

Fluctuations of Periodicity vs Temperature: Cubic Nanoparticle Molecular Dynamics using NAMD

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In this practice, the thermalization of a cubic gold (Au) nanoparticle was studied using the molecular dynamics package NAMD [1], for different temperature settings. All the generated material can be found in our github repository [2]. The data treatment and 3D plots were done using VMD [3], while the other plots were generated using Python.

1 The Initial Settings

Initially, a cubic arrangement of 6x6x6 Au atoms was designed, as shown in Figure 1.(a) in the Van der Waals radius ball representation or in Figure 1.(b) as smaller balls (the CPK representation). As it is shown in Figure 1.(b), the designed configuration's lattice parameters are not strictly periodic, but show a little deviation from perfect periodicity.

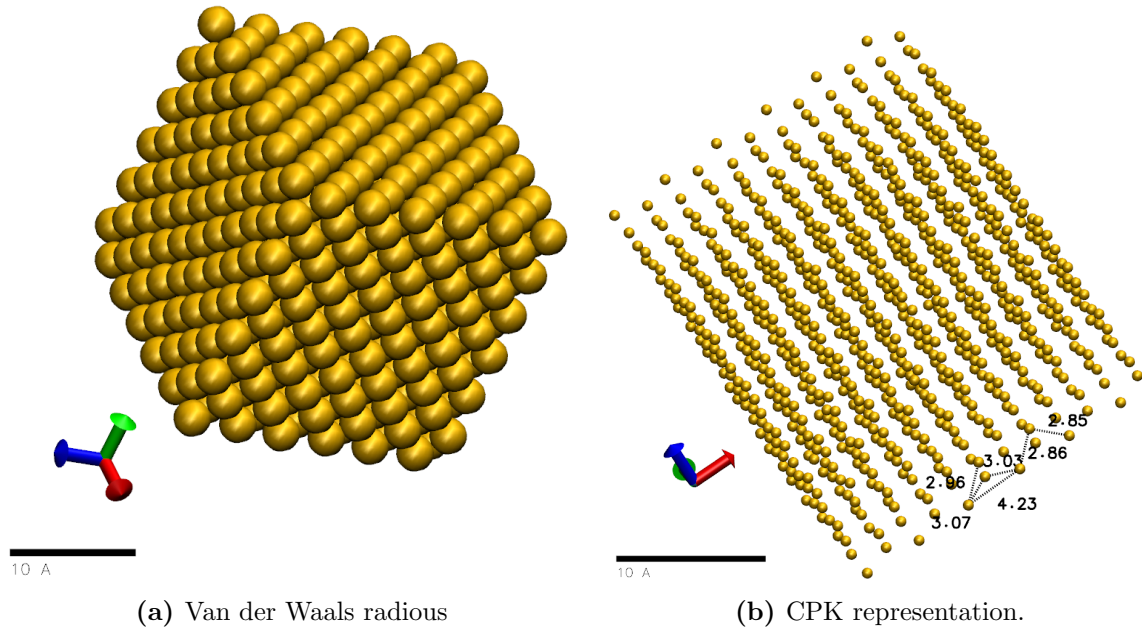


Figure 1: Graphical representation of the initial state employed in the simulations. Note how in (b) we show the distances for some of the atoms. The scale has 10 Å.

2 Molecular Dynamics Settings

Using VMD we simulate the time evolution of the system within a molecular dynamics thermostat, by setting three different thermostat temperatures, [10, 300, 1500](K), at a constant number of particles, volume and temperature (an NVT configuration). The simulation box was chosen to be of $50\text{Å} \times 50\text{Å} \times 50\text{Å}$, with a time-step of 2 fs , simulating 1 ns , with a minimization of 5000 steps and outputting results every 1 ps . The force field was chosen to be the one due to the Lennard-Jones potential

$$V(\vec{x}_i, \vec{x}_j) = \varepsilon \left[\left(\frac{R}{\|\vec{x}_i - \vec{x}_j\|} \right)^{12} - 2 \left(\frac{R}{\|\vec{x}_i - \vec{x}_j\|} \right)^6 \right] \quad (1)$$

where \vec{x}_i, \vec{x}_j are the center of mass positions of two of the Au atoms, ε is the stabilization energy at the minimum of the potential energy and R is close to the potential minimum radial distance. We used $\varepsilon = -5.29 \text{ kcal/mol}$ and $R = 2.951 \text{ \AA}$, following the results by Ref. [4].

