

Molecular Dynamics

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1 Introduction

Atomistic simulations are a key tool for determining both micro- and macroscopic thermodynamic properties of materials. Ideally, quantum mechanical calculations could be performed for any given system to provide maximum accuracy, however these are unrealistically expensive to simulate in even very simple systems containing more than around a hundred atoms. There exist essentially two methods for determining physical quantities such as temperature and pressure as statistical averages over a restricted set of states: the molecular dynamics and Monte Carlo methods. Molecular dynamics is a widely used method for studying classical many-particle systems. It consists essentially of integrating the equations of motion of the system numerically. It can therefore be viewed as a simulation of the system as it develops over a period of time. Its greatest advantage is that it not only provides a way to evaluate expectation values of static physical quantities; dynamical phenomena, such as transport of heat or relaxation of systems far from equilibrium can also be studied. Monte carlo on the other hand considers all possible occupations of phase space, whether they are realized in time or not. Which can be a powerful tool when time integration schemes are limited due to the complexity of the system but are computationally overkill for a well behaved system.

The solutions of the equations of motion describe the time evolution of a real system although obviously the molecular dynamics approach is approximate for the following reasons. Firstly, the system sizes in such simulations are much smaller than those of experimental systems. The finite size aspect is felt through the presence of the boundary, which can often be highly influential if not dominant in the physics of the system. The convention adopted in the vast majority of molecular simulations is to use periodic boundary conditions. Secondly, the numerical integration algorithm is not infinitely accurate. This forces us to make some optimum choice between speed and accuracy: the larger the integration time step, the more inaccurate the results of the simulation[1]. In this work, we will investigate these downsides as well as the general development of a simple MD solver and compute basic thermodynamic properties for solid-phase crystalline Argon using the simple two-body Lennard-Jones potential.

2 Methodology

2.1 Lennard-Jones potential

The Lennard-Jones potential is an effective potential that describes the interaction between two uncharged molecules or atoms. It is represented by the following equation:

$$V(\mathbf{r}_i, \mathbf{r}_j) = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^6 \right] \quad (1)$$

where $R = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of atom i and atom j . The parameters σ and ε represent the distance in which the inter-particle potential is 0 and the depth of the potential respectively. The r^6 term describes the attractive potential, while the r^{12} term is responsible for the repulsive potential. The Verlet Algorithm entirely depends on the force exerted on each particle in a given timestep and how that changes previous positions and velocities which is determined analytically from the LJ potential:

$$\mathbf{F}(\mathbf{r}_i(t)) = \sum_{j \neq i} 24 \left[2 \left(\frac{1}{R} \right)^{14} - \left(\frac{1}{R} \right)^8 \right] (\mathbf{r}_i(t) - \mathbf{r}_j(t)) \quad (2)$$

One can note how the potential is attractive for two molecules approaching each other until a certain point in which the system diverges and the potential becomes very repulsive. This strong repulsive force is intuitive considering the particles cannot simply diffuse through each other. The attractive potential at larger distance is a bit less intuitive. It arises from the induced dipole moment interactions between the particles. In the gas and liquid states of a material, we can expect multiple collisions between atoms. Everytime there is a collision, the electron cloud of each atom deforms due to the fields of the colliding atom. This deformation will create unsymmetric electron clouds and thus create a dipole. This dipole-dipole interactions in these collisions is responsible for the attractive potential found in the Leonard-Jones Potential.

Once force is determined, we can investigate the actual dynamics of the system. An equation of motion is now written using Newton's classical laws for the i^{th} atom:

$$\frac{d^2 \mathbf{r}_i(t)}{dt^2} = \frac{\mathbf{F}(\mathbf{r}_i(t))}{m} = \mathbf{F}(\mathbf{r}_i(t)) \quad (3)$$

Given proper initial conditions, these $3N$ ordinary differential equations are integrated in time to simulate the argon atoms dynamics.

