \in [2300 - 2310] \text{K}$ (The melting point have been taken to be the highest energy gap between two consecutive points).

Two other ways to see this phase transition are to look at the total energy and the pressure as a function of the temperature. The result show a similar melting point for the three plots.

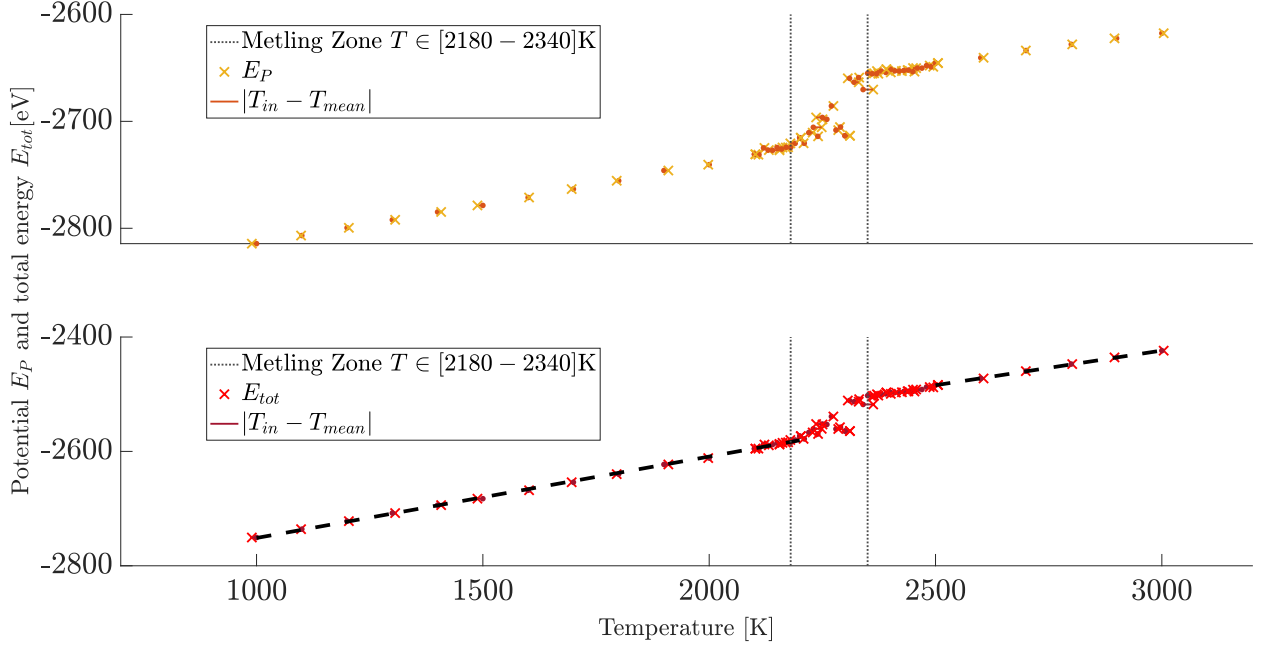


Figure 5: Potential energy E_P and total energy E_{tot} [eV] as a function of the temperature T [K] for the platinum

Finally one can also plot the pressure P in the platinum as a function of the temperature.

