

# The Lennard Jones Potential



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**Keywords:** Molecular dynamics, Statistical mechanics, Lennard Jones, heat capacity  
26<sup>th</sup> August, 2025

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## Abstract

The heat capacity as a function of temperature for a system of  $N$  particles in three dimensions that interact through the Lennard Jones potential is computed. The values that we obtain from simulation are shown not to be consistent with the values that would be expected for a system of  $3N$  classical harmonic oscillators. This system instead undergoes a phase transition from a solid to liquid phase at a temperature of 1.6 natural units.

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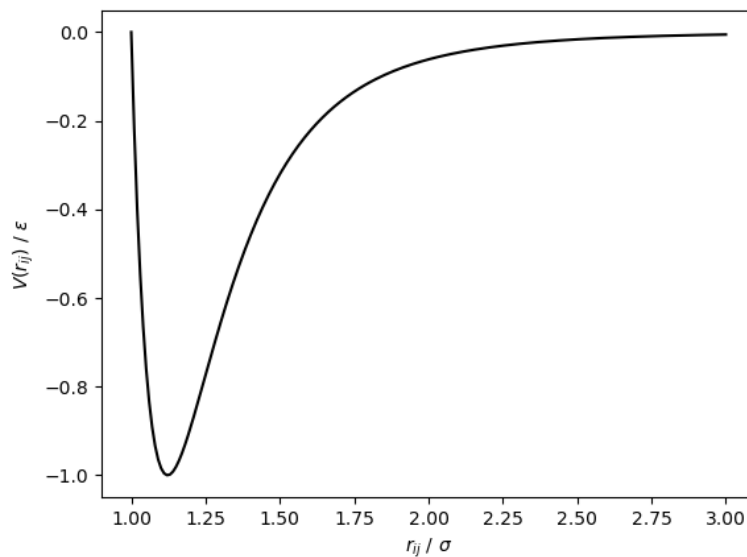
## 1 Introduction

To obtain accurate values for the many-body potential energy of a system of  $N$  atoms one must solve the time-independent Schrodinger equation. As solving this equation is computationally expensive a common alternative approach is to express the many body potential energy,  $V(\{\mathbf{x}\})$ , for  $N$  atoms using the following sum:

$$V(\{\mathbf{x}\}) = \sum_{i=1}^N V_1(\mathbf{x}_i) + \sum_{i=2}^N \sum_{j=1}^i V_2(\mathbf{x}_i, \mathbf{x}_j) + \sum_{j=3}^N \sum_{i=2}^j \sum_{k=1}^i V_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k) + \dots \quad (1)$$

In this expression,  $V_1(\mathbf{x}_i)$  is a one-body potential that describes how each atom interacts with any external fields.  $V_2(\mathbf{x}_i, \mathbf{x}_j)$  and  $V_3(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k)$  are then 2 and 3 body potentials that describe the interactions between pairs and triples of atoms respectively. One can expand this expression further and introduce sums of 4 and 5 body potentials over all possible quadruples or quintuples of atoms. However, for a system of atoms or ions researchers have found that one can get accurate values for the potential energy even when the expansion above is truncated at second order so only include one and two body terms are included. Furthermore, because it is rare to study systems that interact with an external field, the one-body term can also be set to zero.

In equation 1,  $V_2(\mathbf{x}_i, \mathbf{x}_j)$  is a suitably-parameterized function of the distance between atom  $i$  and  $j$  that is fitted to results from experiments or more-expensive, quantum calculations of the potential. In this work, we will investigate a system of atoms that interact through the Lennard Jones potential. The energy of each pair of atoms thus depends on the distance



**Fig. 1.** The Lennard Jones potential that acts between a pair of atoms as a function of the separation between the two atoms.

between the atoms in the manner described below:

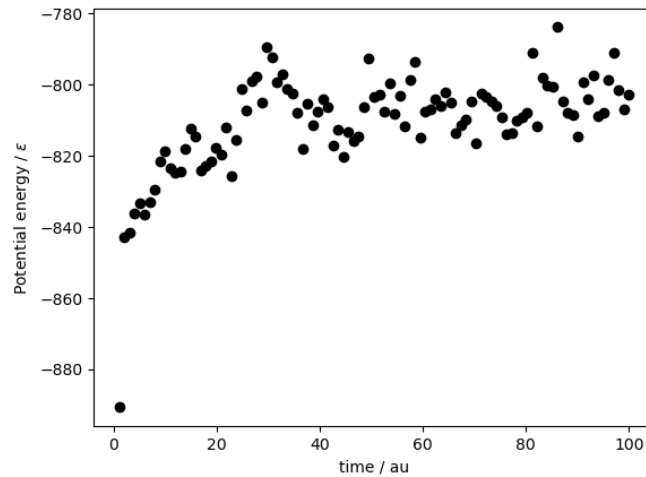
$$V_2(\mathbf{x}_i, \mathbf{x}_j) = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^6 \right]$$

In this expression  $r_{ij}$  is the distance between atom  $i$  and atom  $j$  and  $\sigma$  and  $\epsilon$  are parameters that will be set equal to one in what follows.

Figure 1 shows a plot of  $V_2(\mathbf{x}_i, \mathbf{x}_j)$  as a function of  $r_{ij}$ . The potential is close to zero when  $r_{ij}$  is large, which reflects the fact that the interaction between atoms has a limited range. For intermediate values of  $r_{ij}$  the potential is attractive. The potential is attractive in these regions because of dispersive, dipole-induced interactions between atoms. However, when  $r_{ij}$  gets small the potential becomes repulsive as the atoms have a finite size and having the electron clouds around different nuclei overlapping is energetically unfavourable.

In the remainder of this report the heat capacity for a system of  $N$  atoms that interact through the Lennard Jones potential is examined using molecular dynamics simulations. We show that the results are not consistent with what would be expected with the predictions of classical equipartition for a system of  $3N$  harmonic oscillators. Instead the atoms in this system undergo a phase transition from a solid to a liquid configuration at a temperature of about 1.6 natural units.

Details of the bench marking we did to ensure that the averages that we extract from MD are converged provided in section 2. In section 3 we then report the heat capacity as a function of temperature and compare what is observed for our  $N$  atoms of Lennard Jones with what would be expected for a system of  $3N$  classical harmonic oscillators. We show that there is a



**Fig. 2.** The values the potential energy took during a 10000 step simulation. You can see that the energy settles down to a constant value after 40 natural units and that the system is thus equilibrated after this point.

peak in the heat capacity for the Lennard Jones particles that occurs because the solid melts at a temperature of 1.6 natural units. The report finishes with a short conclusion in section 4

## 2 Methods

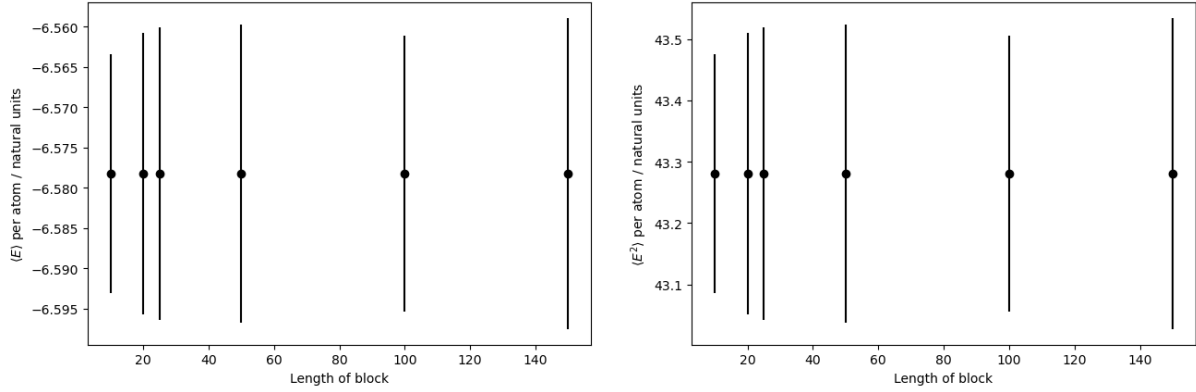
In this report, we studied a system of 108 particles with a mass of 1 in a cubic box with sides that have a length of  $3(2^{2/3}) \sigma^*$ . When calculating distances between particles we used the minimum image convention so this system of 108 atoms is assumed to be repeated periodically in all directions and throughout all of space. Temperature was kept fixed by performing Langevin dynamics using a timestep of 0.005 natural units and a friction of 0.1 natural units.

