Classical Molecular Dynamics of Gold

Lab 4

Atomistic and Quantum Simulations of Materials

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The topic of this report is the study of the properties of Gold through classical Molecular Dynamics simulations. The program used in all the exercises is General Utility Lattice Program (GULP).

Gold is modeled by the Embedded Atom Method (EAM). It is necessary due to the fact that the system is a metal, and we need to account for the characteristic nature of the metallic bond, where the electrons are free to move inside the solid.

We also assume that the system is ergodic, so that the ensemble averages can be computed through time averages.

The goal is the study of the melting of Gold. At room temperature (298.15 K) and ambient pressure (1 atm) the stable crystalline form of Au is face-centered-cubic (fcc), and by changing the temperature obviously this stable structure changes. As already said, in order to describe this system the EAM potential is adopted and the supercell method used. The melting point of Gold is at $1337K$, so in order to look at the phase transition we consider temperatures in the range $800K - 2000K$. The minimum supercell size, in order to have not too large fluctuations of the quantities we are interested in, is $2 \times 2 \times 2$. The equilibration time used is $2ps$.

1 Exercise 1: Testing simulation parameters

In this first problem we focus on the study of the convergence of the parameters needed to perform a simulation with an adequate precision. In particular we investigate the size of the best time step, the size of the supercell and the length of the production run.

1.1 Task A

The first goal is to find a good time step for our simulations. It should allow to save computational time and at the same time it leads to small integration errors. We then perform several MD simulations with different time steps and we test the convergence of the time step by looking at the energy conservation in the NVE ensemble. In order to have an idea about the size of energy fluctuations we need to calculate the variance of the energy. It can be done through Equation (1).

$$\sigma_A^2 = \frac{1}{t_{run}} \sum_{t=1}^{t_{run}} \left(A(t) - \langle A \rangle_{run} \right)^2 \tag{1}$$

where A is the sampling quantity, an example could be the total energy E or the temperature of the system T.

Here we use the highest temperature of 2000 K, and the smallest supercell size $2 \times 2 \times 2$ that we will use later. This choice is dictated by the fact that the periods of oscillation of the system get shorter at high temperature and for small supercell size. As a consequence, if the time step converges for the highest temperature and for the smallest supercell size, it will always converge in our calculations.

The Verlet algorithm used here implicitly assumes that velocities and accelerations are constant over each time step. Then, in general by considering the vibrational period of the lattice, a good choice is to split it into 100 segments. In the case of Gold, a safe time step is then $1 fs$.

Keeping this in mind, we choose to simulate the system with time steps in the range $[1 fs - 10 fs]$. The production run is set to $10 ps$ while the sampling step is $0.02 ps$.
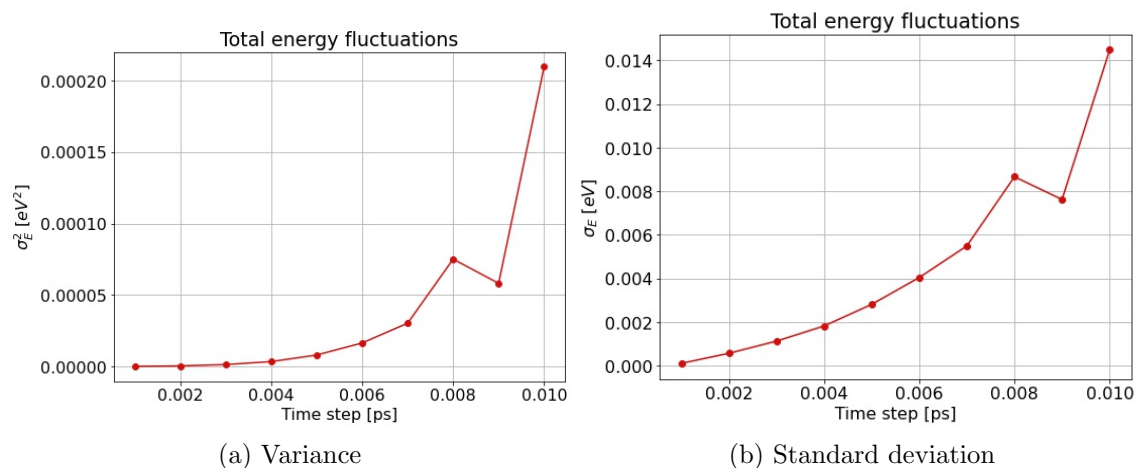

(a) Variance   (b) Standard deviation

Figure 1: Variance and standard deviation of the total energy as a function of the time step.

By looking at Figure 1, it's possible to see that, as expected, the size of the fluctuations of the energy decreases as the time step becomes smaller. An acceptable value for the time step is $0.004 ps$. It's assures the convergence of the energy, indeed the fluctuations are only about $\sigma_E = 0.002$, and also it isn't too expensive from a computational point of view. By using a smaller time step we would spend too much time without gaining a significant difference in the value of the energy.

It's also interesting to plot the energy as a function of time for the converged run. In this way it's possible to directly see how the energy fluctuates in time, and check if there is a drift. Figure 2 is obtained by adopting the time step chosen before: the energy oscillates around its mean value with an amplitude around $0.004 \ eV$, as well estimated by the standard deviation. In addition, no signifi-

cant drift in the energy is present in this case, which means that the integration algorithm we are using is good.
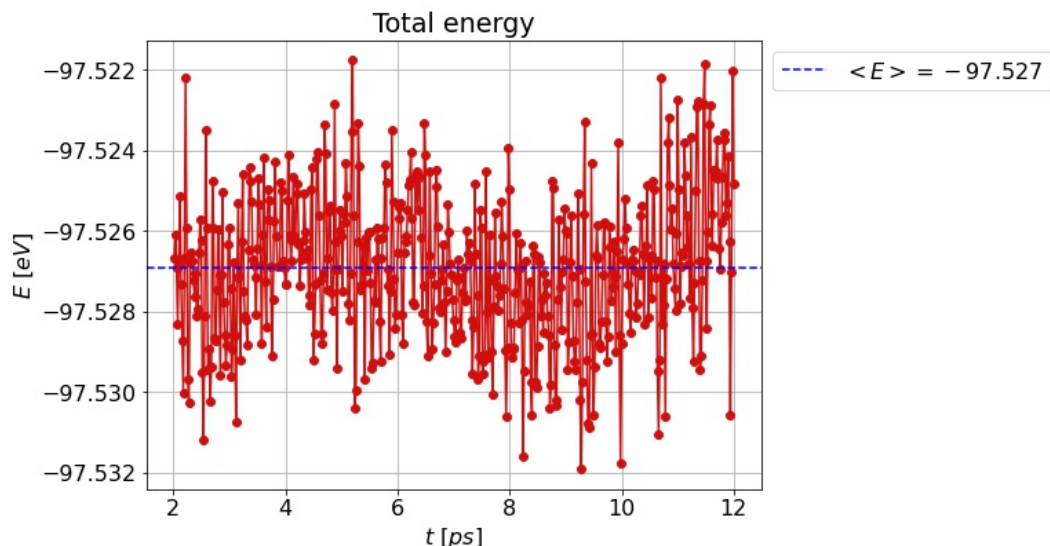

Figure 2: Total energy as a function of time when $\Delta t = 0.004ps$ and its mean value.