2.2 Periodic boundary conditions

Boundary conditions in general are of great importance to most MD simulations intending to resolve physically accurate results. Of course any physical system is of finite size, and thus has different physical interactions on the surface, however the number of atoms in a realistic sample of material that could be used for measurements is most often many orders of magnitude larger than the million or billion scale which leads to a computational bottleneck in some physical systems. Once common example is the goal of modelling protein unfolding dynamics using

MD which poses incredibly complex surface descriptions while still remaining too large to realistically be solved using traditional MD. In our case however we are only interested in bulk material properties and phase transitions, so we can safely assume that the surface effects are simple and the structure is so large that they can be effectively ignored and replaced by a periodic boundary condition, i.e modelling the system as infinite extent.

How the periodic boundary conditions is chosen has some flexibility but is important as the BC will dictate how the potential is computed for atoms near the boundary as well as how it behaves if it crosses the boundary. Formally, the most accurate method would utilize *minimum image convention* to compute the accelerations between particles in the periodic FCC lattice.

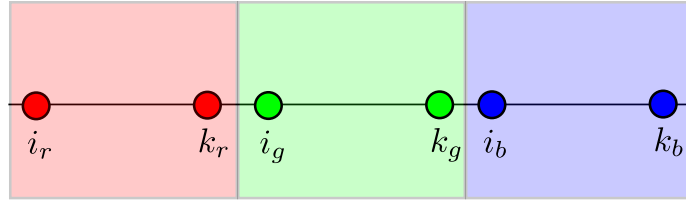


Figure 1: The minimum image convention illustration in one dimension.

An illustration of the method is shown in Figure 1. If $R_{i_g k_r} = |\mathbf{r}_{i_g} - \mathbf{r}_{k_r}|$ is less than $R_{i_r k_r} = |\mathbf{r}_{i_r} - \mathbf{r}_{k_r}|$, then the stronger force with distance $R_{i_g k_r}$ is used for computing the acceleration and the weaker force with distance $R_{i_r k_r}$ is neglected. Since the lattice is periodic, then the minimum image convention can be written in algorithm:

- If $R_{ik} = |\mathbf{r}_i - \mathbf{r}_k| > \frac{L}{2}$
 - If $R_{ik} > 0 \rightarrow R_{ik} = R_{ik} + L$
 - If $R_{ik} < 0 \rightarrow R_{ik} = R_{ik} - L$

This can be visually seen using Figure 1. When the two particles in the red unit cell are separated by a distance larger than half the unit cell size, then the second particle is translated by the unit cell dimension to compute the distance between the red particle and the green particle.

In this work we rely on the simpler approach which entails simply moving particles which leave the computational domain. If the updated particle position is outside of the computational domain, then its position is merely shifted by the size of the computational domain $\mathbf{r}_i \rightarrow \mathbf{r}_i + L$.

2.3 Flowchart

The overall workflow is presented in the given flowchart, which is summarized as follows:

1. Initialize particle positions and momenta.
2. Compute forces on particles.
3. Integrate equation of motion.

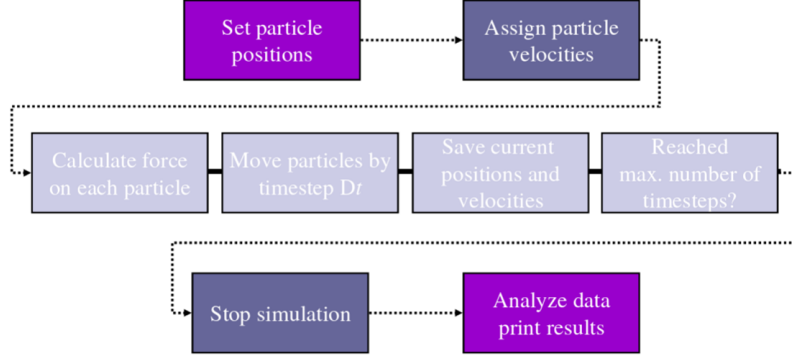


Figure 2: MD simulation workflow

4. Measure relevant quantities.
5. Repeat (2)-(4) for the designated period of time.
6. Compute averages.

2.4 Initial conditions

We set up our simulation for Argon in the FCC crystalline configuration as shown in Fig.3.

