Phase transitions in a one dimensional atom chain

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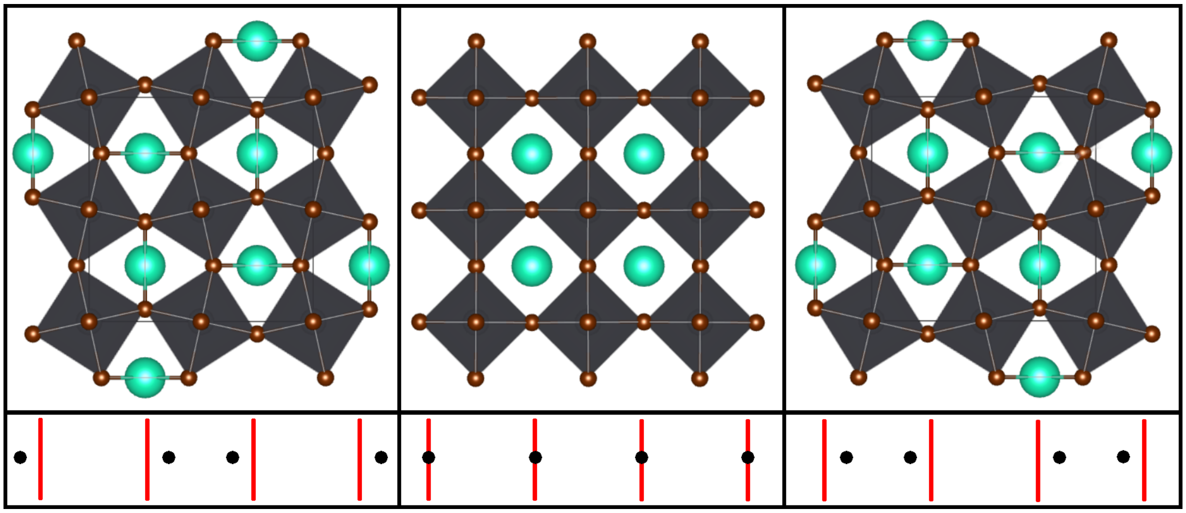

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Abstract

In this thesis we are set out to find if a simplified model can be constructed that captures phase transitions that occur in perovskites. The model is a one dimensional atom chain modeled after certain anharmonic phonon modes of a $CsPbBr_3$ perovskites. We simulate our model in a Molecular Dynamics (MD) simulation. We first cover the derivation of our model after which we discuss the methods we implement and use in the simulation of the model. After this, the results of the simulation are covered. We find that phase transitions in our model analogous to the phase transitions of $CsBrPb_3$ do occur, but because of an unspecified parameter in our model the resulting phase transition temperatures can not be compared to values found in literature. We discuss the results and conclude that further research is needed on the model to solve the problem of the unspecified parameter. If this is done then the model could be compared with other research to see if the model can lead to a better understanding of phase transitions in a crystal. We conclude that until further research is done model should only be used as a purely theoretical model and the results of our model should not be directly linked to a real system.

Contents

1 Introduction

Recent research on photovoltaic cells has turned to alternative materials to increase efficiency and reduce costs for solar cells. One of such materials which is being turned to is perovskites. Perovskites are crystals of the form ABX_3, with A and B being cations and X being an anion. The perovskites most commonly looked at for solar cells are hybrid organic-inorganic lead or tin halide based materials, where B = Pb, Sn and X = I, Br, Cl for example [1]. Due to research in recent years the photovoltaic efficiency of these materials has seen a rapid increase, recently surpassing efficiency limits of silicon based technology [2]. Perovskites are also relatively cheap to produce and manufacture, making these materials commercially very attractive. However, there are still problems concerning the stability of the material, keeping it from being implemented in the market. Because of this, further research is needed to improve the stability. In the field of computational physics one factor limiting this research is computational power. Simulating this crystal can take up to many years even on the most sophisticated supercomputers. Many methods have already been proposed and implemented to try and circumvent this issue such as the use of machine learning to model the crystal [3] [4].