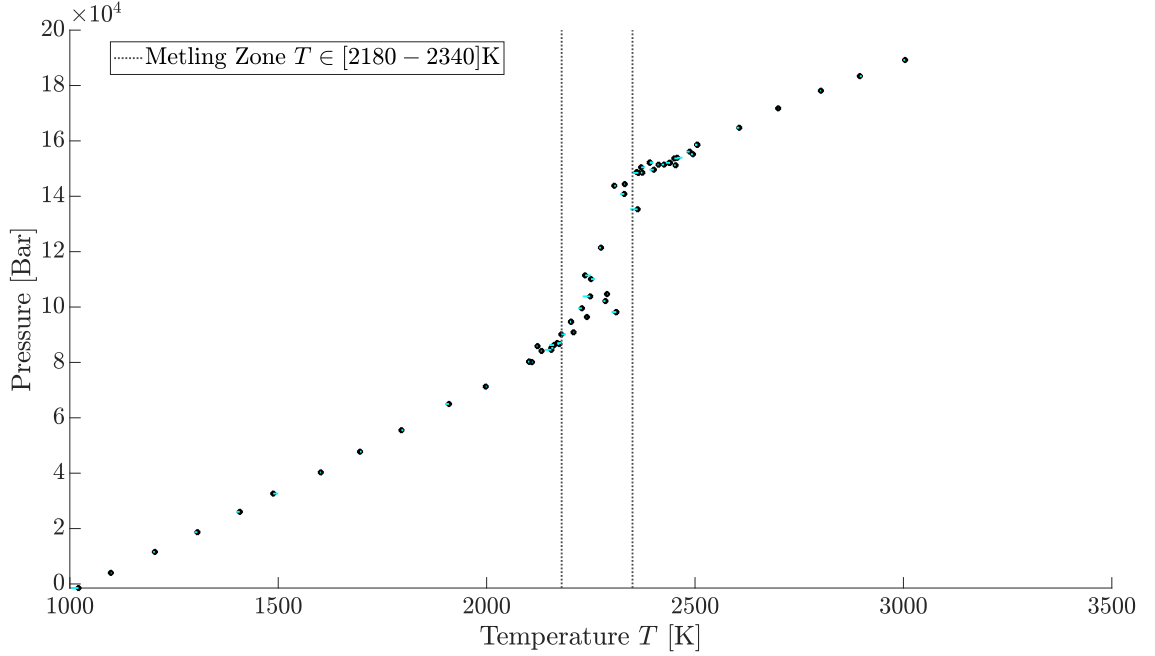


Figure 6: Pressure P [bar] as a function of the temperature T [K] for the platinum

As expected this plot shows the same result for the melting zone and melting point as the caloric curve. It can be noted that the phase transition in both the total energy and the pressure are less visible than for the caloric curve.

4.2 Heat capacity at constant volume

Another way to estimate the phase transition is the heat capacity at constant volume C_V . It can be computed using two methods. First noticing that it is related to the variance of energy as:

$$C_V = \frac{\sigma_{E_{tot}}^2}{k_b T^2} \quad (5)$$

where the Boltzmann's constant is $k_b = 1.380649 \cdot 10^{-23} \text{ J}\cdot\text{K}^{-1}$. It also should be added that the heat capacity is an extended quantity, its value depends on the number of atoms in the simulation cell (256 atoms for the case of a super cell size of 4).