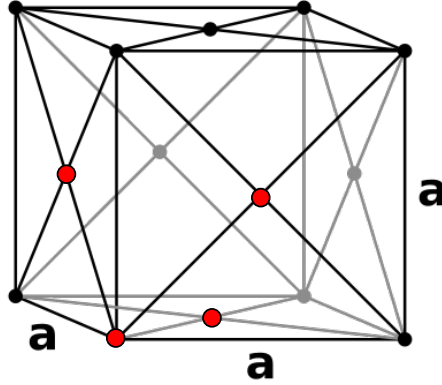


Figure 3: The face centered cubic (FCC) initial particle positions for the Velocity Verlet algorithm. Red atoms comprise the primitive unit cell

Corresponding velocities will be assigned randomly based on the Maxwell-Boltzmann distribution:

$$P(x) = \frac{\exp \left[- (x - x_0)^2 / (2\sigma)^2 \right]}{\sqrt{2\pi\sigma^2}} \quad (4)$$

Generating these random velocities was done with a box-muller based method outlined as such:

- Generate random number between 0 and 1
- Use Box-Muller transform: $Z = \sqrt{-2 \ln U_1} \cos(2\pi U_2)$ to transform random number into random variables on a normal distribution
- Scale the normal distribution to temperature to get velocity $v = T^{-0.5} Z$

Since the random initial velocities are distributed around zero, the total momentum will not be exactly zero. To prevent the system drifting in space, the random initial velocities are transformed to a center of mass reference frame:

$$\mathbf{v}_0 \rightarrow \mathbf{v}_0 - \frac{1}{N} \sum_{i=1}^N \mathbf{v}_i \quad (5)$$

Now if using an NVT-ensemble where temperature is desired to be fixed, temperature rescaling will need to be performed as the randomly generated velocity will often have fluctuations leading to the temperature not being exact at first iteration. As a solution we can run the simulation for some iterations with temperature fixed and rescale them at each step until the result is unchanging.

$$\mathbf{v}_0 \rightarrow \sqrt{\frac{3(N-1)T_{\text{desired}}}{\sum_{i=1}^N \mathbf{v}_i^2}} \mathbf{v}_0 \quad (6)$$

2.5 Timestepping

Our ODE then is integrated in time using the well known Velocity Verlet Algorithm[2], which is derived from Taylor expansions. This algorithm updates both particle position and velocities in a three step process:

1. Define $\mathbf{a}_i(t) = \mathbf{F}(\mathbf{r}_i(t))$
2. $\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \mathbf{v}_i(t)\Delta t + \frac{1}{2}\mathbf{a}_i(t)\Delta t^2$
3. $\mathbf{a}_i(t + \Delta t) = \mathbf{F}(\mathbf{r}_i(t + \Delta t))$
4. $\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2} [\mathbf{a}_i(t + \Delta t) + \mathbf{a}_i(t)]\Delta t$

Here, Δt is the time step size of the time integration. The Velocity Verlet algorithm requires initial conditions for both particle positions and velocities, and will compute updated positions, velocities, and accelerations at each time step.

2.6 Compute thermodynamic properties from statistics

Using the trajectories over time, we compute the following physical properties

- **Energy:** The total energy in each time-step is measured. The total energy $E = K(t) + U(t)$ is conserved by classical Newtonian dynamics. Potential is determined with Lennard-Jones while the kinetic energy is

$$K(t) = \frac{1}{2} \sum_{i=1}^N |v_i(t)|^2 \quad (7)$$

• **Temperature:** The instantaneous temperature is computed from the equipartition theorem which states that the kinetic energy equals $\frac{1}{2}Nk_B T$ per degree of freedom. In the case of argon

$$K = \frac{3}{2}Nk_B T \quad (8)$$

• **Pair correlation function $g(r)$:** The static pair correlation function $g(r, r')$ is proportional to the probability of finding a particle at r from any other particle r' , so it describes how density varies as a function of distance from a reference particle. In the canonical ensemble it is given by

$$g(r) = \frac{1}{4\pi N \rho r^2} \left\langle \sum_{i \neq j} \delta(r - r_{ij}) \right\rangle \quad (9)$$

We can use this function to determine where phase transitions may occur

• **Diffusion coefficient:** The diffusion coefficient is related to the variance of the square of the displacement $\langle r^2 \rangle$ as

$$\langle r^2 \rangle = 6Dt \quad (10)$$

The value should be zero for a solid but non-zero in a liquid. So this also can be used to determine melting.