To study these perovskites with a reduced computational cost we propose a simplified model of the crystal which we hope characterises certain properties of a real perovskite. Specifically, we are set out to find if such a simplified model can accurately portray phase transitions. Due to anharmonic phonon modes in the perovskite and upon increasing the temperature, the perovskite has a second order phase transition from a tetragonal to a cubic phase [5]. We would like to capture these anharmonic properties of the perovskite in our simplified model such that an analogous phase transition occurs. We will construct our model after specific eigenmodes of a $CsPbBr_3$ perovskite which exhibit anharmonic behaviour. Our model will be a one dimensional atom chain coupled with an anharmonic double well potential where we only look at nearest neighbour interactions. It already has been shown that 1D atom chain models are able to describe second order phase transitions such as a 1D Ising model [6]. Our model will be simulated using a molecular dynamics (MD) simulation where we sample from the canonical ensemble. Here the number of atoms, the volume and the temperature are kept constant. The temperature is kept constant with a Langevin thermostat and we use periodic boundary conditions. Second order phase transition theory will be used to find the phase transition temperature (T_c) where the order parameter will be the peak positions of the probability density function of the positions of the atoms relative to their equilibrium positions.

We find that our model does show behaviour analogous to a phonon eigenmode of a real perovskite crystal. Furthermore, a second order phase transition occurs at a specific temperature. For high temperatures we find that on average the atoms are positioned at their harmonic equilibrium positions. That is, the equilibrium positions of the atoms in the same atom chain but with a harmonic nearest neighbour potential, where all the distances between neighbouring atoms are equal. For lower temperatures we find that the atoms are on average equally distributed between the two well positions of the double well potential. In the probability density function of the atoms this can be seen as a transition from two peaks for temperatures lower than than T_c to one peak for higher temperatures. Because of the way the potential of our model is structured we can not yet compare the results of the model to the perovskite. A method is proposed which would make it possible that this can be done, however this fell out of the scope of this project and has not been tested as of now. The results do show us that it can be possible to construct a simplified model which captures phase transitions. This could lead to a better understanding of such phase transitions, as less computing power is needed to get results. For now these results cannot be coupled to actual perovskites or other crystals, but further research could bring change in this issue. We propose that for now, the model should be primarily used as an analogous toy model, to better get a grasp of the mechanisms behind phase transitions.

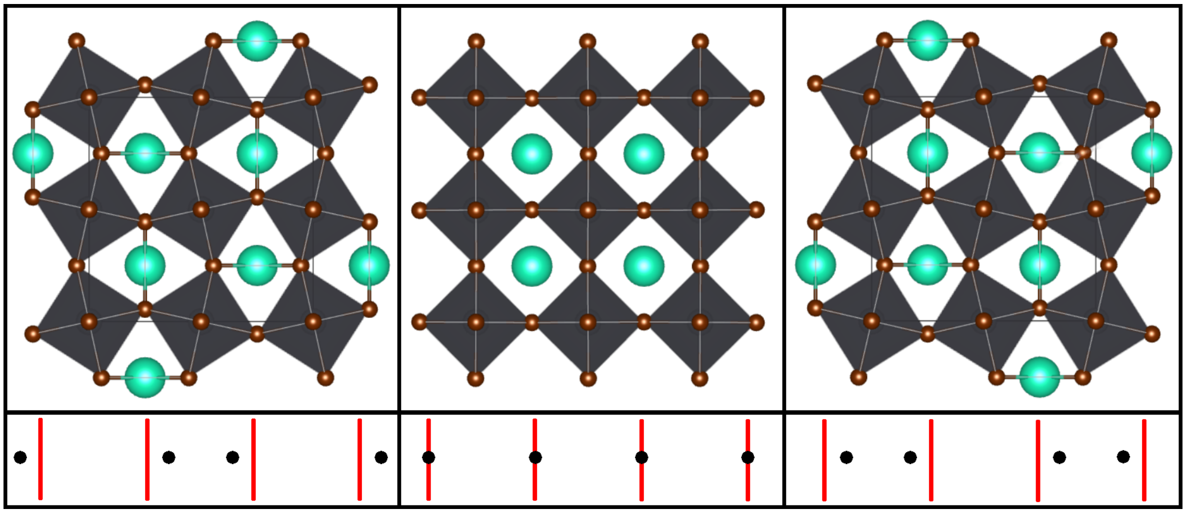


Figure 1: Frozen phonon modes of $CsPbBr_3$ and the analagous states of the atom chain. The deviation from the positions of the atoms in the 1D chain (black dots) to their harmonic equilibrium positions (red lines) correspond to the rotation of the $PbBr_6$ octahedra in the perovskite.