It's also possible to see from Figure 1 that the fluctuations of the energy significantly vary with the step size. As expected from the theory, they decrease while the time step becomes always smaller. Indeed, by adopting a smaller time step in the simulation, we obtain a reduction of the integration error, which scales with some powers of Δt depending on the integration algorithm. In this case, we are using the standard Verlet algorithm (2).

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + a(t)\Delta t^2 + O(\Delta t^4)$$
$$a(t) = -\frac{1}{m}\nabla V(r(t)) \tag{2}$$

Here, the integration error scales with the 4th order of the time step. Indeed it's possible to see in Figure 3 that a 4th order polynomial is a very good fit for the values of energy fluctuations.
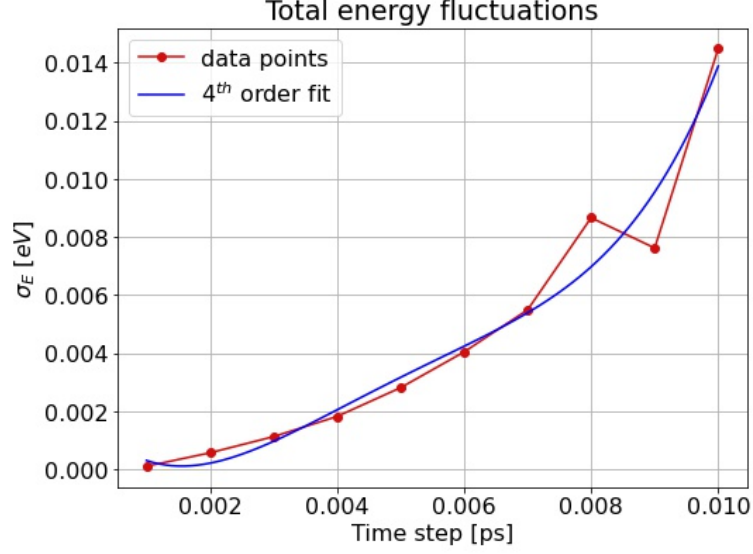
3

Figure 3: Fit of the energy fluctuations σ_E with the curve $y = 8.92 \ 10^6 x^4 - 1.74 \ 10^5 x^3 + 1.24 \ 10^3 x^2 - 2.74x + 1.97 \ 10^{-3}$.

1.2 Task B

Now that we have chosen the time step, we need to decide also the size of the supercell we want to use. In order to do so, we have to look at the fluctuations of the temperature. As it has been done before, the standard deviation of the temperature for every size of the supercell is calculated. Then it is also normalized with the target temperature of the case. We consider acceptable fluctuations that are the 5% of the target temperature.

We test the convergence, with respect to the supercell size, for both the lowest and the highest temperature, respectively $T = 800K$ and $T = 2000K$. The adopted range of supercell sizes is from 2 to 6 unit cell in each direction. So the size will be $2 \times 2 \times 2$, $3 \times 3 \times 3$ and so on, until $6 \times 6 \times 6$. The other parameters are set as in the previous task.

The variance of the temperature is calculated again as in (1) and the deviation standard by taking the square root of it. Then, in order to be able to compare the size of the fluctuations with the target temperature, the ratio $\sigma_T \ / \ T$ has been performed. Then it's possible to individuate the size of the supercell which allows to get convergence, for a threshold of 5% as already said before. From Figure 5 we deduce that a good size for the supercell of our system is $4 \times 4 \times 4$.
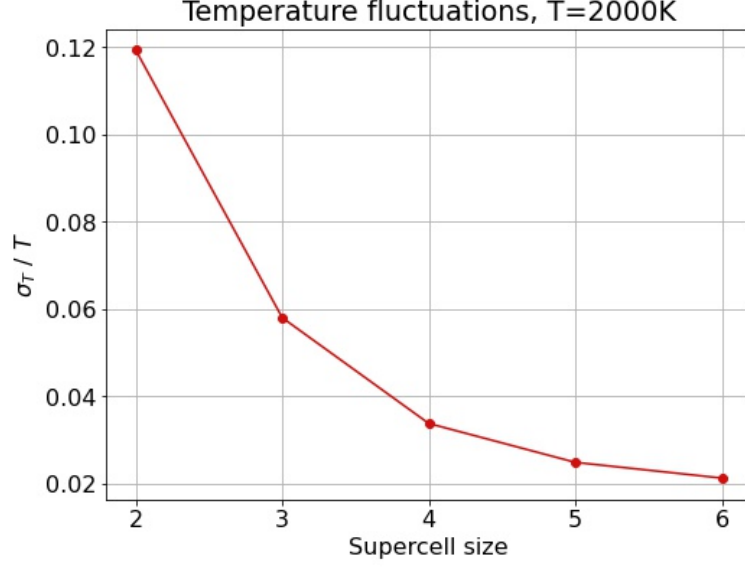
Figure 4: Standard deviation of the temperature divided by the target temperature of $2000K$ as a function of the supercell size.

In order to see how the fluctuations decrease with the size of the system, a linear fit of $log(\sigma_T^2)$ is performed against $log(N)$, where N is the number of the atoms in the system and it is found by multiplying the number of unit cell in the supercell by 4, that are the atoms in a single unit cell. It is found that the best fit is given by the line in (3).

$$y = -1.076\ x + 14.574 \tag{3}$$

It's then possible to deduce that the size of temperature fluctuations decreases in an exponential way while the dimension of the system increases.