Note from the closest atom distances shown in Figure 1.(b), that we set initially the Au atoms at around the distance $R = 2.951 \text{ \AA}$ which yields close to the minimum Lennard-Jones potential energy which would be the 0 K situation if perfectly arranged. In particular, we compute this initial configuration to have a null kinetic energy and a total/potential energy of $-30468.6551 \text{ kcal/mol}$.

3 Results as a function of Thermostat Temperature

We now analyze the obtained results for each of the thermostat temperatures.

3.1 Instantaneous Temperature Thermalization

By the equipartition theorem, we can get the instantaneous temperature of the system by computing the average atomic kinetic energy. With this, we obtain the results in Figure 2. Since the initial conditions in all three cases are due to 0 kinetic energy, the plots start at an instantaneous $T = 0 \text{ K}$, but rapidly depart to the range around the thermostat temperatures. In the insets of the figure, we wrote the mean and standard deviations obtained with the last 500 iterations of the simulations. We find that in average the temperature is practically that of the thermostat in all three cases at those times, which suggests a correct thermalization with the reservoir. It is noteworthy that the fluctuations (quantified by the standard deviations in the insets) around this value are non-negligible in all three cases, which is a consequence of the finiteness of the number of degrees of freedom. As it was also expectable, the greater the thermostat temperature, the fluctuations are bigger.

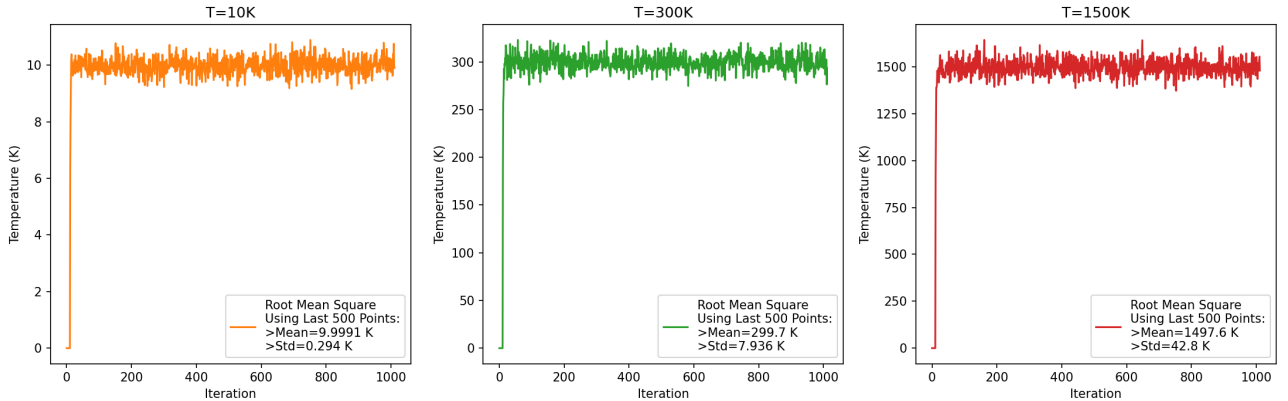


Figure 2: Instantaneous temperature at each iteration of the simulation, for the three thermostat temperatures (T), shown in the title of each plot. In the inset the average and standard deviation computed with the last outputted 500 iterations can be found.

3.2 Energy Thermalization

Next we analyze the dynamics of energy. In Figure 4 we plot the time evolution of the kinetic energy of the system, which can be seen to follow a same profile as the instantaneous temperature, up to a scale factor. This is because that temperature was computed as proportional to the kinetic energy.