2 Model

Our simplified model will be a one dimensional atom chain with a potential similar to that of the potential energy landscape of a phonon mode of $CsPbBr_3$. A phonon mode in a crystal is a periodic motion of the crystal lattice at a single frequency. Phonons can be thought of as quantized sound waves in a material, just as photons can be thought of as quantized light waves. The displacement of particles in a phonon mode can be described mathematically as [7]:

$$\vec{u}_j(\vec{n},t) = \text{Re}\left[\epsilon_j^{\vec{s}}(\vec{q})e^{i(\vec{q}\cdot\vec{n}-\omega^s(\vec{q})t)}\right] \tag{1}$$

where $\vec{u}_j(\vec{n},t)$ = the displacement of atom j in unit cell $\vec{n}$ at time t, $\epsilon_j^{\vec{s}}(\vec{q})$ = the phonon eigenvector for atom j at normal mode s with wave vector $\vec{q}$ and $\omega^s(\vec{q})$ = the frequency of the phonon. The phonon eigenvector specifies the direction of motion for each particle in the unit cell.

The movemement that is described by equation (1) can be seen in figure 1 for the q=M1-mode. Taking a phonon movement and calculating or deriving the potential energy along it, we get the potential energy landscape for the phonon mode. A similar process can be done for our 1 dimensional atom chain and we want that the potential landscapes of both systems are similar. Because the phase transitions are thought to arise because of anharmonic phonon modes we will be investigating the q=M- and q=R-modes, which exhibit anharmonic behaviour [5].

To calculate the potential landscape of these modes in $CsBpBr_3$ we move each atom a certain distance along its phonon eigenvector as specified in equation (1) and calculate the corresponding potential energy. The phonon eigenvectors and the calculation of the potential energy for each resulting atom configuration was obtained with the help of the CMS group of University of Twente by implementing a machine learning force field [3] [4]. This is a method which approximates the force field which describes the crystal with the help of machine learning, to reduce computational cost of a simulation.

The results for the potential landscapes for $CsPbBr_3$ can be seen in Figure 2 for the q=M1-, R1-, R2- and R3-modes. It can be seen that there are two wells in potential energy. These wells ensure that the ground state is a state where the octahedra comprised of 6 Bromine atoms are rotated slightly around

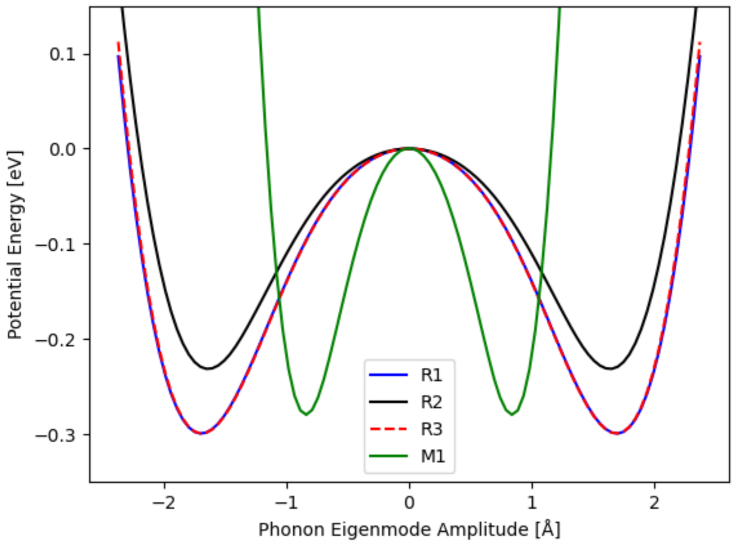


Figure 2: The anharmonic q=R1, R2, R3 and M1 (blue, black, red and green respectively) phonon eigenmodes of the perovskite $CsPbBr_3$.

the Lead atom in an alternating sequence as shown in Figure 1. We will see this configuration for low temperatures. For higher temperatures the system will on occasion get enough energy to jump from one well to the other. For a high enough temperature the atoms will have so much energy that they ”ignore” the potential hill all together, resulting in a cubic phase where on average the atoms are on their equilibrium positions instead of one of the two wells.