• **Thermal Conductivity:** Using the green-kubo formula we can get an estimate of thermal conductivity from time averaged heat currents

$$\lambda = \frac{1}{3Vk_B T^2} \int \langle j(0)j(t) \rangle dt \quad (11)$$

where j is the macroscopic heat current given by

$$j(t) = \sum_i v_i E_i + \frac{1}{2} \sum_{i < j} r_{ij} [F_{ij} \cdot (v_i + v_j)] \quad (12)$$

and can be analyzed for error using the heat autocorrelation function:

$$\sigma(\langle j(0)j(t) \rangle) \approx \frac{2t}{t_{\text{run}}}^{1/2} \langle j^2 \rangle \quad (13)$$

$$\sigma(\lambda) = \frac{\Delta t}{3k_B V T^2} \sqrt{\sum_t \sigma^2(\langle j(0)j(t) \rangle)} \quad (14)$$

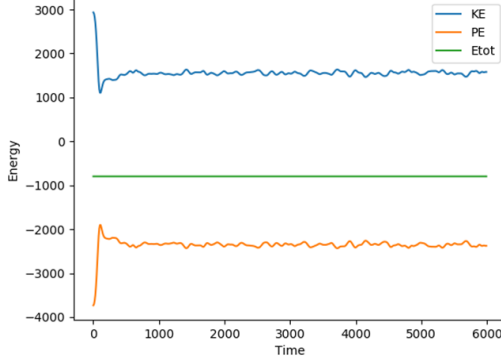


Figure 4: Equilibration phase for an NVE system of N=108 atoms at T=200K

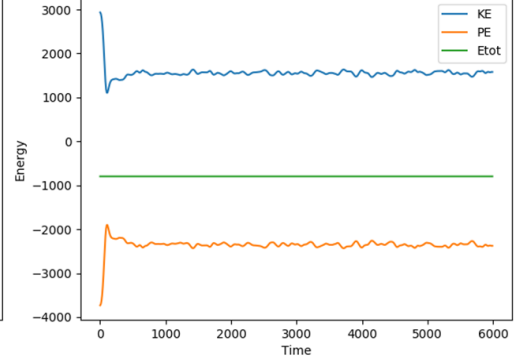


Figure 5: Equilibration phase for an NVE system of N=108 atoms at T=500K

2.7 Reduced Units

Lastly, we have adopted natural (reduced) units. This means that all quantities of interest are put to unity, so we do not work with very large or very small numbers. An advantage is that the equations of motion become simplified.

The following basic units are put to unity:

- length: $\sigma = 3.405$ angstrom for argon
- energy: $\epsilon = 119.8 \text{ degK}$ for argon
- mass: $m = 39.9$ amu for argon
- Boltzman's constant: $k_B = 1.381e - 23 \text{ J/K}$

Other derived reduced quantities are time $t^* = t\sqrt{\epsilon/m\sigma^2}$, temperature $T^* = k_B T/\epsilon$, and density $\rho^* = \rho^3$.

For simplicity we will indicate the unit of time as Δt .

3 Results

For most tests we use N=108 atoms (found to be sufficiently unaffected by surface effects) or N=500 atoms with a timestep of 10fs.

3.1 Temperature ratio - NVE

In NVE we set the initial velocities according to our prescribed energy and then they evolve into equilibrium naturally. Thus the temperature will change accordingly. We can verify this behavior by first checking that total energy is indeed conserved,

Throughout the equilibration, the kinetic energy drops to about a half of its initial value. Coinciding with this behavior, we now determine how the

temperature changes over the equilibration phase. This is necessary for determining what initial temperature to set the system at to analyze thermodynamic properties at a fixed final temperature. This result is given in Fig.6. We find the relationship to be approximately a factor of 1/2 between initial and final temperature i.e $T_f = \frac{1}{2}T_i$.