The same has been performed also at $T = 800K$, just to check that also in this case a supercell of 4 unit cell in each direction is enough to make the temperature to converge. Figure 6 perfectly confirms this.
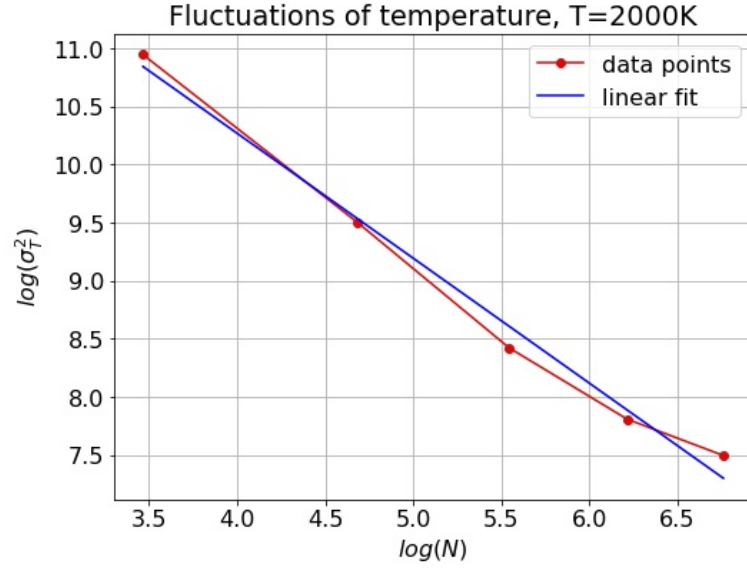
Figure 5: Linear fit of the logarithm of the variance of the temperature as a function of the logarithm of the number of atoms in the supercell.
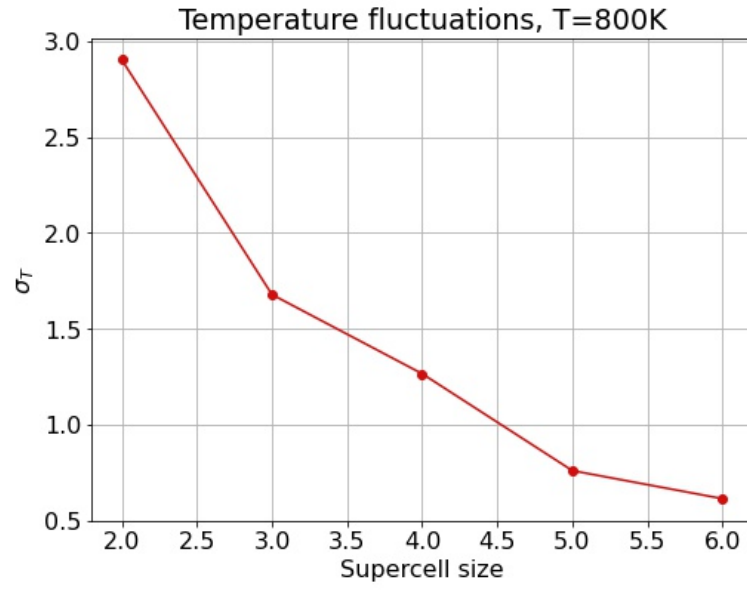

Figure 6: Standard deviation of the temperature divided by the target temperature of $800K$ as a function of the supercell size.

1.3 Task C

The last parameter we have to study is the length of the production run. Theoretically it should converge with respect to all the quantities we are interested in, but check the convergence with respect to each one of them would be a very long process. Another shorter way is to look at the velocity auto-correlation function (VACF), showed in Equation (4). It describes when a trajectory looses its memory, which means it is not correlated anymore to the starting point.

$$VACF(t) = \frac{1}{3N} \sum_{I}^{N} \sum_{\alpha=1}^{3} \langle V_{I_\alpha}(t) \, V_{I_\alpha}(0) \rangle \tag{4}$$

where $V(t)_{I_\alpha}$ is the velocity of a particle I at time t in direction α. When its value starts fluctuating around 0, it means that the decorrelation time t_c of the system has been reached. We need then to simulate the system with a production run at least as longer as the decorrelation time.

It's important to specify that the estimate of the decorrelation time should be done at the lowest temperature. This is a consequence of the fact that the system in this case has less energy, velocities are lower and more time is needed to 'forget' the initial conditions. We want to adopt a series of parameters that guarantees a good sampling for all the temperatures we investigate, so we study the production run only for $T = 800K$. Then at $T = 2000K$ the decorrelation time will be shorter, so that we are sure that our production run is long enough also in this case.

Then we perform a $2ps$ equilibration and a $50ps$ production run in order to be able to individuate t_c. Time step and supercell size are fixed as found before.
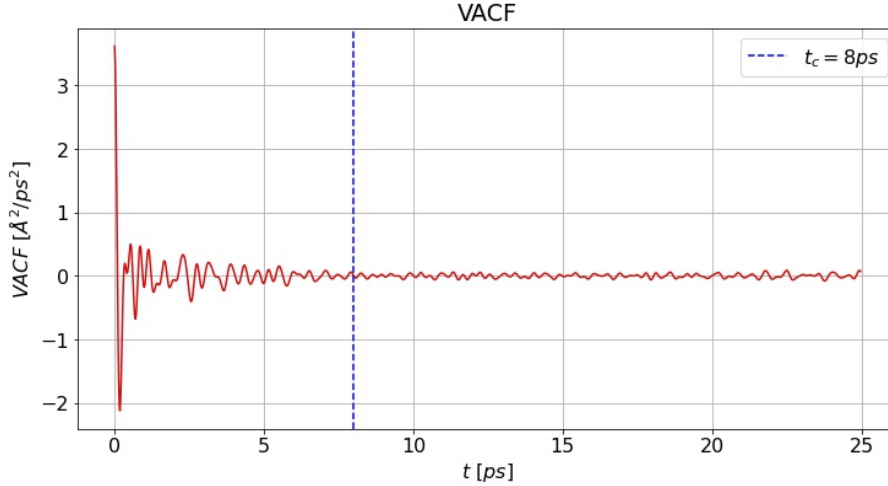

Figure 7: Velocity auto-correlation function of the system and decorrelation time t_c.

As it's possible to see in Figure 7, around $8ps$ the oscillations of the VACF start becoming dramatically small. We can then approximate the decorrelation time of the system as $t_c = 8ps$ and set all our successive calculation to have a production run equal to this amount of time.