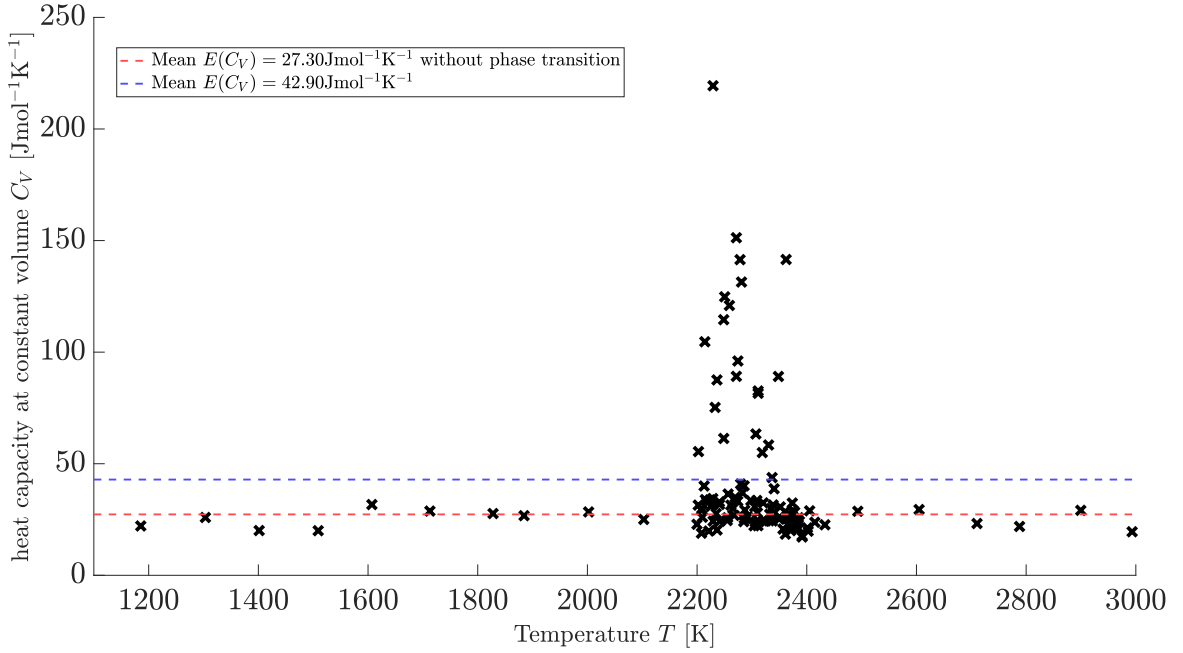


Figure 7: Potential energy E_P and total energy E_{tot} [eV] as a function of the temperature T [K] for the platinum

It is possible to find a value in the literature for the heat capacity at a temperature $T = 1000\text{K}$ of $C_V = 29.32\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ [3], whereas the computed value give, outside phase transition, for $T = 1000\text{K}$ a value $C_V = 27.30\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Both are in the same values range. At the melting point, the heat capacity can reach values greater than $C_V > 150\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ but it seems that this explosion around the melting point is really chaotic as is oscillate a lot. Using the original definition of this quantity, eq.6, the second way in order to determine the heat capacity at constant volume is:

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = \left(\frac{dU + PdV}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \quad (6)$$

where we used the second principle of thermodynamics and the fact that $dV = 0$. Then by discretizing this equation it is possible to compute C_V as:

$$C_V = \frac{U_i - U_{i+1}}{\Delta T} \quad (7)$$

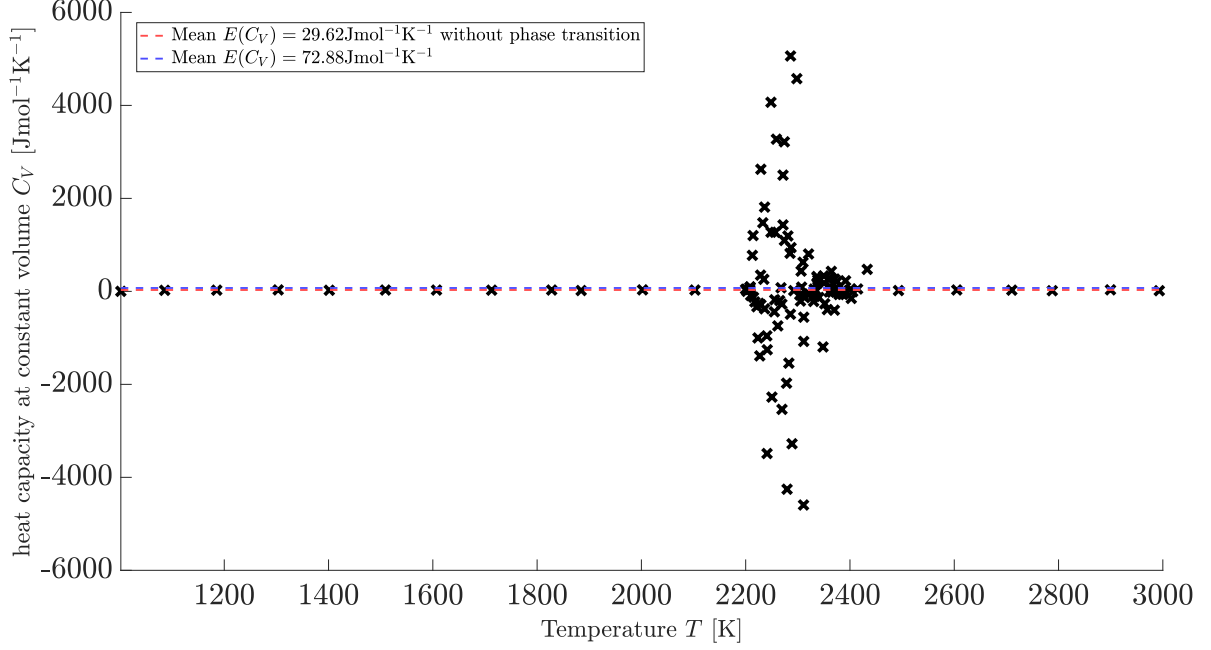


Figure 8: Potential energy E_P and total energy E_{tot} [eV] as a function of the temperature T [K] for the platinum

This time, the Fig.8 shows values for C_V of $C_V = 29.62 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ but the observed trend is the same than the previous one, the heat capacity increases a lot near in phase transition (values around 2300K are around 200 times higher than the mean without phase transition). A slight difference here is that with this definition, C_V also have negative value around the melting point, the curve look a bit symmetric around the mean $E(C_V) = 72.88 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Nevertheless for both cases, whereas the phase transition is clearly visible, the melting point is much harder to determine using the plot of the heat capacity than looking at the caloric curve.

4.3 Equation of state

As we are no looking at NVT simulations, the volume is put to be a constant of the system, nevertheless it is still possible to plot the equation of state (the volume as a function of the temperature. Indeed we want to vary the volume at an ambient pressure. Thus it is possible, by changing the cell parameter in the input to have different volume for NVT calculations and then taking the pressure which corresponds to the ambient one. The same process can also be applied to find the volumetric thermal expansion coefficient α and the isothermal bulk modulus K_T .

4.4 Radial distribution functions (RDF)

Radial distribution functions measure the density of atoms as a function of the distance. As it can be experimentally determined, it is an interesting property to compute. It will be computed up to the maximum radial distance in the cell.