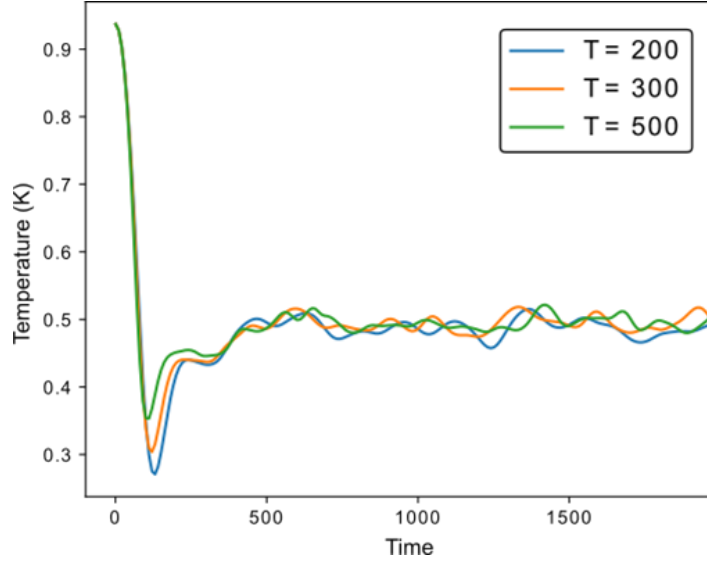


Figure 6: Temperature over time ratio for NVE with several temperatures. The dropping of the initial values to about half is consistent with the behavior seen in the kinetic energy

3.2 Melting and Pair Correlation

The systems behavior should change drastically after a phase transition. Visualization of the atomic structure in Fig.7 give clear indications of melting occurring near $T=300K$. we further investigate by looking at the pair correlation function for a known solid phase and a predicted liquid phase ($T = 70K$ and $T = 350K$) in Fig.??

3.3 Diffusion

Determining the exact melting temperature is a difficult calculation to perform rigourously however we can get an estimate for our initial lattice density using the diffusion constant. Using $N=500$ atoms in this case we can see in Fig.11 how the diffusion constant evolves over temperature. For solids this coefficient should be zero while liquids, non-zero. This result becomes non-zero at around $T=300K$ so we estimate the melting temperature to be in this vicinity. To match with experimental values would require altering the density of our initial structure and attempting to match the overall phase diagram of Argon i.e volume in addition to temperature.

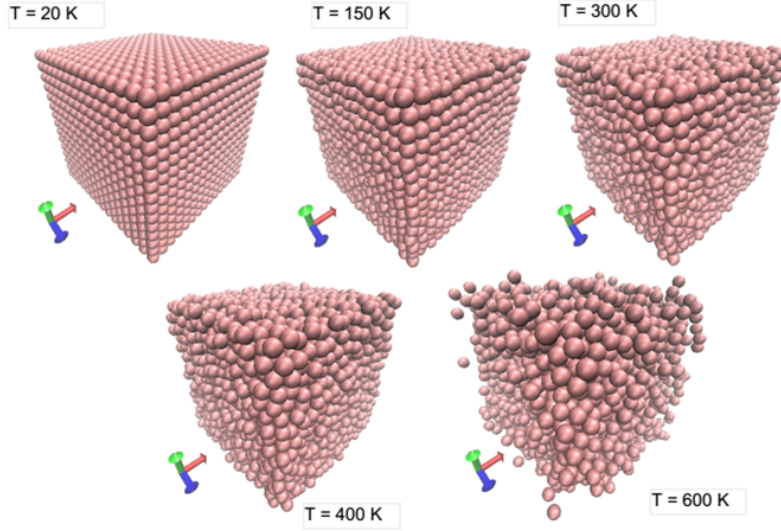


Figure 7: Crystal visualization over series of temperatures. By $T=300\text{K}$ approximately there is a noticeable loss of ordering in the atoms. We expect a phase transition to occur near this point.

3.4 velocity rescaling - NVT

Moving on now to the NVT ensemble we first verify equilibration is taking place as expected and that our thermostat is working properly i.e the velocity rescaling.

3.5 Thermal Conductivity

Generally thermal conductivity calculation require a larger simulation cell ($N=500$) and longer run times ($> 10^5$ time steps). First we can analyze the heat autocorrelation to predict what behavior to expect for thermal conductivity which is shown in Fig.14 for several solid phase temperatures.