We can derive how the value of VACF(0) is related to the average kinetic energy through some simple passages, as shown below.

$$
\begin{aligned}
VACF(0) &= \frac{1}{3N} \sum_I^N \sum_{\alpha=1}^3 \langle V_{I_\alpha}(0) \; V_{I_\alpha}(0) \rangle \\
&= \frac{1}{3N} \sum_I^N \sum_{\alpha=1}^3 \langle V_{I_\alpha}^2(0) \rangle \\
&= \frac{1}{3N} \sum_I^N \frac{2}{m} \langle \frac{1}{2} m \overrightarrow{V}_{I_\alpha}^2(0) \rangle \\
&= \frac{1}{3N} \frac{2}{m} \sum_I^N \langle E_{kin,I} \rangle \\
&= \frac{1}{3N} \frac{2}{m} \langle E_{kin} \rangle
\end{aligned}
\tag{5}
$$

It's then possible to check this result by looking at one of the trajectories obtained from the previous run. For example, here we choose to compute the average kinetic energy for the trajectory with $\Delta t = 0.004ps$, $T = 800K$, supercell size of $4 \times 4 \times 4$. We obtain the following.

$$
\begin{aligned}
VACF(0) &= 3.62 = 36206.37 \; \frac{m^2}{s^2} \\
\frac{1}{3N} \frac{2}{m} \langle E_{kin} \rangle &= \frac{1}{3 \; 4(4^3)} \frac{2}{196.96 \; u} \; 47.04 \; eV = 36071.83 \frac{m^2}{s^2}
\end{aligned}
\tag{6}
$$

As it's possible to see, the two calculated quantities are very similar. This confirms our previous finding.

2 Exercise 2

We can now proceed with the estimation of the melting temperature of Gold. In order to do so, some MD simulations in the NVT ensemble are needed. As said before, we will consider the range of temperatures $800K - 2000K$ with a resolution of $100K$. All the other parameters have been set as found in Exercise 1

($\Delta t = 0.004ps$, supercell size $4 \times 4 \times 4$, production run $8ps$). Starting from these data then several ways exist for the estimation of a phase transition temperature. They include: looking at which temperature the caloric curve presents a discontinuity, identifying when the radial distribution function dramatically changes its behaviour, finding the transition to diffusive behaviour by looking at the diffusion coefficient, looking for a divergence in the fixed-volume heat capacity.

2.1 Task A

The first way we decide to follow is the one which involves the caloric curve.

We calculate the average of potential energy per atom as a function of the temperature, known also as caloric curve. It's shown in Figure 8. Also the pressure and total energy are calculated from the results of the simulations, see Figure 9 - 10.

It's known that when a phase transition happens in a material, its caloric curve presents a discontinuity. As it's possible to see from Figure 8, an evident discontinuity is present in the averaged potential energy of Gold. It corresponds at a temperature between $1500K$ and $1600K$. We can deduce then that this is the range of temperatures in which the melting temperature of Gold is located. We can't provide here a more precise estimate due to the low resolution in temperature, but it can be done by performing more MD simulations with a smaller temperature step.
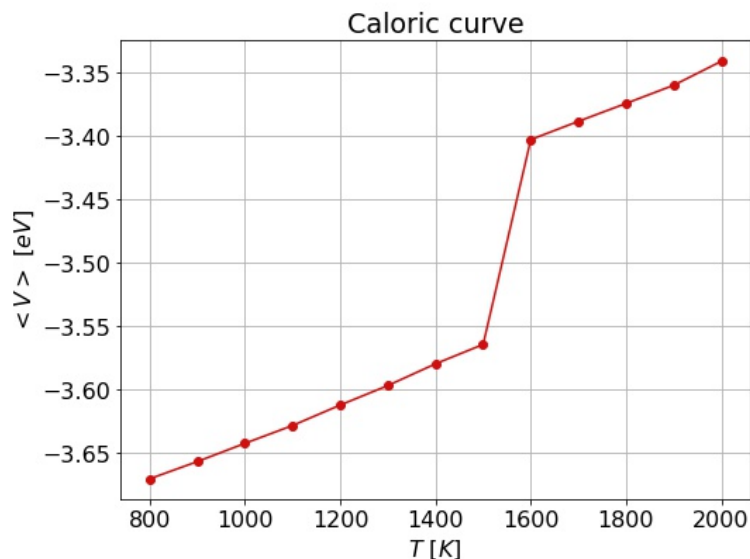
Figure 8: Average potential energy per atom as a function of the temperature. Calculated in NVT ensemble.
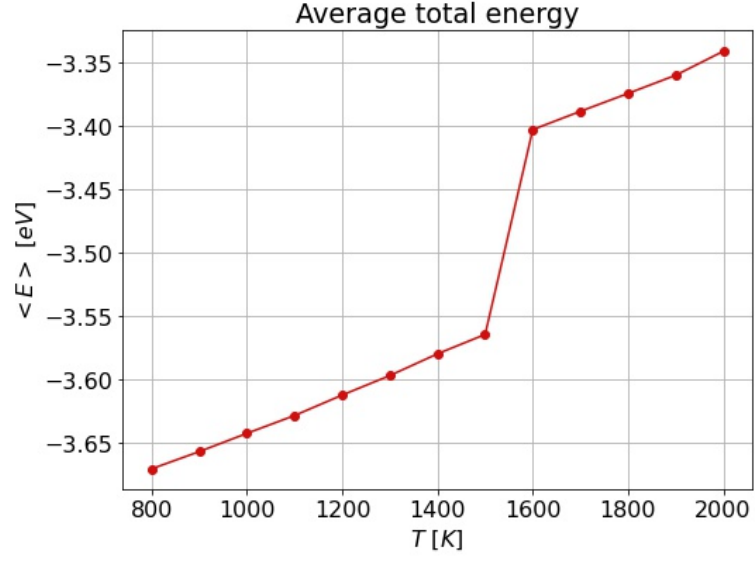
Figure 9: Average total energy as a function of the temperature. Calculated in NVT ensemble.
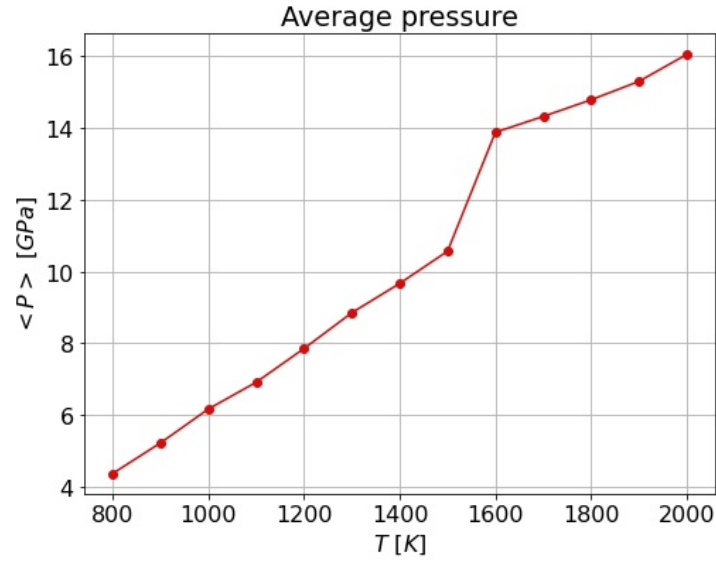

Figure 10: Average pressure as a function of the temperature. Calculated in NVT ensemble.