In Figure 5 we find the time evolution of the potential energy and the total energy of the system for each case of thermostat temperature. As did the kinetic energy, these quantities appear to thermalize around the values computed and shown in the insets. Note how in the $T = 10 \text{ K}$ case, the thermalization energy ($-31099.3 \text{ kcal/mol}$) is lower than the energy of the initial configuration (-30468.6551

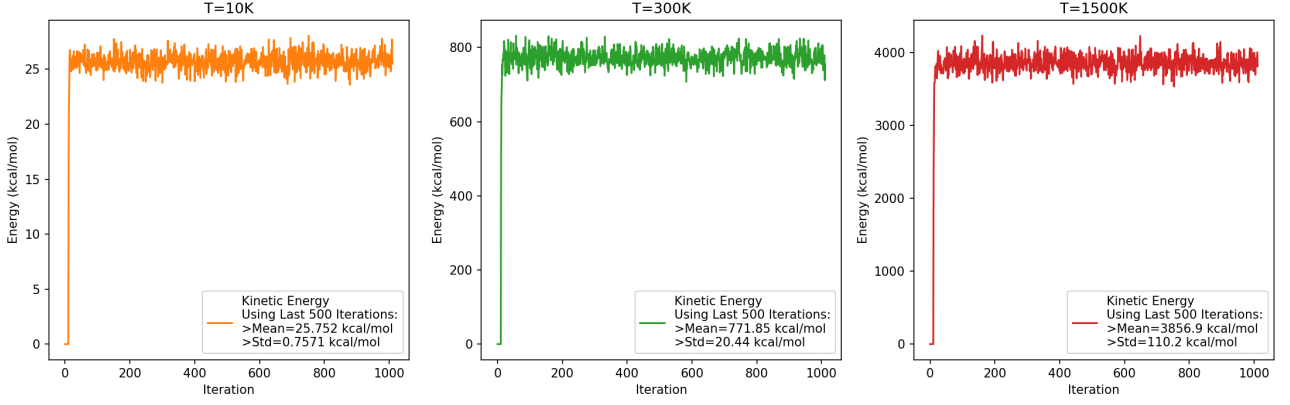


Figure 3: Van der Waals radius

Figure 4: System kinetic energy evolution with iterations. The insets show the mean and standard deviation computed with the last outputted 500 iterations.

kcal/mol). This means that the initial configuration we set was not the ground state (as we anticipated from the fact that the inter-atomic distances were not perfectly periodic). Meanwhile, for the other two thermostat temperatures, both the potential and total energies are less negative, and thus indicate a lower stability of the system as compared to the initial configuration. All this calls for the analysis of the lattice parameters and their time fluctuations in each thermostat temperature to confirm the loss or gain of periodicity.

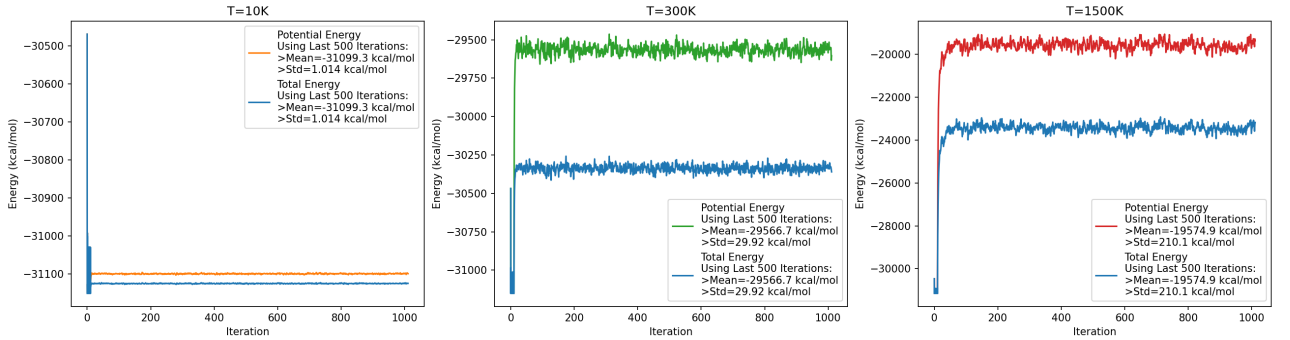


Figure 5: System potential and total energy evolutions with iterations. The insets show the mean and standard deviation computed with the last outputted 500 iterations. T refers to the thermostat temperature.