Notice as temperature increases, the heat current autocorrelation function decays faster. This is due to the fact that there are more scattering processes when the temperature increases which will lower thermal conductivity. It also will lead to less accuracy using Green-Kubo as the time averaging scheme has less temporal history of relevant phenomena to average over. This is consistent with the computed thermal conductivity as presented in Fig.15.

4 Conclusion

Thermodynamic properties of solid Argon was examined by a molecular dynamics method both in the canonical (NVT) and microcanonical (NVE) systems. Lennard-Jones potential was a sufficiently accurate choice given the simplicity and accuracy of the results when used with a velocity verlet energy-conserving integration scheme. We were successfully able to observe a melting phase tran-

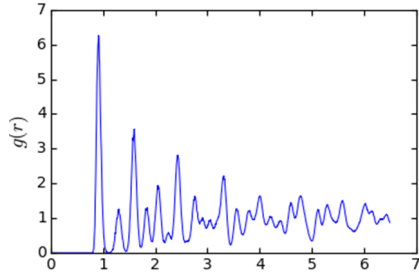


Figure 8: Solid phase $T=70K$

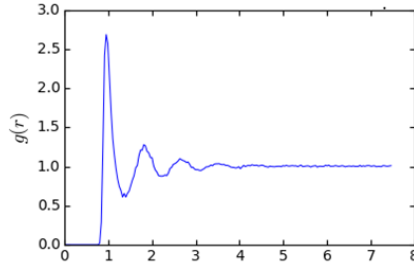


Figure 9: Liquid phase $T=350K$

Figure 10: Pair correlation function for the known solid phase of $T=70K$ is significantly staggered with many distinct peaks. This is expected for solids as the particles are all located at distinct sites separated by some distance dictated by crystal symmetry. In the liquid case is significantly smoothed out meaning the distribution of particles radially is more uniform. This is the case when there is less order in the structure i.e liquid and gaseous phases.

sition as well as the corresponding pair correlations of each phase. This was verified by the computation of the diffusion coefficient and finding its non-zero value to begin somewhere around $T=300K$ indicating a solid-liquid phase change. Additionally NVT calculations were carried out for thermal conductivity using the Green-Kubo formulation which was found to be very accurate using only Lennard-Jones potential.

We did not encounter any specific case of error accumulation but it was found that smaller timesteps lead to smaller errors unsurprisingly. This can introduce bottlenecks when the goal of the simulation is to determine properties of multi-scale systems where there is large disparity in the timescales of relevant physical phenomena.

References

- [1] Loup Verlet. Computer "experiments" on classical fluids. i. thermodynamical properties of lennard-jones molecules. *Phys. Rev.*, 159:98–103, Jul 1967.
- [2] M. Hjorth-Jensen. Lecture notes in computational physics, 2015.
- [3] F Clayton and D N Batchelder. Temperature and volume dependence of the thermal conductivity of solid argon. *Journal of Physics C: Solid State Physics*, 6(7):1213, 1973.

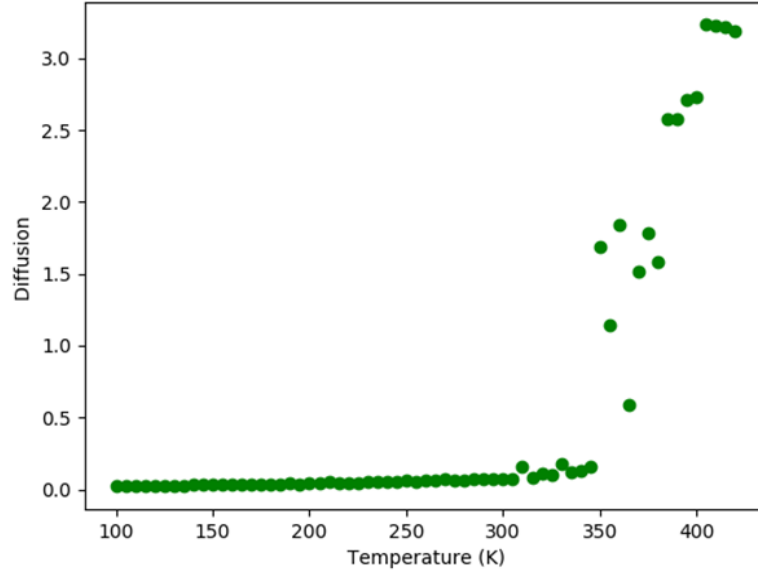


Figure 11: Diffusion constant as a function of temperature from final temperature values of 100K to 500K. Note we had to explicitly include the determinend $T_f = \frac{1}{2}T_i$ relationship we determined earlier