Also in the plots of the averaged total energy and pressure there is a discontinuity in the same range of temperatures. This is obviously due to the fact that these two quantities are strictly related to the averaged potential energy.

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2.2 Task B

We want now to estimate the melting temperature of Gold through another technique, which consists in looking at the radial distribution function (RDF) of the system (Equation 7).

$$g(r) = \frac{1}{\rho_0} \frac{1}{N} \sum_{I=1}^{N} \frac{\langle n_i \rangle}{4\pi r^2 \Delta r}$$
$$n_i = \sum_{J=1, J \neq I} n_i(I, J) \tag{7}$$
$$n_i(I, J) = \begin{cases} 1 & \text{if } r - \Delta r/2 < r < r + \Delta r/2, \\ 0 & \text{otherwise} \end{cases}$$

where ρ_0 is the mean density of the material, N the number of atoms and n_i an histogram collecting the location of the atoms with respect to the distance from atom I.

The RDF is a measure of the 'internal structure' of the system, indeed, it is the normalized density of atoms as a function of the distance from one generic atom. It should present a different behaviour depending on the phase of the material. For instance, the RDF of a solid shows sharp peaks, while a liquid has a broader and smoother RDF. Consequently, by studying the RDF of Gold at different temperatures, we should be able to recognize some differences in its behaviour at the transition temperature.

From the data collected in the previous task and by using the python script `rdf.py` it's possible to automatically compute the RDF. A good bin-size is found by using 100 bins.

If we look at Figure 11 we see that there is a clearly different behaviour of the RDF at temperatures under $1500K$ and above $1600K$. In particular, until the temperature of $1500K$ has been reached, it shows sharp and well defined peaks which suggest, as already mentioned before, a solid structure. On the other hand, above $1600K$, the function $g(r)$ is smoother and it has less peaks. It's then possible to confirm, thanks to this analysis, that the melting temperature of Gold is in between $1500K$ and $1600K$. The same observation about the resolution is applicable also in this case.
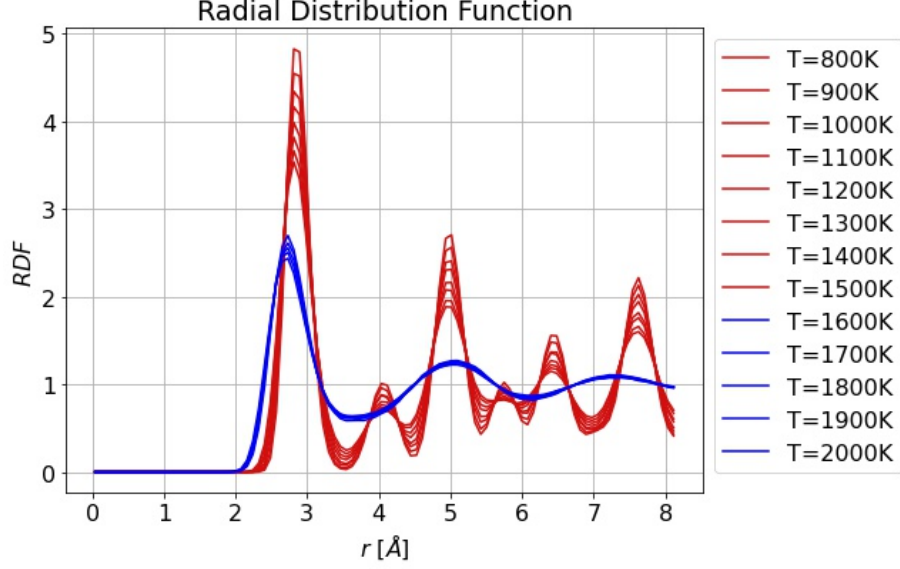
Figure 11: Radial distribution function of Gold at different temperatures.

From the RDF it's also possible to calculate the coordination number of the system, which corresponds to the number of nearest neighbour atoms for each atom in the system. It can be estimated through the integration of the first peak of the radial distribution function. The integral of the RDF is automatically calculated by the script `rdf.py` previously used to compute the RDF. Then by only looking at the value of $\int RDF(r)$ up to the value of r which corresponds to the first minimum of RDF, we obtain the coordination number. Obviously, in our case we have to treat two different phases of the system which have different RDF curves. We decide to look at the highest and the lowest temperatures we have simulated, in order to not being affected by the phase transition of the system.

At $T = 800K$, in the liquid phase, the integral reveals to be equal to 12.01. While at $T = 2000K$ it is 11.96. So, they are both approximated to 12. See Figure 12. This is explained by the fact that, by looking again at Figure 10, it's possible to see that the pressure of the system at $T = 2000K$ is far higher than the one at lower temperatures. Consequently, what happens is that even if the atoms are moving faster in the liquid phase than in the solid one, they are also obliged to stay closer to each other by the high pressure. So that, at the end the number of nearest neighbour atoms is the same in the two phases.
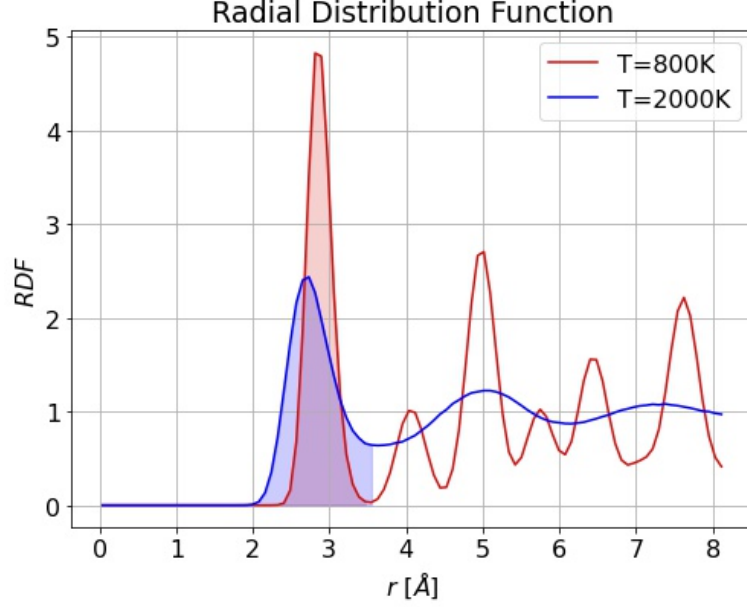
Figure 12: Radial distribution function of Gold at $800K$ and $2000K$. The shaded areas correspond to the integrals that reveal the coordination number of the system.