Figure 2 shows how the potential energy changes over the course of a 10000 step simulation that was run using these parameters at a temperature of  $0.6 \frac{k_B T}{\epsilon}$  and that was started from a perfect face centered cubic structure. You can see that the energy has settled down to a reasonably constant value after about 40 natural units. When collecting statistics for analysis we thus discarded the first 50 natural units of the simulation as we assumed that it would take this long for the system to equilibrate.

To calculate the heat capacities in section 3 we need to determine the average energy,  $\langle E \rangle$ , and  $\langle E^2 \rangle$ . As MD will give us an approximate average, we also need suitable estimates for the errors on these quantities. These errors for a 95% confidence limit are determined by block averaging. Figure 3 shows how the estimates of the errors depends on the lengths of the

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\*The Lennard Jones potential has a minimum at  $2^{1/6} \sigma$ . When the lattice spacing in an FCC crystal is  $a$  then the distance between an atom and its nearest neighbour is  $\frac{a}{\sqrt{2}}$ . By setting  $a = 2^{2/3} \sigma$  we thus ensure the separation between each atom and its nearest neighbour has a value where the potential is minimised.



**Fig. 3.** The dependence of the estimates of  $\langle E \rangle$  (left) and  $\langle E^2 \rangle$  (right) on the sizes of the blocks that they were computed from. The averages (black dots) do not depend on the size of the blocks. However, you can see that when the blocks are small the error on the average (length of lines) is underestimated.

blocks that we use. This figure was generated by running a 200000 step MD simulation at a temperature of  $0.6 \frac{k_B T}{\epsilon}$  in which statistics were collected every 200 steps.

Figure 3 shows that the error on the ensemble averages is underestimated when blocks with less than 50 statistics are used. We thus use blocks with a length of 200 to calculate all averages in what follows.

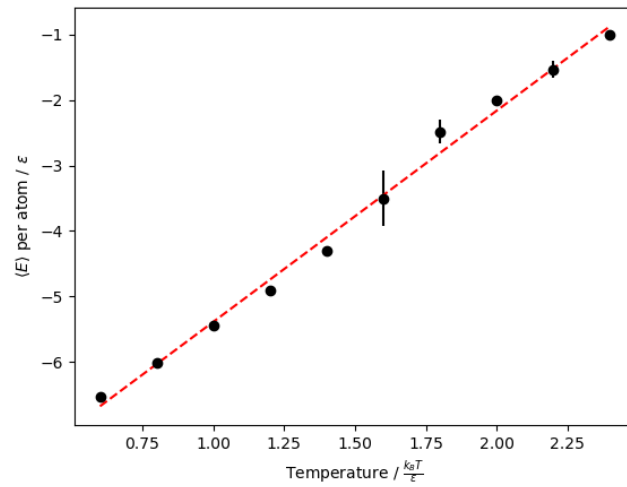
### 3 Results

Figure 4 shows how the average energy per atom for our system of 108 particles changes with temperature. The black dots in this figure are ensemble averages that were calculated from 200000 step MD simulations at each of the temperatures. Averages were extracted from these simulations in the manner described in section 2. The red dashed line is a line of best fit through these points. This line has a gradient of approximate 3.22, which is consistent with what would be expected for a system of harmonic oscillators. However, you can clearly see that some of the average energies we obtain are quite far from this line. Errors, most of which are smaller than the sizes of the points were computed on the averages. You can see that some of the differences between what is observed for this system and the predictions for a system of harmonic oscillators are statistically significant.