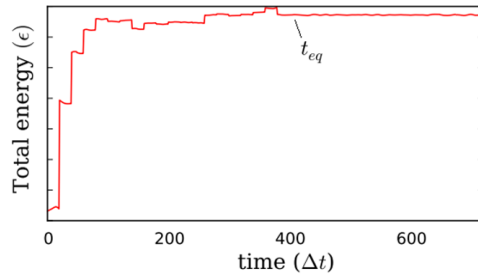


Figure 12: Energy during equilibration phase for an NVT system of N=108 atoms at T=200K. Rescaling of velocity is performed every 20 iterations

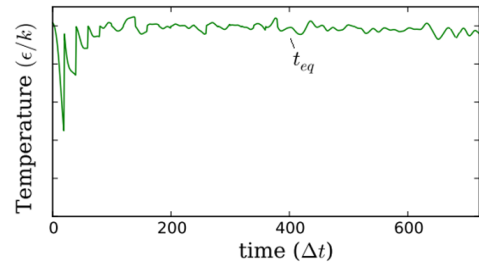


Figure 13: Temperature during equilibration phase for an NVT system of N=108 atoms at T=200K. Rescaling of velocity is performed every 20 iterations

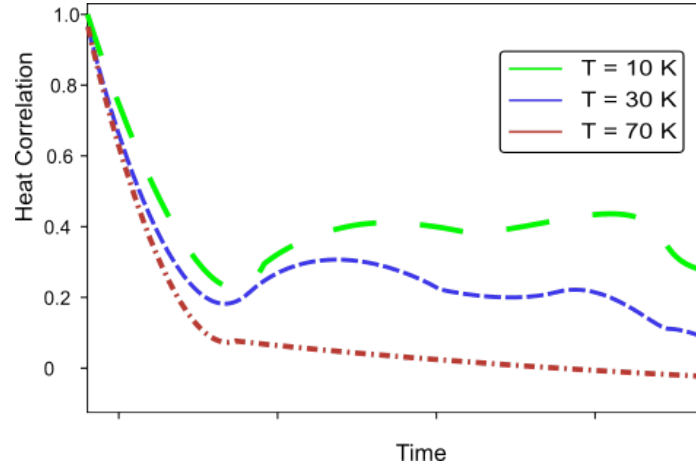


Figure 14: Heat Correlation at temperatures at 10K, 30K and 70K respectively

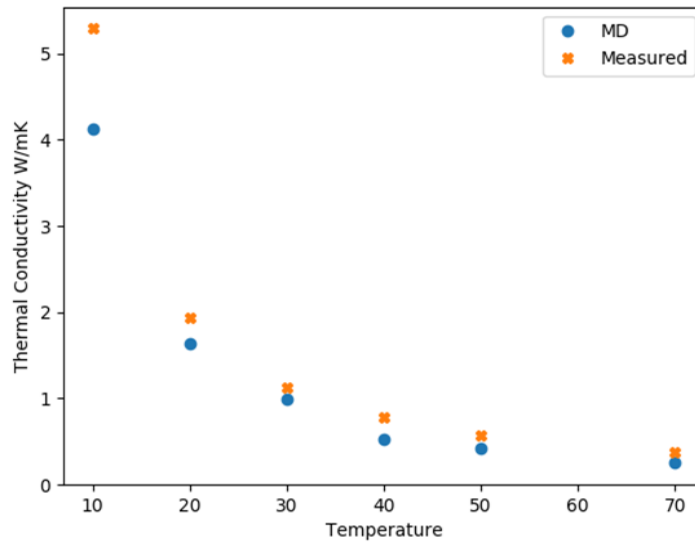


Figure 15: Thermal conductivity values of solid argon from 10K to 70K. The black circles are experimental values taken from Ref.[3]