Now that we know some properties of the phonon modes of $CsPbBr_3$ we can start with constructing the simplified model. We will want to construct a potential which ensures similar or analogous movement to the rotating $PbBr_6$ octahedra as mentioned before. Because the movement of the atoms are confined to one dimension with periodic boundary conditions this movement will be an alternating pattern of being left or right of the atom equilibrium positions as shown in Figure 1. When moving the atoms from one to the other side of their equilibrium positions and calculating the potential energy of all atom configurations along this movement we should get a potential landscape similar to the one obtained from the perovskite. A first try for an interaction potential which achieves this is a nearest neighbour quartic approximation:

$$V = \sum_{i=1}^{N} V_{i,i-1} = \sum_{i=1}^{N} -\frac{a}{2}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^2 + \frac{b}{4}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^4 \tag{2}$$

Here, V = the total potential energy, $V_{i,i-1}$ = the interaction potential between two atoms i and $i-1$, r_i = the position of the $\mathrm{i_{th}}$ atom and d_{eq} = the distance between the equilibrium positions of two neighbouring atoms. In general, $d_{eq} = L/N$, the length of the chain divided by the number of atoms. Note that we have periodic boundary conditions, so $r_0 = r_N$. The reason we do a quartic approximation is to keep the model simple. We mainly do this because we can work out properties such as the well depth h and well position X_0 for our model, which we want to be equal to the well depth and well position of the potential landscape of the perovskite. The q=R2 potential landscape with its quartic approximation can be found in figure 3. When looking at the distances between the atoms in the ground state we expect an alternating pattern of short and long distances. This potential works in the sense that the energy for the system is minimized if the distances between atoms are either long or short. To obtain analogous behaviour to a phonon mode of $CsPbBr_3$ we would want the successive distances between neighbouring atoms to be alternatingly short or long, similar to the alternating $PbBr_6$ octahedra. However, our potential doesn't specify a specific pattern for the nearest neighbour distances for which the energy is minimized. The energy is minimized if there is the same amount of short as long distances, given that $d_{eq} = L/N$. The pattern of the nearest neighbour distances does not matter. To actually force the ground state to be an alternating pattern of long and short distances we need a slight modification to the interaction potential:

$$V = \sum_{i=1}^{N} V_i + V_{i,i-1} = \sum_{i=1}^{N} k(\vec{r}_i - \vec{r}_{ieq})^2 - \frac{a}{2}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^2 + \frac{b}{4}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^4 \tag{3}$$

Where r_{ieq} is the equilibrium position of the i_{th} atom. The added term V_i is an on-site harmonic potential. If k is high enough this makes sure that the atoms can not deviate from their equilibrium positions too much. This in turn forces the ground state to be the alternating pattern of short and long distances like we want.

We now need to set parameters k, a and b such that the potential landscape is the same as that of a anharmonic phonon mode of a perovskite. If we move the atoms a distance X from their equilibrium positions in a left or right alternating fashion we get:

$$|\vec{r}_i - \vec{r}_{ieq}| = X \tag{4}$$

$$||\vec{r}_i - \vec{r}_{i-1}| - d_{eq}| = 2X \tag{5}$$

plugging (4) and (5) in (3)

$$V = \sum_{i=1}^{N} (k-2a)X^2 + 4bX^4 = N((k-2a)X^2 + 4bX^4) \tag{6}$$

To make this landscape similar to the landscape of the perovskite we will set k, a and b such that the positions of the wells X_0 and the well depth h are similar. In our system X_0 and h are given by:

$$X_0 = \pm\sqrt{\frac{2a-k}{8b}} \quad h = \frac{N}{16b}(2a-k)^2 \tag{7}$$

The well depth of the potential landscape of the perovskite scales with the number of unit cells in the system which is equivalent to the number N of atoms in our 1D model. We divide with N when solving for a and b:

$$a = \frac{k}{2} + \frac{h}{X_0^2} \quad b = \frac{h}{4X_0^4} \tag{8}$$

Note that h is now given as the well depth due to the contribution of one unit cell of the perovskite. Because a is in units of J m^{-2} we redefine:

$$k^* = \frac{k}{X_0^2} \tag{9}$$

So for our final potential we have:

$$V = \sum_{i=1}^{N} V_i + V_{i,i-1} = \sum_{i=1}^{N} \frac{k}{X_0^2}(\vec{r}_i - \vec{r}_{ieq})^2 - \frac{k+2h}{4X_0^2}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^2 + \frac{h}{16X_0^2}(|\vec{r}_i - \vec{r}_{i-1}| - d_{eq})^4 \quad (10)$$