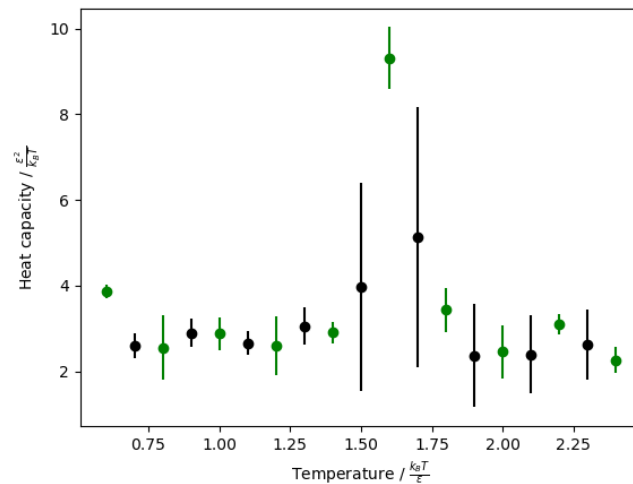
The gradient of the line in figure 4 is an estimate of the heat capacity of the system. We can refine this estimate by taking finite differences. The heat capacities, as well as errors that indicate a 95% confidence limit on our estimates, that we obtain using this approach are shown in black in figure 5.

We can also estimate the heat capacity in an MD simulation using:

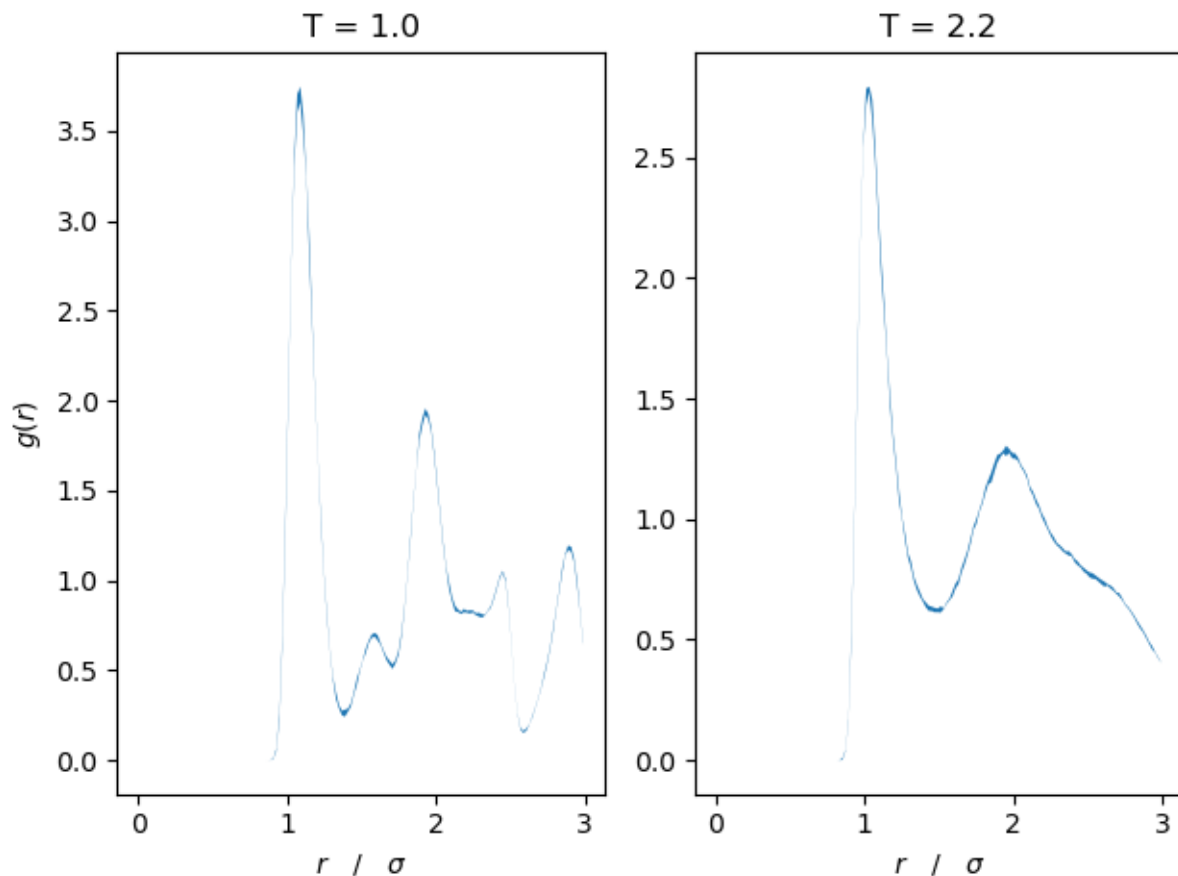
$$C_v = \frac{1}{k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2)$$



