

The Quantum Lennard Jones Potential



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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 in a way that incorporates nuclear quantum effects. These calculations are performed by determining the characteristic frequencies from the 0 K structure and assuming that each of these frequencies can be treated as a quantum harmonic oscillator at all temperatures. In the conclusions we demonstrate that this approach is not really suitable for studying solid systems as anharmonic effects play a significant role in determining the properties of materials.

1 Introduction

In a previous report, I studied a system of interacting particles. Each pair of particles in the system interacted through the Lennard Jones potential:

$$V_2(\mathbf{x}_i, \mathbf{x}_j) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (1)$$

In this expression r_{ij} is the distance between atom i and atom j and σ and ϵ are parameters that were set equal to one.

The previous report used classical molecular dynamics (MD) simulation to calculate how the heat capacity of a system of 108 particles that interact through this potential changed with temperature. In doing these calculations I assumed that my system was composed of classical particles. However, in reality atoms follow the laws of quantum (and not classical mechanics). In this report, I am thus going to determine how the heat capacity of this system is affected by harmonic nuclear quantum effects.

The remainder of this report is laid out as follows. I first introduce the theory and approximations I am making by considering the heat capacity of a single particle on the energy landscape given in equation 1 in section 2. I then use this theory to calculate the heat capacity as a function of temperature for a system of 108 Lennard Jones particles in section 3. In doing these calculations I assume that the system can be thought of as a series of independent harmonic oscillators at all temperatures. In section 4 I discuss why this approach is flawed and probe the dynamic behaviours of the system at finite temperature.

2 Heat capacity for a diatomic

Consider a single particle on the Lennard-Jones energy landscape. If this particle is at position x its energy is:

$$V(x) = 4\epsilon \left[\left(\frac{\sigma}{x} \right)^{12} - \left(\frac{\sigma}{x} \right)^6 \right] \quad (2)$$

We can find the lowest-energy position for this particle by differentiating the above expression with respect to x to arrive at:

$$\frac{dV}{dx} = 4\epsilon \left[-12 \left(\frac{\sigma^{12}}{x^{13}} \right) + 6 \left(\frac{\sigma^6}{x^7} \right) \right] = 24\epsilon \left(\frac{\sigma^6}{x^7} \right) \left[1 - 2 \left(\frac{\sigma}{x} \right)^6 \right] \quad (3)$$

If we are at a minimum in the potential this derivative must equal zero so:

$$0 = 1 - 2 \left(\frac{\sigma}{x} \right)^6 \quad \rightarrow \quad x = \sqrt[6]{2}\sigma$$

For points close to this minimum we can determine an approximate value for the energy of the diatomic by using a Taylor series truncated at second order as follows:

$$V(\sqrt[6]{2}\sigma + \delta) = V(\sqrt[6]{2}\sigma) + \left(\frac{dV}{dx} \right)_{\sqrt[6]{2}\sigma} \delta + \left(\frac{d^2V}{dx^2} \right)_{\sqrt[6]{2}\sigma} \frac{\delta^2}{2!} + \dots$$

Inserting $\sqrt[6]{2}\sigma$ into equations 2 and 3 and inserting the results into the Taylor series above gives:

$$V(\sqrt[6]{2}\sigma + \delta) = -\epsilon + \left(\frac{d^2V}{dx^2} \right)_{\sqrt[6]{2}\sigma} \frac{\delta^2}{2!} + \dots$$

The second derivative of V with respect to x is then:

$$\left(\frac{d^2V}{dx^2} \right) = 4\epsilon \left(\frac{\sigma^6}{x^8} \right) \left[156 \left(\frac{\sigma}{x} \right)^6 - 42 \right]$$

Evaluating this at $\sqrt[6]{2}\sigma$ and inserting the result into our Taylor series gives:

$$V(\sqrt[6]{2}\sigma + \delta) = -\epsilon + \frac{486\epsilon}{\sqrt[3]{2}\sigma^2} \frac{\delta^2}{2!}$$

The second term in this expression is the potential for a Harmonic oscillator with $k = \frac{486\epsilon}{\sqrt[3]{2}\sigma^2}$ and thus $\omega = \sqrt{\frac{486\epsilon}{\sqrt[3]{2}m\sigma^2}}$ with m being the mass of our particles. We can write the following expression for the energy levels of this system by approximating it as a harmonic oscillator:

$$E_n = -\epsilon + \left(n + \frac{1}{2} \right) \hbar\omega \quad \text{with} \quad n = 0, 1, 2, \dots$$