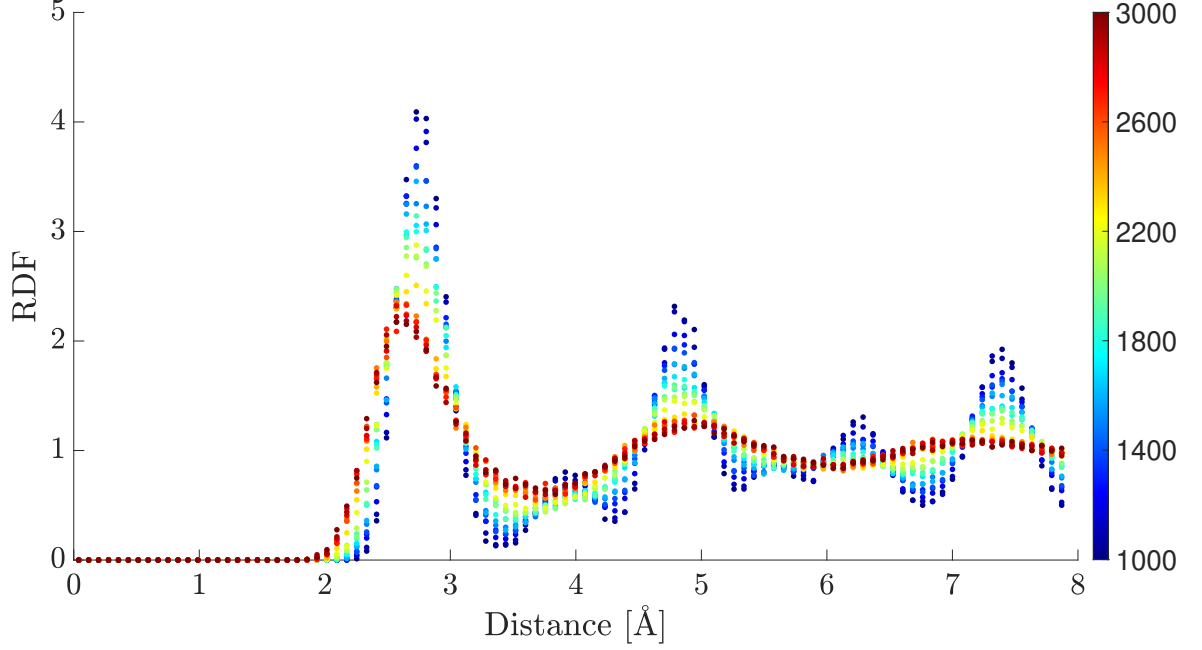


Figure 9: Radial distribution function (RDF) as a function of the distance $x[\text{\AA}]$

Before reaching the melting point, Fig.9 illustrates that at lower temperatures, the radial distribution function (RDF) exhibits greater instability with distance compared to higher temperatures. Additionally, as the temperature increases, the RDF plots converge near the phase transition. This means that beyond this transition, the RDF curve will no longer depend on the temperature variations.

4.5 mean square displacement (MSD)

The mean square displacement is a property that allows us to see if atoms can move freely or are bound to their position, it can be determined as:

$$MSD(t) = \frac{1}{3N} \sum_i^N \sum_{\alpha}^3 \langle |R_{i,\alpha}(0) - R_{i,\alpha}(t)|^2 \rangle, \quad (8)$$

LAAMPS give directly MSD for each Δt , we can the plot the MSD as a function of the temperature.

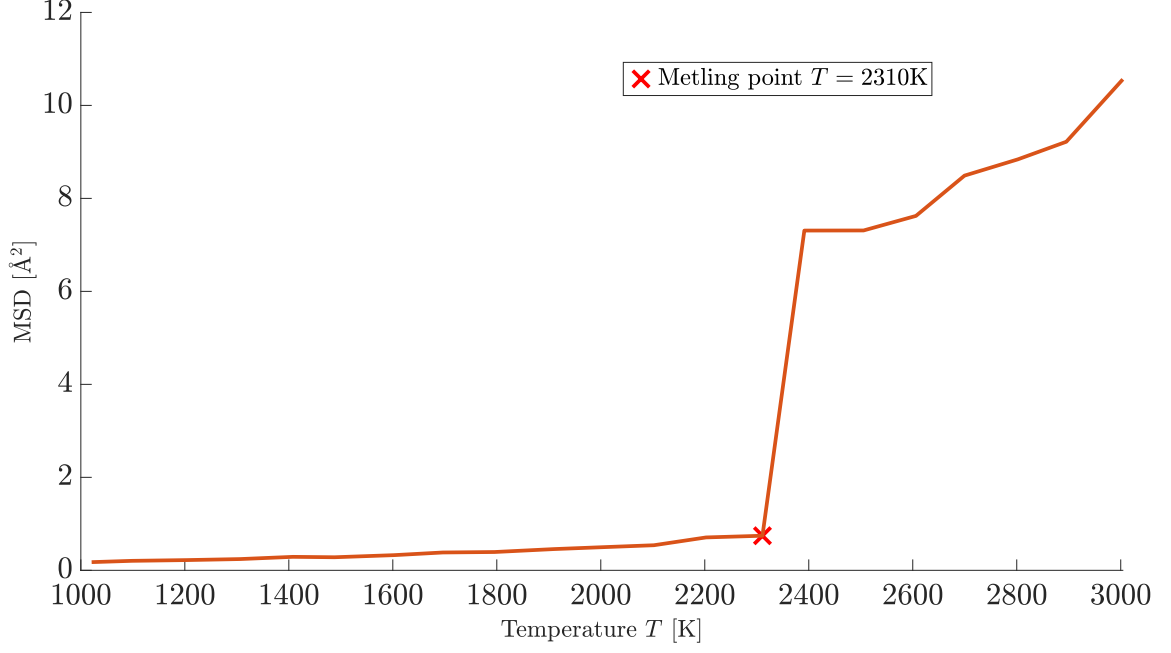


Figure 10: Radial distribution function (RDF) as a function of the distance $x[\text{\AA}]$

It is here clear that the melting point is $T_c = 2310$ K. The gap between the MSD before and after the melting point make total sense. Indeed in the solid phase, the atoms are clearly constant by the lattice structure of the solid whereas when going into the liquid phase, those same atoms will have a lot more freedom around their initial position.