3.3 Lattice Parameters and Root Mean Square Displacements

We plot in Figure 6 the thermalized and initial configurations of the system, with some example inter-atomic distances linking the same atoms in all plots, such that they represent the final simulation times. Indeed, we can already visually assert that the $T = 10K$ thermalized configuration is more regular than the initial configuration, as can be seen from the perfect ordering of the atoms in the bulk of the particle. It can also be seen that while for $T = 300K$, the structure has still got a cubic configuration, by $T = 1500K$, the nanoparticle loses its shape and becomes a drop with the inter-atomic distances wildly deviating from those of perfect periodicity.

These configurations are not static and fluctuate in time differently as a function of the thermostat temperature. In Figure 7 we plot the time evolution of the root mean square displacement of the instantaneous configurations relative to a reference frame. Note the mean and standard deviation of these time-series (in the thermalized regime) written in the insets of the figure. The mean displacements of the $T = 10K$ configuration are two orders of magnitude smaller than the bonding distance we set for the Lennard-Jones potential, meaning that the atoms only slightly vibrate around the con-

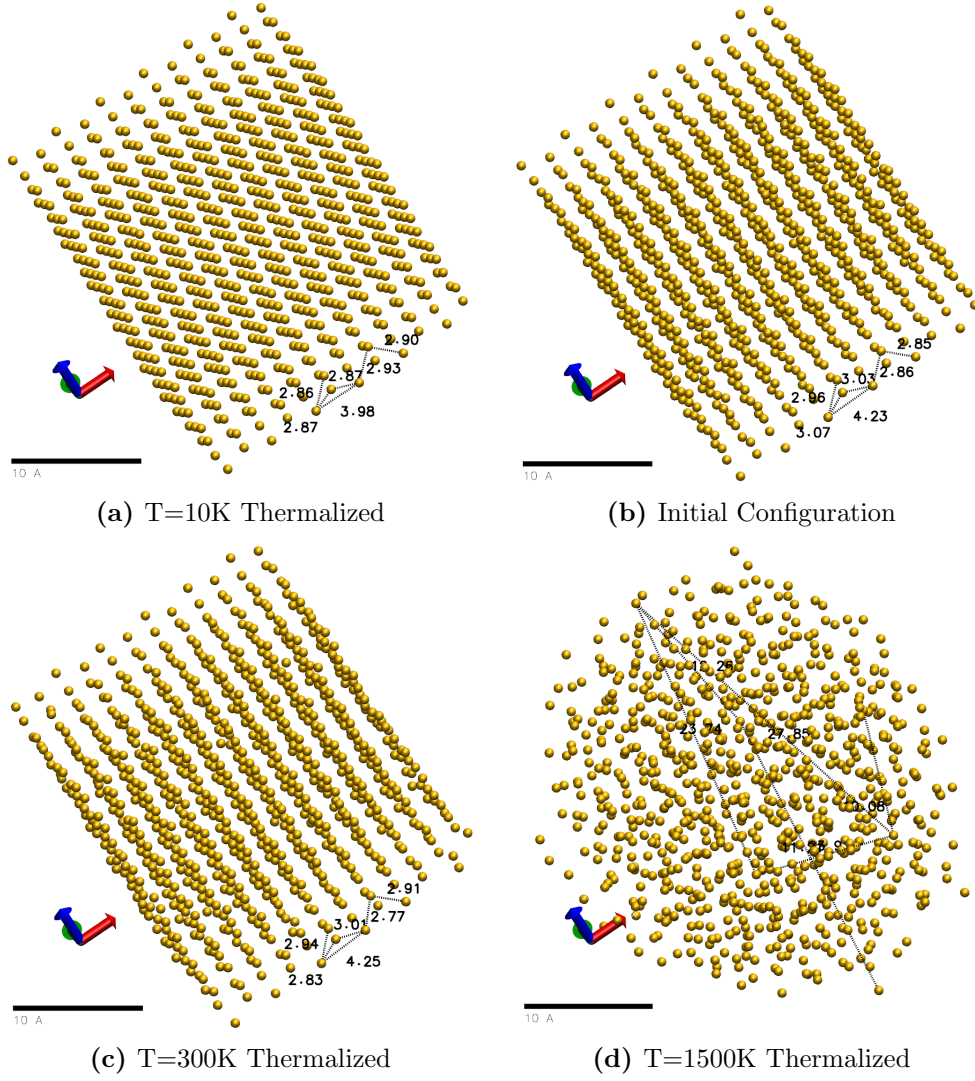


Figure 6: CPK representation of the thermalized and initial configurations, showing example inter-atomic distances.