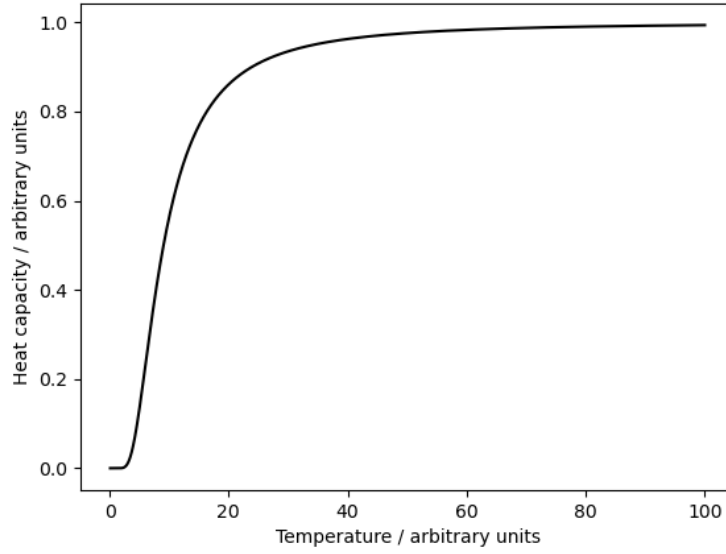


Fig. 1. The heat capacity for a single particle sat on the Lennard Jones energy landscape as a function of temperature.

For this harmonic oscillator the partition function is:

$$Z = \frac{\exp\left(\frac{\epsilon}{k_B T}\right) \exp\left(-\frac{\hbar\omega}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)}$$

and the average energy is:

$$\langle E \rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right) = -\epsilon + \hbar\omega \left[\frac{1}{2} + \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \right]$$

The heat capacity of the particle must therefore be:

$$C_v = \left(\frac{\partial \langle E \rangle}{\partial T}\right) = \frac{\hbar^2 \omega^2}{k_B T^2} \left[\frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} + \frac{\exp\left(-\frac{2\hbar\omega}{k_B T}\right)}{\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right]^2} \right] \quad (4)$$

Figure 1 shows a plot of this heat capacity as a function of temperature. As always we are operating in a system of natural units so ϵ , σ and m have been set equal to one. As we do not know the values of \hbar in this system of units we have also set it equal to one. You can clearly see from this figure that the heat capacity tends to zero when the temperature is low. At high temperatures the heat capacity saturates to the value of 1.0 that would be expected from classical equipartition.

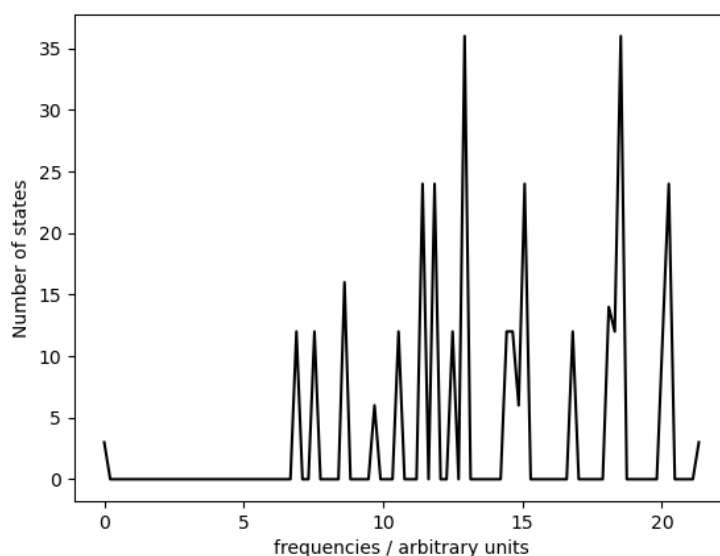


Fig. 2. The spectrum of frequencies that were obtained by diagonalising the Hessian for a system of 108 Lennard Jones particles

Figure 1 suggests that nuclear quantum effects have a significant effect on the heat capacity of this system for temperatures up to $40 \frac{k_B T}{\epsilon}$. For temperatures lower than this value the heat capacity has a value that is less than the value of 1 which is predicted by classical equipartition. This rough calculation suggests that we were perhaps wrong to treat the particles classically in the previous molecular dynamics assignment. In the following sections we will thus use the theory outlined in this section to calculate the heat capacity in a way that incorporates (harmonic) nuclear quantum effects.