Once the MSD plotted, one can obtain the self-diffusion coefficient (D) as:

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{dMSD(t)}{dt} \approx \frac{MSD_i - MSD_{i+1}}{6\Delta t}, \quad (9)$$

where $d = 3$ is the dimension of the system for a $t > t_c$.

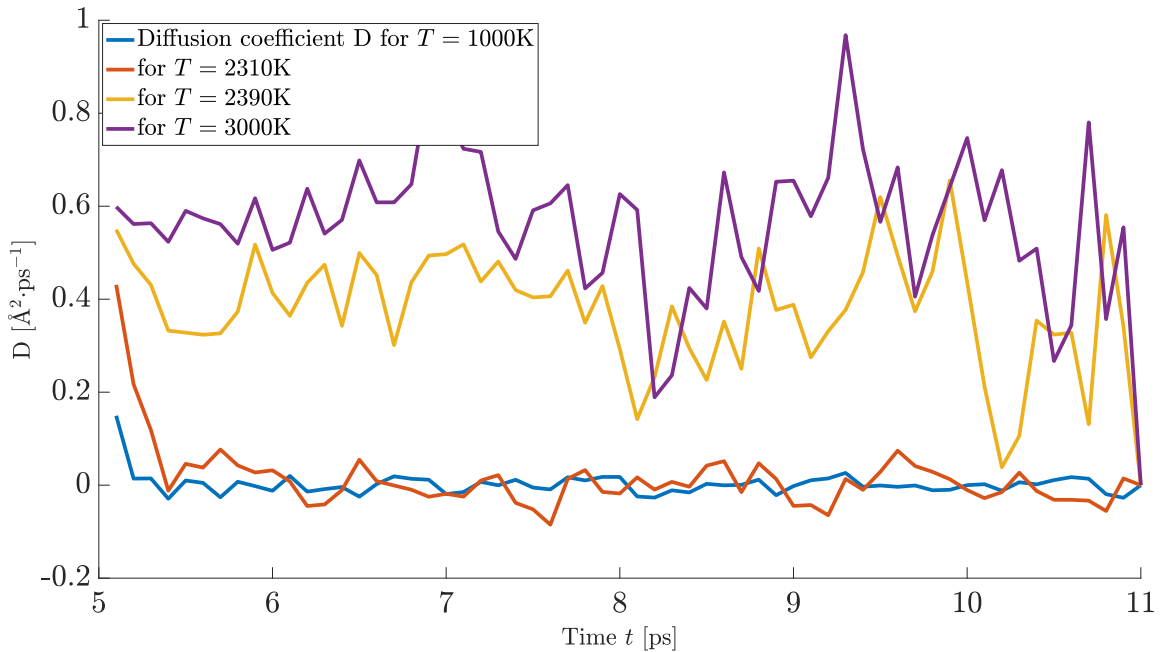


Figure 11: Radial distribution function (RDF) as a function of the distance $x[\text{\AA}]$

As expected, the diffusion coefficient D increases a lot after the melting point $T = 2310\text{K}$, this can be seen both in Fig.10 and Fig.11.

References

- [1] *LAMMPS Documentation*. URL: <https://docs.lammps.org/Manual.html>.
- [2] Laurent Villard. *Physique numérique I-II*. URL: https://moodlearchive.epfl.ch/2021-2022/pluginfile.php/77901/mod_resource/content/9/physnumbook_21_1.pdf.
- [3] Yoichi Takahashi Harumi Yokokawa. “Laser-flash calorimetry II. Heat capacity of platinum from 80 to 1000 K and its revised thermodynamic functions”. In: *The Journal of Chemical Thermodynamics* (1979).