2.3 Task C

Other two important quantities can be calculated from such simulations. They are the diffusion coefficient (D) and the mean-square displacement (MSD), and they are defined as in Equations (8), (9).

$$\text{MSD}(t) = \frac{1}{3N} \sum_{I}^{N} \sum_{\alpha=1}^{3} \left\langle |R_{I\alpha}(t) - R_{I\alpha}(0)|^2 \right\rangle \tag{8}$$

$$\text{D} = \frac{1}{2d} \lim_{t \to \infty} \frac{d}{dt} \text{MSD}(t) \tag{9}$$

where, in our case, the dimensionality is $d = 3$.

As it's possible to see these two quantities are related to each other. In particular, once the mean-square displacement is known, it's possible to calculate the self-diffusion coefficient. Indeed, the MSD, after a short period of time in which it has a quadratic trend, it tends to infinity linearly and it's easy to calculate its derivative. By knowing the slope of the line the diffusion coefficient can be easily calculated.

Due to the fact that the MSD is an index of how fast the atoms are moving inside the system, we can use this quantity to identify in which conditions the behaviour of the system changes because of the phase transition.

Starting from the data collected before, the MSDs shown in Figure 13 have been calculated through the use of the script `msd.py`.
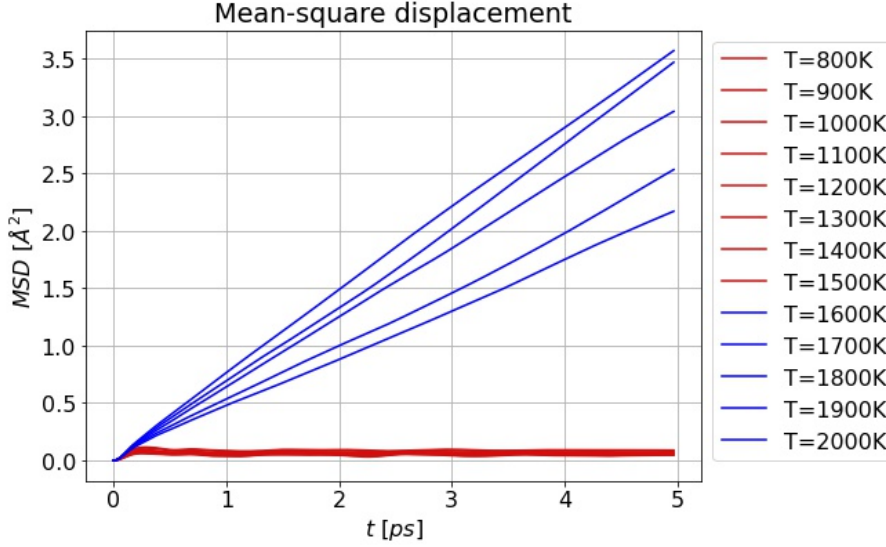

Figure 13: Mean-square displacement of Gold at different temperatures.

It's possible to easily distinguish two different types of behaviours at different temperatures: the first takes place at temperatures below $1500K$, and it is represented by a curve very close to zero, the other one is visible above $1600K$ and it is represented by a line with a significant slope. We are able to recognize the liquid phase of the system in the lines with larger slopes. Indeed in this case the atoms are moving a lot from their initial position and this fact is represented through higher values of MSD, which indicates exactly how much, in average, the atoms are moving. On the other hand, in a solid the atoms are strongly bonded to their positions in the lattice, so that their vibrations are small. This situation is represented by the red group of lines in Figure 13.

In both cases, the linear behaviour starts after at most $0.5ps$, so that after this period of time it's possible to extract the slope of the line in order to calculate D. By averaging the values obtained for $dMSD/dt$ from the script used before, and that are located in the linear regime, the diffusion coefficients in Table 1 have been found. It's possible to see a clear difference between the values of the diffusion coefficients below $1500K$ and above $1600K$. As already said in the previous sections, we confirm once again that the transition temperature is inside this range.

T	$d\mathrm{MSD}/dt \ [\mathring{A}^2/ps]$	$D \ [\mathring{A}^2/ps]$
$800K$	$-7.559 \ 10^{-4}$	$-1.25 \ 10^{-4}$
$900K$	$-5.256 \ 10^{-4}$	$-8.76 \ 10^{-5}$
$1000K$	$-7.855 \ 10^{-4}$	$-1.30 \ 10^{-4}$
$1100K$	$+4.778 \ 10^{-4}$	$+7.96 \ 10^{-5}$
$1200K$	$-4.456 \ 10^{-4}$	$-7.42 \ 10^{-5}$
$1300K$	$+3.155 \ 10^{-4}$	$+5.25 \ 10^{-5}$
$1400K$	$-7.187 \ 10^{-4}$	$-1.19 \ 10^{-4}$
$1500K$	$-6.463 \ 10^{-4}$	$-1.07 \ 10^{-4}$
$1600K$	0.426	0.709
$1700K$	0.500	0.083
$1800K$	0.605	0.101
$1900K$	0.695	0.115
$2000K$	0.711	0.118

Table 1: Derivative in time of mean square displacement and diffusion coefficients at different temperatures.

Now, we perform an additional analysis for the liquid phase. We look at how the logarithm of the diffusion coefficient changes as a function of the inverse of the temperature. In Figure 14 these data are shown together with a linear fit. The line used for the fit is described by Equation (10), so that the slope is equal to $-4376.95 \ K$.

$$y = -4376.95 \ x + 0.104 \tag{10}$$

This analysis is important because related to the equation that describes the evolution of diffusion coefficient with temperature. It's the so called Arrhenius equation, shown in (11).

$$D(T) = D_0 \ e^{-\frac{E_A}{k_B T}} \tag{11}$$

where E_A is the activation energy for the reaction and k_B the Boltzmann constant. This equation is commonly used to describe the rate of reaction of a chemical or physical process.