3 Heat capacity from 0K structure

As in the previous report, I studied a system of $N = 108$ 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. The interaction between each pair of particles in this system was then calculated using the Lennard Jones potential that was given in equation 1.

We used the BFGS algorithm as implemented in ASE to minimise the energy of the particles. We then used ASE to calculate the matrix of second derivatives at this minimum energy configuration numerically. Frequencies for a set of orthonormal modes were obtained from this Hessian matrix by diagonalising it and computing the square roots of the resulting eigenvalues. Figure 2 shows the spectrum of frequencies that were output by this procedure.

The heat capacity for each of the $3N$ frequencies shown in figure 2 were calculated using equation 4. The graph shown in figure 3 shows the sum of these $3N$ heat capacity values

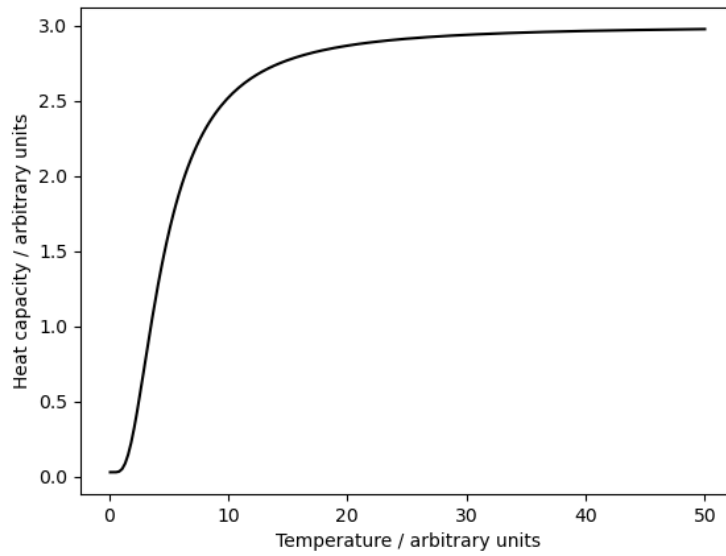


Fig. 3. The heat capacity for the system of 108 Lennard Jones particles as a function of temperature. This result was obtained by calculating the heat capacity as a function of temperatures for each of the frequencies shown in figure 2 using equation 4. The graph shows the sum of all these heat capacities divided by N .

divided by N . In other words, figure 3 shows the per atom heat capacity for our system. You can once again see that the heat capacity per atom is considerably lower than the value of three that would be predicted from the classical equipartition theorem. It would thus appear that nuclear quantum effects also have a substantial effect on the heat capacity of this system.

4 Conclusions

The results from the previous sections of this paper suggest that nuclear quantum effects have a significant effect on the heat capacity up to quite high temperatures. In the proceeding sections, however, we have assumed that $\hbar = \epsilon \sqrt{\frac{\epsilon}{m\sigma^2}}$. This assumption is likely incorrect and illustrates why we cannot rely on theory alone. We need experiments to determine the ratios between physical constants such as Planck's constant the masses of the atoms and the position and depths potential well that describes the interaction between atom. In other words, we need experiments to determine the values of the parameters (σ and ϵ). If we want to include nuclear quantum effects, we cannot simply set all the parameters equal to one as we have done in these reports and hope to obtain results that tell us about the nature of reality.

Lennard Jones has most famously been used to simulate Argon. Reasonable parameter values for argon are $\epsilon = 0.997$ kJ/mol, $\sigma = 3.4$ Å and $m = 0.040$ kg/mol. Planck's constant is 3.99×10^{-13} kJ s/mol and Boltzmann's constant is 0.00831 kJ/mol. These parameter values were inserted into equation 4 to determine heat capacity as a function of temperature curve for a single atom of Argon rolling about on the pair potential that is shown in figure 4. You can