If we now set the parameters h and X_0 to be the well depth and the well position respectively, we can make sure that the potential landscape of our model is similar to the one of the perovskite, while also making sure that it exhibits analogous behaviour as the perovskite. We do face a new problem however. By including the on-site harmonic term our potential now includes an extra degree of freedom in the form of parameter k. Our potential has three parameters but we only get enough information from the perovskite potential landscape to set two. Extra information about the perovskite is needed to determine k. We ran out of time to successfully find a method to do this. This problem will be discussed in more detail in section 5. This does mean that for now we can not properly compare the results of our model to properties of $CsPbBr_3$ like we intended. To continue on we will try to make an educated guess for this parameter to still get some results. We will also look at how the phase transition varies with k.

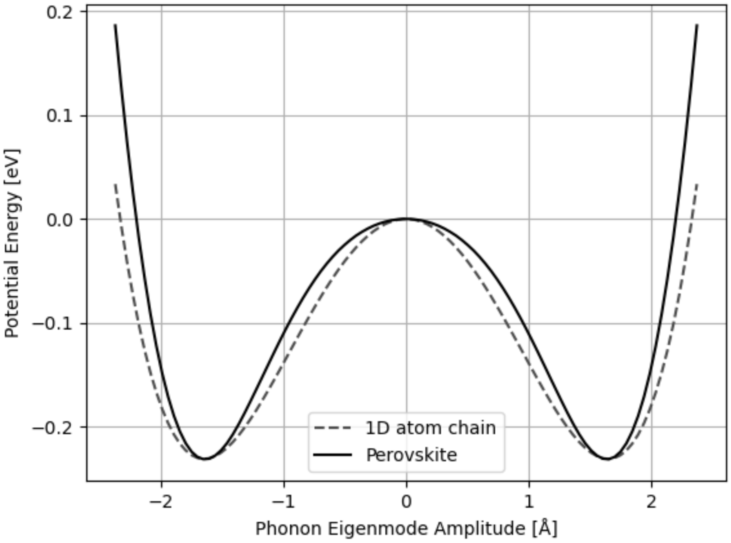


Figure 3: Potential landscape of the R2 phonon mode of $CsPbBr_3$ (black) and its quartic approximation (dashed grey)

Although we cannot derive k from the potential landscape, we can derive an inequality which the parameter should satisfy. That is, if we want the alternating behaviour of the atoms as previously described we should have that k satisfies:

$$k \geq \frac{h}{2} \quad (11)$$

The reasoning is as follows: suppose that there is a single defect in the system. That is, all atoms are alternatingly a distance X_0 right or left of their respective equilibrium positions R_{ieq}, except for one atom. We should have our potential constructed in such a way that the potential energy for this atom is minimized if the atom is in the correct well of its interaction potential. In particular, there should only be one minimum. From this follows that the force on the defective atom is only zero when the atom is at the position for which the energy is the lowest. The force on an atom i is given by the negative gradient of the potential with respect to the coordinates of atom i. Calculating this force for the potential specified in equation (10) we get:

$$\begin{aligned}\vec{F_i} = -\nabla_i V = \vec{f_i} + \sum_{j=i\pm1} \vec{f}_{i,j} = \\ -2\frac{k}{X_0^2}(\vec{r}_i - \vec{r}_{ieq}) - \sum_{j=i\pm1}\left[\frac{k+2h}{2X_0^2}(|\vec{r}_i - \vec{r}_j| - d_{eq}) - \frac{h}{4X_0^4}(|\vec{r}_i - \vec{r}_j| - d_{eq})^3\right]\frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|}\end{aligned} \tag{12}$$

We now study the scenario as described earlier, where the system is in its ground state except for one atom. We track the distance between the position of the atom r_i from its equilibrium position r_{ieq}. From this we get:

$$\vec{r}_i - \vec{r}_{ieq} = Y, \quad |\vec{r}_i - \vec{r}_{i-1}| = d_{eq} + Y - X0, \quad |\vec{r}_i - \vec{r}_{i-1}| = d_{eq} - Y + X0 \tag{13}$$