By taking the logarithm on both sides of (11) is then possible to obtain an estimate of the two factors D_0 and, more important, E_A. This last quantity is the activation energy (per molecule) of the reaction. It is the energy needed by the system to start the melting process.

$$log(D(T)) = log(D_0) - \frac{E_A}{k_B} \frac{1}{T} \tag{12}$$

15

$$
\begin{cases} log(D_0) & = 0.104 \\ -\frac{E_A}{k_B} & = -4376.95 \ K \end{cases}
\begin{cases} D_0 = e^{0.104} = 1.11 \ \mathring{A}^2/s \\ E_A = 4376.95 \ k_B = -6.04 \ 10^{-20} J \end{cases}
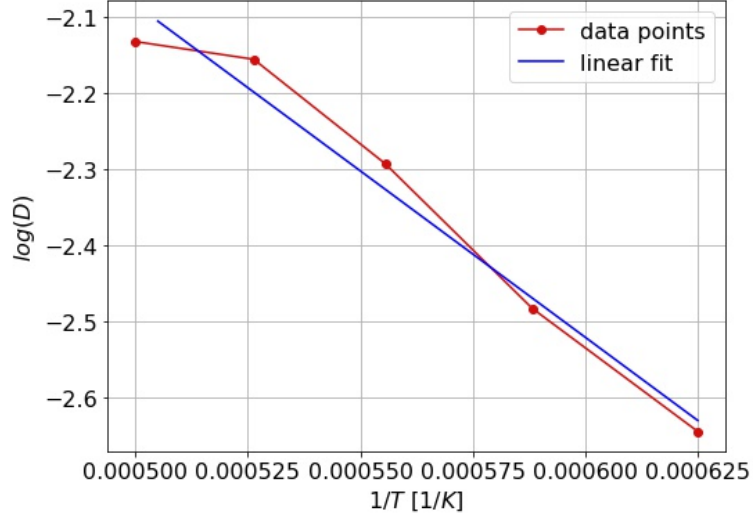\tag{13}
$$

Figure 14: Logarithm of the diffusion coefficient D (when the system is in the liquid phase) as a function of $1/T$ and linear fit.

2.4 Task D

We now want to compute the fixed-volume heat capacity as a function of temperature starting from the total energy fluctuations in the NVT ensemble. This is the last way we follow in order to estimate the melting point of Gold. According to the theory, when a first-order phase transition has place, a divergence in the heat capacity C_V appears.

By using Equation (14), and the data collected before, it's possible to obtain Figure 15. Nevertheless, it's difficult to see a discontinuity in the range of temperatures where we were expecting it (between $1500K$ and $1600K$). Indeed, we know that the resolution in temperature is very low. Then we decide to run some more simulations in the range cited above to be able so see clearly the discontinuity.

The results of these additional simulations are shown in Figure 16.

$$
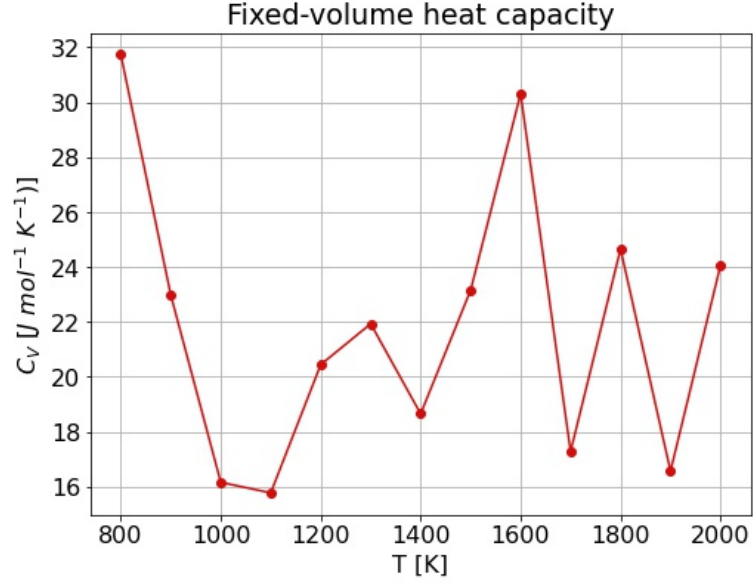C_V = \frac{\sigma_E^2}{k_B T^2}
\tag{14}
$$

Figure 15: Fixed-volume heat capacity as a function of temperature.

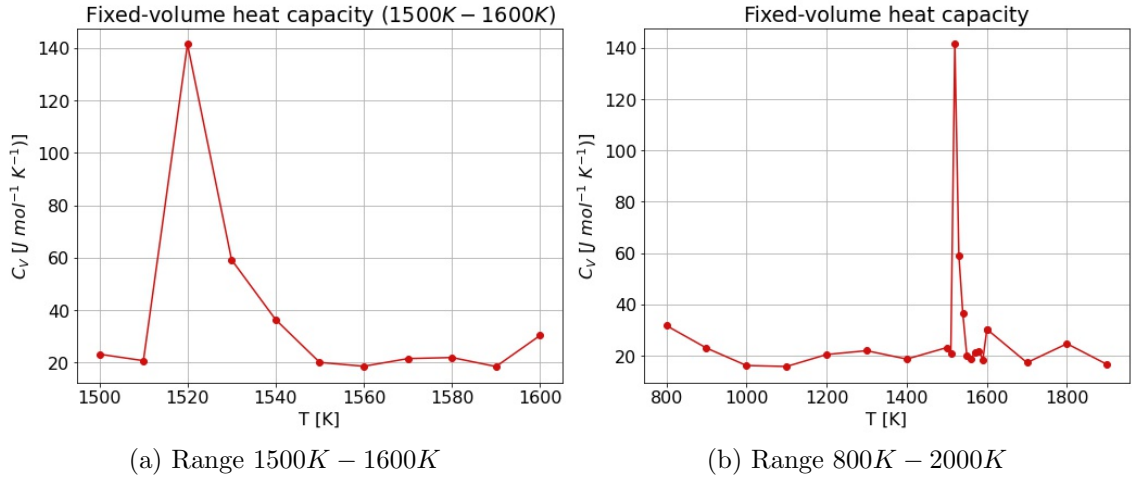(a) Range $1500K - 1600K$

(b) Range $800K - 2000K$

Figure 16: Fixed-volume heat capacity as a function of temperature, with additional runs in range $1500K - 1600K$.

Now the divergence is easy to see, and it corresponds to the temperatures between $1510K$ and $1520K$. It means that a phase transition is happening in such conditions for Gold. With these more calculations then we are able to estimate with higher resolution the melting temperature of Gold. They indicate that it is

located just at the beginning of the range found in the previous tasks. As already said it is in range $1510K - 1520K$.

Although, this estimation doesn't correspond very well to experimental data which indicate a melting temperature of gold of $T_{exp} = 1337K$.

In conclusion, the estimations done in Exercise 2 don't really agree with the experimental data. However, it's known that MD calculations usually overestimate this quantity. Indeed, the definition of melting temperature is 'temperature at which solid and liquid phase coexist'. But in MD, without a seed (of liquid material) inside the solid phase, we usually see a overheating of the system before the transition happens. As a consequence, the estimation of the melting temperature is $20 - 30\%$ higher than T_{exp}. This is exactly what we have seen for Gold. The same problem is present when the process is studied in the opposite direction, so when from liquid phase we want to find the temperature at which the system becomes solid. A possible solution for this issue would be to simulate the system in a different phase condition: 50% solid and 50% liquid. Then the goal would be to find the temperature at which these two phases coexist at equilibrium. However, this kind of simulation requires a more complex set up.