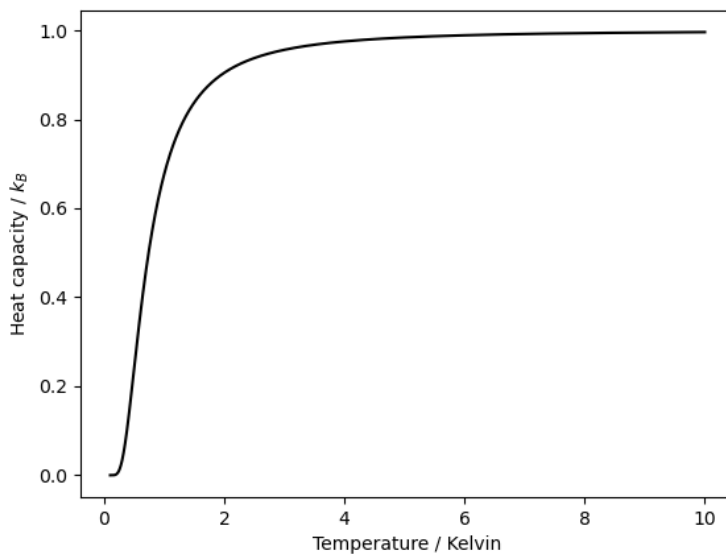


Fig. 4. The heat capacity for a single particle of argon sat on the Lennard Jones energy landscape with the parameters described in the text as a function of temperature.

see that nuclear quantum effects on the heat capacity are negligible at all temperatures above 4 K. We were thus correct to treat the atoms as classical particles in our previous simulations.

Even if we were to properly incorporate the units, there is a further problem with the analysis in this report. We have assumed that the system behaves like a harmonic oscillator at all temperatures. In other words, we have assumed that the anharmonicity of the potential does not play a significant role in determining the properties of the system. Given that we observed a phase transition from a solid to a liquid phase in the previous report anharmonicity must play a more significant role than we have assumed here.

Although I cannot calculate the Hessian at finite temperature, I can get information on the vibrational behaviour at a particular temperature by computing the velocity autocorrelation function. Figure 5 shows what I obtain for this function at temperatures of 0.5 and $3.0 \frac{k_B T}{\epsilon}$. To calculate these autocorrelation functions I first ran 50000 steps of constant temperature molecular dynamics with a timestep of 0.005 natural units starting from the ideal FCC structure with a lattice parameter of $2^{2/3}$. During this equilibration stage a Langevin thermostat with a friction of 0.1 natural units was used to maintain the temperature. This constant temperature equilibration was followed by second equilibration stage of 20000 steps in which the temperature was also kept constant. Velocity autocorrelation functions were then computed from NVE simulations with 50000 steps. These production runs were split into 5 blocks so as to have five independent estimates for the autocorrelation function. The error bars for the autocorrelation function that were obtained by averaging over these five estimates are narrower than the widths of the lines in figure 5.

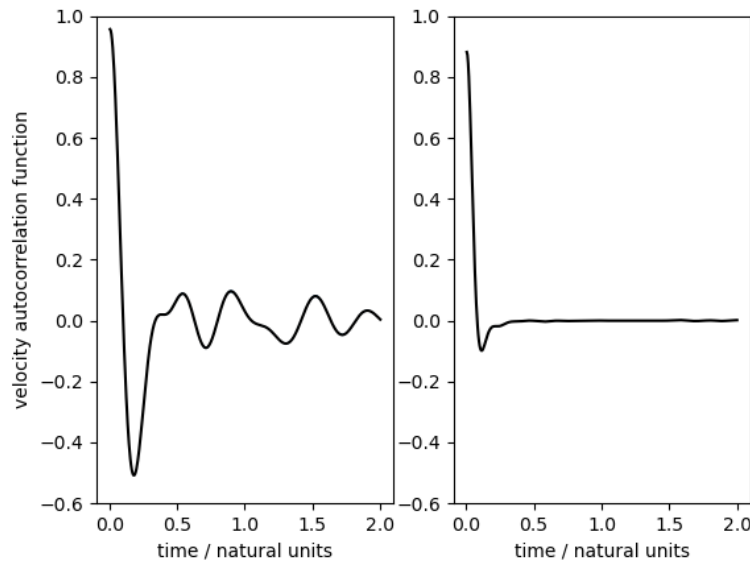


Fig. 5. Velocity autocorrelation functions for the system of Lennard Jones particles that were studied in this work at temperatures of 0.5 (left) and $3.0 \frac{k_B T}{\epsilon}$. To make y-axis scales on the two curves comparable I divided the velocity correlation functions by the temperature, which (by equipartition) is equal to the value of the autocorrelation function at $t = 0$.