figuration shown in Figure 6. For the $T = 300K$ case, the displacements happen in the order of a tenth of the inter-atomic bonding, meaning now the configurations vary appreciably, but still preserving the lattice. However, the mean displacements for $T = 1500K$ are one order of magnitude bigger than the bonding, meaning, as already suggested by Figure 6, that the nanoparticle becomes very fluid and loses most of its periodic structure, but still the atoms are confined to a bounded sphere in space. This is the behaviour of liquid state, meaning that the nanoparticle appears to be fused by such a temperature. All this suggests that we should analyze the loss of periodicity more quantitatively.

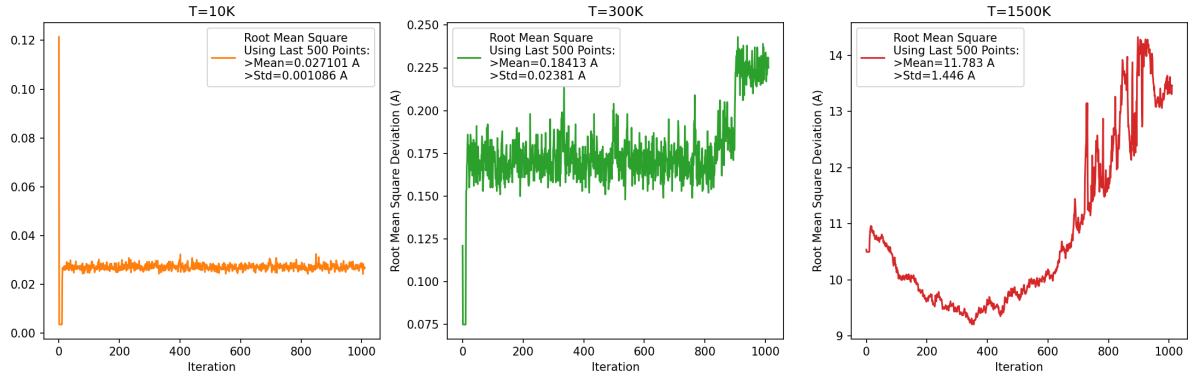


Figure 7: Average root mean square deviations relative to reference configurations as a function of iterations. The insets show the mean and standard deviation computed with the last 500 iterations.

3.4 Radial Density Functions

In order to obtain a better intuition of the loss of periodicity, we compute the radial density functions for each thermostat temperature, as plotted in Figures 8 and 9.

By the mere glance at the top two plots in Figure 9, we can see that the initial configuration is indeed less periodic than the thermalized one at $T = 10K$, since the peaks of the $T = 10K$ thermalized one, are the finest and discretest of all. Interestingly, we see that the $T = 300K$ case and the initial configurations show very similar profiles, suggesting that their average lattice configurations are very akin to each other. Finally, for the case of $T = 1500K$ we find a complete loss of the discreteness of the peaks, suggesting indeed the liquid state.

Regarding the quantitative information, all of the plots have their first peak, indicating the distance to the first neighbours in average, at around 2.85 Å. This is in excellent agreement with the chosen Lennard-Jones potential minimum and the inter-atomic distances we found in Figure 6. It is noteworthy that the $T = 1500K$ case still shows in average such a peak distance to the closest neighbours. This is in contrast with what could happen if the nanoparticle was in gas state at that temperature, reinforcing the statement that it is in liquid state.

Finally, we see that the second peak appearing in the structured cases, happens at around 4.05 Å. This successfully matches the second closest inter-atomic distances shown in Figure 6.

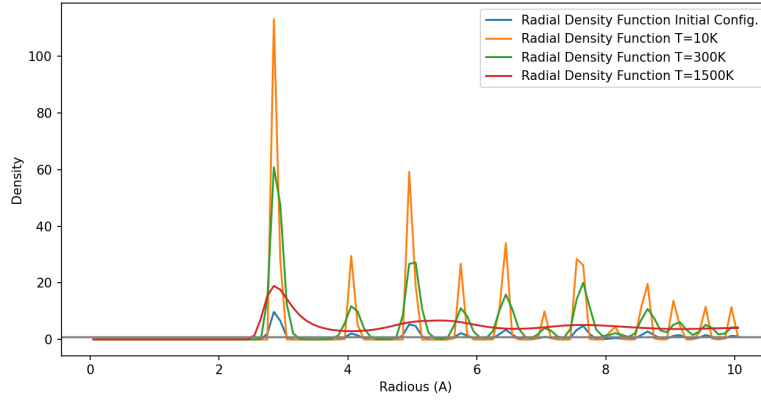


Figure 8: Integrated average radial density as a function of the radius from the atoms.