**Fig. 4.** The average energy per atom for the system of 108 Lennard Jones atoms that has been studied in this work. The black points are the results from simulation, while the red line is a line of best fit that was plotted through these points. Error bars that show the 95% confidence limit on our estimates of the averages are shown for all points. However, many of these error bars are smaller than the dots that have been used in the plot.



**Fig. 5.** The heat capacity per atom for the system of 108 Lennard Jones atoms that has been simulated in this work. As discussed in the text, the green points were calculated from the fluctuations in the energy, while the black points were calculated using finite differences. The error bars indicate the 95% confidence limit on our estimates of the heat capacity.



**Fig. 6.** Radial distribution functions for our Lennard Jones system at a temperatures above and below the peak in the heat capacity. For both curves the width of the lines indicate the 95% confidence limit on the estimate of the radial distribution function that was obtained from the simulation.

The estimates that we get for the heat capacity using this formula are shown in green in figure 5.

Figure 5 shows that the heat capacity has a marked peak at about  $1.6 \frac{k_B T}{\epsilon}$ . This behaviour is in marked contrast to the behaviour of a system  $3N$  classical harmonic oscillators, which has a heat capacity that does not depend on temperature.

To determine the physical origin for the peak in the heat capacity in figure 5 we calculated the radial distribution functions at temperatures above and below the peak. The distance between 0 and  $3 \sigma$  was divided into 150 equally spaced bins when calculating these radial distribution function and once again block averaging was used to obtain an error on our estimate. The final result are shown in figure 6. You can see that the radial distribution function is considerably more structured when it is obtained at temperatures that are lower than the position of the peak in the heat capacity. Much of this structure disappears when the radial distribution function is calculated at the higher temperatures. This suggests that the system undergoes a structural transition at a temperature of around 1.6 natural units. In other words, there is some loss of structural order at this temperature.

To further investigate the change in structure we measured the extent to which the environment around each of the atoms atom resembles the environment in the ideal fcc crystal. We can calculate whether the environment around atom  $i$  resembles the environment in the ideal fcc structure by calculating the following quantity:

$$s_i = \frac{1}{\sum_{j \neq i} \sigma(r_{ij})} \sum_{j \neq i} \sigma(r_{ij}) \left[ \frac{(x_{ij}y_{ij})^4 + (x_{ij}z_{ij})^4 + (y_{ij}z_{ij})^4}{r_{ij}^8} - \frac{27(x_{ij}y_{ij}z_{ij})^4}{r_{ij}^{12}} \right]$$

In this expression the sums run over all the atoms in the system.  $x_{ij}$ ,  $y_{ij}$  and  $z_{ij}$  are the components of the vector connecting atom  $i$  to atom  $j$  and  $r_{ij}$  is the magnitude of this vector. The function  $\sigma(r_{ij})$  ensures that we only consider the first coordination sphere around atom  $i$  as it is given by:

$$\sigma(r_{ij}) = \begin{cases} 1 & \text{if } r_{ij} < 1.5 \\ 0 & \text{otherwise} \end{cases}$$