Clear differences in the system's behaviour are evident from figure 5. When the temperature is low the velocities remain correlated for longer periods of time. These correlations are indicative of the fact that atoms are oscillating around lattice sites as they would be expected to do in a solid. When the temperature is raised, however, these correlations disappear as the atoms in the liquid are no longer oscillating around their lattice sites.

The evident differences in the autocorrelation functions in figure 5 suggest that the assumptions that were made to compute the heat capacity in section 3 are not reasonable. If the system were behaving as a harmonic oscillator we would expect to see the oscillations in the velocity autocorrelation function that we see at $0.5 \frac{k_B T}{\epsilon}$ at all temperatures.

We can compute the vibrational density of states at finite temperature by computing the Fourier transform of the velocity autocorrelation function * Figure 6 shows the estimates for the densities of states at 0.5 and $3.0 \frac{k_B T}{\epsilon}$ that were obtained by applying this procedure. These density of states were from NVE MD runs of 500000 steps in which configurations were stored every 10 steps. To generate initial configurations for these production calculations we ran an equilibration that was identical to that performed for the calculation of the autocorrelation function. The production trajectory was also once again split into 5 blocks so that block averaging could be used to determine the errors on our estimate of the density of states. These errors are smaller than the widths of the lines in figure 6

*Or by doing a fast-Fourier transform on the time series of velocities directly and taking advantage of the convolution theorem as we have done here.

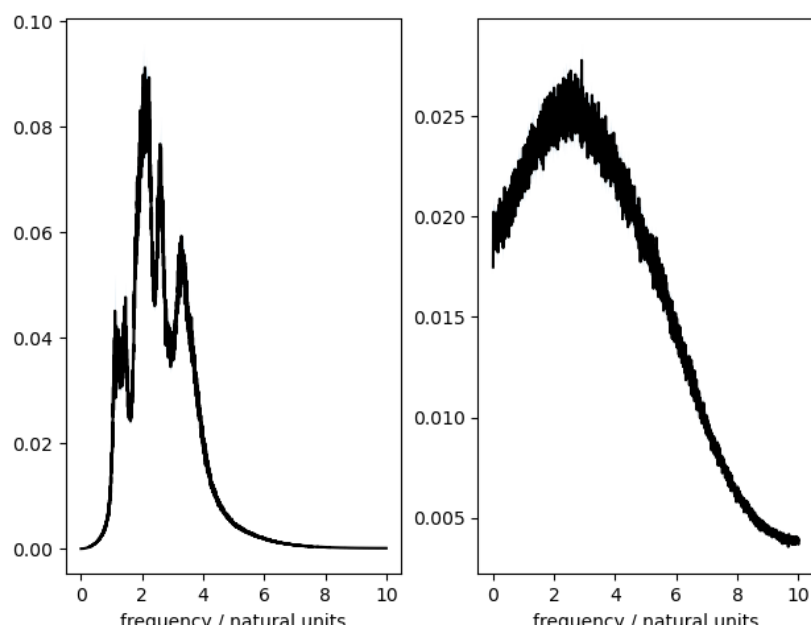


Fig. 6. Vibrational density of states for the system of Lennard Jones particles that were studied in this work at temperatures of 0.5 (left) and $3.0 \frac{k_B T}{\epsilon}$. Density of state plots were normalised so that the area under each curve is equal to one.

The vibrational densities of states at the two temperatures are very different. At the lower temperature there are a number of sharp peaks suggesting that the atoms are oscillating around their lattice sites with certain characteristic frequencies as you would expect to see for a system of harmonic oscillators. At the higher temperature, however, there is only a single broad peak. Another big difference is that value of the vibrational density at zero frequency is zero at the low temperature and non zero for the higher temperature. This result is important as the value of the vibrational density of states at zero frequency is related to the diffusion constant. Consequently, figure 6 is telling us that the atoms are diffusing at the higher temperature and that they are not diffusing at the lower temperature. This result is further evidence that the system is a solid at low temperature and a liquid at higher temperature and that treating it as a harmonic oscillator at all temperatures is not a reasonable assumption.