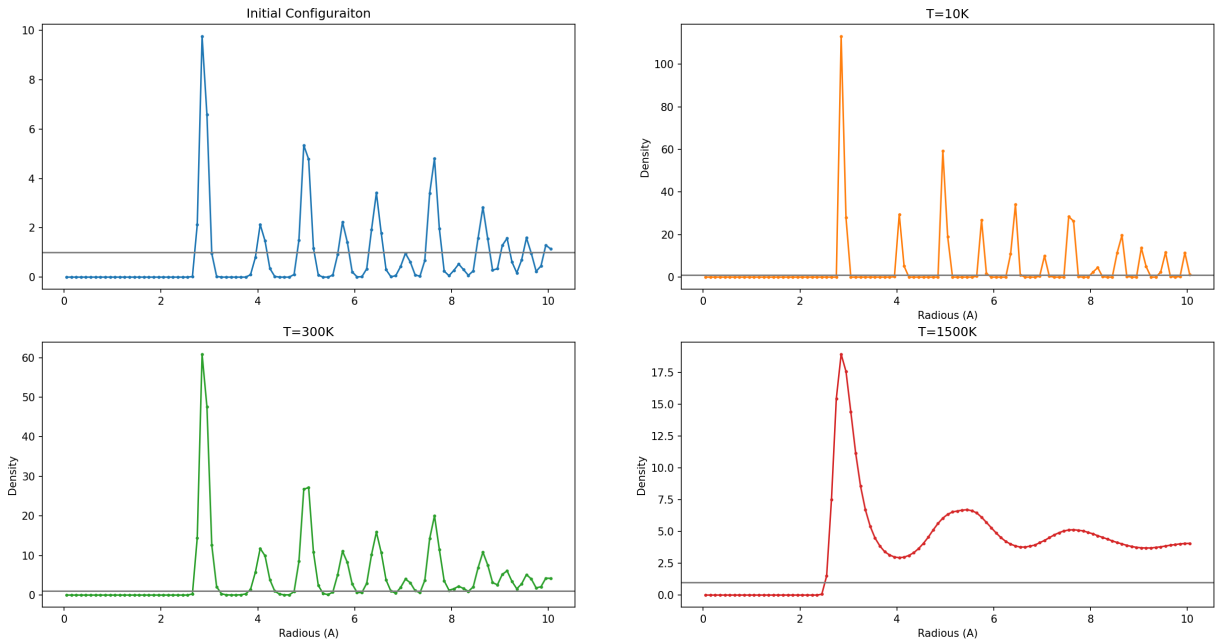


Figure 9: Integrated average radial density as a function of the radius from the atoms.

References

- [1] J. C. Phillips, D. J. Hardy, J. D. Maia, J. E. Stone, J. V. Ribeiro, R. C. Bernardi, R. Buch, G. Fiorin, J. Hénin, W. Jiang, *et al.*, “Scalable molecular dynamics on cpu and gpu architectures with namd,” *The Journal of chemical physics*, vol. 153, no. 4, p. 044130, 2020.
- [2] “Github repository with the python scripts and notebook generated for the report.” https://github.com/Oiangu9/_Miscellaneous/tree/main/SSN.
- [3] W. Humphrey, A. Dalke, and K. Schulten, “VMD – Visual Molecular Dynamics,” *Journal of Molecular Graphics*, vol. 14, pp. 33–38, 1996.
- [4] H. Heinz, R. Vaia, B. Farmer, and R. Naik, “Accurate simulation of surfaces and interfaces of face-centered cubic metals using 12- 6 and 9- 6 lennard-jones potentials,” *The Journal of Physical Chemistry C*, vol. 112, no. 44, pp. 17281–17290, 2008.