Figure 7 shows estimates of the free energy for a single atom as a function of the following linear transform of this quantity <sup>†</sup>:

$$\kappa_i = \frac{80080s_i}{2717 + 16 \times 27} + \frac{16(27 - 143)}{2717 + 16 \times 27}.$$

The free energies surfaces in figure 7 were calculated by constructing histograms. Block averaging was again used when calculating these histograms. The range of values between -0.5 and 1.1 was divided into 70 bins and, because all the particles are indistinguishable, all 108 atoms in each frame of the trajectory were used when accumulating statistics.

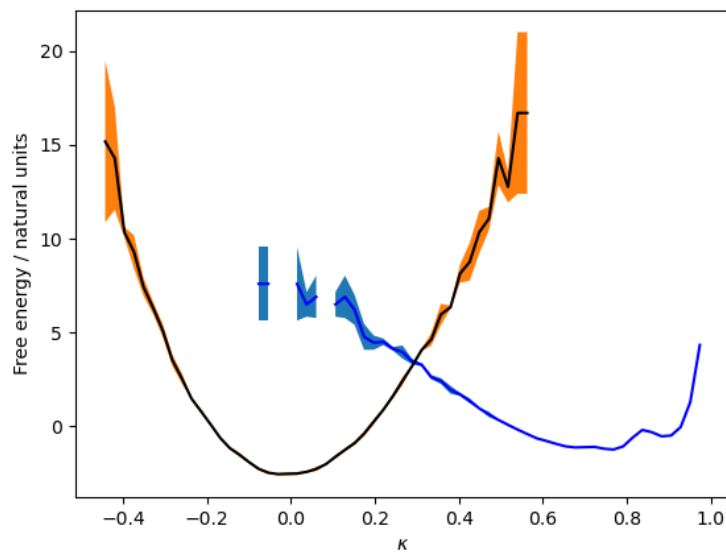
When the temperature is low there is a minimum in the free energy for values of the order parameter,  $\kappa$ , of around 0.8. The environment around each atom in these configurations thus closely resembles that seen in the FCC crystal. When temperature is high you can see that this minimum disappears and is replaced by a minimum at 0.0. The structure thus melts at the higher temperature and the FCC structure disappears.

## 4 Conclusions

Simulations of a system of 108 particles that interact through a Lennard Jones potential have been performed. Multiple evidences that the system undergoes a transition from solid to liquid at a temperature of 1.6 natural units have been provided. The analysis with the FCC order parameter that was presented in figure 7 suggests that an analogy with the two-level system can be used to understand this system. There is a peak in the heat capacity similar to the one observed in figure 5 for two-level system which occurs because the ratio of the

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<sup>†</sup>Transforming  $s_i$  in this way ensures that  $\kappa_i$  equals 1 when the environment around atom  $i$  resembles that in the fcc crystal and 0 when there is no orientational order around atom  $i$ . In other words,  $\kappa_i$  is zero when the arrangement of atoms resembles what would be seen if atoms were placed randomly on a sphere.



**Fig. 7.** Free energy surfaces for a single particle of Lennard Jones as a function of the  $\kappa$  order parameter that was defined in the text. The blue curve shows the free energy calculated from a simulation that was run at a temperature of 1.0 natural units while the black curve is the free energy surface that is obtained for a temperature of 2.2 natural units. You can see that the atomic environments resemble those found in a perfect fcc crystal at the lower temperature but that this structure has melted at the higher temperature. The shaded regions indicate the 95% confidence limit on our estimate of the free energy.

number of atoms in the two levels changes little at high and low temperatures and rapidly at intermediate temperatures. The peak in figure 5 similarly occurs at temperatures where the ratio of the number of atoms with an environment that resembles that in the solid to the number of atoms with an environment that resembles that in the liquid is changing rapidly.