3 Problem 3

We now want to consider a generic bulk material, and we imagine to run simulations with periodic boundary conditions and a large supercell.

3.1 Task A

It's known that the volumetric thermal expansion coefficient α_V is described by Equation (15).

$$\alpha_V = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p \tag{15}$$

It's possible to determine it through only NVT simulations by following the steps described here.

It's important to remember that simulations in the NVT ensemble, also called canonical ensemble, are such that the number of particles N, the volume V and the temperature T of the system do not change during the simulation. As a consequence, the value of the pressure can't be decided but it is accessible from the output of the simulation. It's also true that if we are simulating a finite system (N is finite) the fluctuations of the average temperature are not zero. However we

neglect this fact here. These three quantities are then fixed at the beginning of the simulation and specified in the input file. In particular, the total number of particles and the volume of the system depend on number of particles and size of one unit cell, and on the number of supercells used.

First of all, it's necessary to have in mind how to estimate the temperature at which a certain volume is at ambient conditions, so that the averaged pressure is 1 atm. By considering a specific volume we have to run several NVT simulations at different temperatures. In this way both the volume and the temperature of the system are constant and known for each simulation. Then, we plot the averaged pressure as a function of temperature and by fitting the function, possibly with an equation of states, it's possible to find the value of T for which the averaged pressure is equal to 1 atm. That value corresponds to the temperature at which the considered volume is the equilibrium.

In a similar way it's possible to estimate the equilibrium volume at several temperatures, that is what's necessary to calculate α_V. Choose a range of temperatures and a value for the step. Consider one temperature at a time and perform several NVT simulations by changing the volume, so that for each simulation volume and temperature are constant and known. At this point it's possible to plot the averaged pressure of the simulations as a function of the volume (and at constant T), and by performing a fit the value of the volume at which P= 1 atm can be found. Also in this case it's possible to use the equation of a known equation of states, that relates P and V, to perform the fit. This procedure then needs to be repeated for all the temperatures chosen at the beginning. We only need to store these temperature-volume points in the T-V space at $P = 1\ atm$ and plot them as a function V(T). A fit with another equation of states that relates V to T can be done also in this case.

By only taking the derivative with respect to T of this function and dividing by the volume, as in Equation (15), it's possible to find the volumetric thermal expansion coefficient.

3.2   Task B

In Exercise 2D we have calculated the fixed-volume heat capacity through Equation 14. However, another way to calculate this quantity exists and it uses only the data already collected in Exercise 2A, which are: averaged potential energy per atom, averaged total energy and pressure of the system as a function of temperature. This method directly comes from the definition of specific heat: it is the heat necessary to increase the temperature of the material by $1K$, while keeping the volume fixed (Equation (16)).

$$C_V = \left(\frac{\delta Q}{dT}\right)_V \tag{16}$$

$$dU = \delta Q - PdV \tag{17}$$

Remembering the first law of thermodynamics (17), and considering the fact that all the simulations we have run are at constant volume, so that $dV = 0$, we get the following result.

$$dU = \delta Q$$
$$C_V = \left(\frac{dU}{dT}\right)_V \tag{18}$$

As a consequence, it's possible to estimate the value of C_V by taking the derivative of the curve of the averaged total energy as a function of the temperature (when the volume is fixed).

As expected, this can be done by using the data collected in Exercise 2A. In particular, we need to avoid the temperature at which the phase transition happens because it is introducing a discontinuity in the energy and there would be issues with the operation of taking the derivative. However, it's also possible to see that the slope of the energy is the same on the two sides of the discontinuity, so that we limit the analysis to the range of temperatures $800K - 1500K$. We also remember that we want to study a bulk material, so that we are interested in the solid phase.

By performing a linear fit of data in Figure 9, with the curve $y = 0.072x - 971.44$ and taking the derivative of it, it's possible to obtain that $(dU/dT)_V = 27.142 \ J/(mol \ K)$. The specific heat in this case is then calculated as a constant value.

In Figure 17 we compare the result obtained here with the one from Exercise 2D.

As it's possible to see, both the methods need a series of NVT simulations to be performed, but obviously they have different features.

The last one we used, which involves Equation (18), provides a constant value of the heat capacity, and it is easily obtained through a linear fit. This can be an advantage due to the fact that there are no doubts about the value of this quantity, there are no oscillations. The other method, involves the calculation of the total energy fluctuations, which obviously have different amplitudes depending on the temperature. As a consequence the value of C_V we can obtain in this way is not constant, instead it varies with the temperature. In this case in then more difficult to have a precise estimate of the value of the heat capacity. But, it's also true that we are able to describe the weak influence that the temperature has on

this quantity. So, at the end, both methods are valid, but by looking at the value found in the literature [1] the method which uses (18) provides a more precise value, even if it's not able to catch the dependence from the temperature.
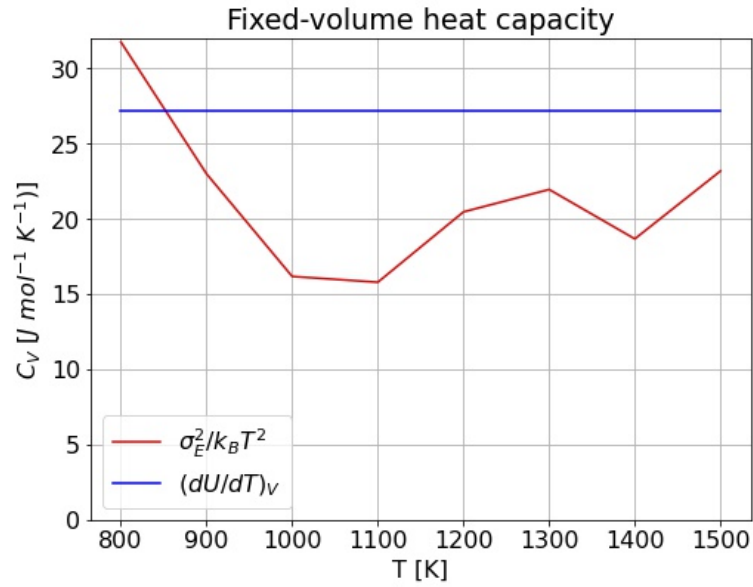

Figure 17: Fixed-volume heat capacity as a function of temperature obtained using two different methods.

References

[1] T.H.Geballe, W.F.Giauque, *The Heat Capacity and Entropy of Gold from 15 to 300K*, J. Am. Chem. Soc. 1952, 74, 9, 2368–2369