Plugging (13) in equation (12) we get:

$$\begin{gathered}\vec{F_i} = -\frac{2k}{X_0^2}Y + \frac{k+2h}{X_0^2}(Y - X_0) - \frac{h}{2X_0^4}(Y - X_0)^3 = 0 \\ -hU^3 + 3hU^2 + (h-2k)U - 2k - 3h = 0, \quad U = \frac{Y}{X_0}\end{gathered} \tag{14}$$

we know that one solution lies at $Y = X_0$, or $U = 1$. We obtain:

$$U = 1, -hU^2 + 4hU + -3h - 2k = 0 \tag{15}$$

Because we seek a potential that has only one minimum, we need the quadratic equation in (15) to not have more than one real solution. That is, the discriminant should be less or equal to zero:

$$D = 4h^2 - 8hk \leq 0 \tag{16}$$

From which equation (11) follows. We note that this derivation also works if we were to replace every X_0 with $-X_0$.

3 Methods

To test the model mentioned in the previous section the atoms will be simulated in a MD simulation. For this a standalone python code was written. In a MD simulation the atoms are simulated as classical particles governed by Newton's equation of motion. The force is given by the negative gradient of the potential with respect to the coordinates of an atom:

$$m\frac{\partial^2 \vec{r}_i}{\partial t^2} = -\nabla_i V \tag{17}$$

In our case the potential is specified as in equation (10). Calculating the force on atom i resulting from this potential we get:

$$\begin{aligned}\vec{F}_i = -\nabla_i V = \vec{f}_i + \sum_{j=i\pm1} \vec{f}_{i,j} = \\ -2\frac{k}{X_0^2}(\vec{r}_i - \vec{r}_{ieq}) - \sum_{j=i\pm1}\left[\frac{k+2h}{2X_0^2}(|\vec{r}_i - \vec{r}_j| - d_{eq}) - \frac{h}{4X_0^4}(|\vec{r}_i - \vec{r}_j| - d_{eq})^3\right]\frac{\vec{r}_i - \vec{r}_j}{|\vec{r}_i - \vec{r}_j|}\end{aligned} \tag{18}$$

Note that for the simulation we only need to calculate $f_{i,j}$ for either $j = i+1$ or $j = i-1$. This is because we can make use of the fact that $f_{i,j} = f_{j,i}$.

As is standard in MD simulations, the integration scheme used to integrate (17) is the velocity-Verlet algorithm. This scheme has a discretization error of $O(\Delta t^4)$ and has the property that it conserves the energy of the system [8]. This last property is especially useful if one were to sample in the microcanonical or NVE ensemble, where the number of atoms, the volume and the energy are to be kept constant. The conservation of energy is one of the main reasons this scheme is often used in MD simulations. The scheme is given by:

$$\begin{aligned}\vec{r}_i(t+\Delta t) &= \vec{r}_i(t) + \vec{v}_i(t)\Delta t + \frac{1}{2m}\vec{F}_i(t)\Delta t^2 \\ \vec{v}_i(t+\Delta t) &= \vec{v}_i(t) + \frac{\vec{F}_i(t) + \vec{F}_i(t+\Delta t)}{2m}\Delta t\end{aligned} \tag{19}$$

Instead of the microcanonical ensemble we sample from the canonical ensemble, where the temperature is to be kept constant. To actually keep a constant temperature we need to make use of a thermostat. A thermostat is a method which is implemented in a MD simulation such that it ensures a specific average temperature of the system. This is often done by simulating a coupled heat bath to the system. One of the simplest is the Anderson thermostat, which simulates a collisions with particles from a heat bath by drawing velocities from a Gaussian distribution. This distribution has zero mean and a specific variance which ensures that the mean temperature of the system is as desired. Although the Anderson thermostats is one of the simplest to implement, we will be using the Langevin thermostat [8]. This thermostat remodels Newton's equation of motion:

$$m\frac{\partial^2 \vec{r}_i}{\partial t^2} = -\nabla_i V - \gamma m \vec{v}_i + \sqrt{2m\gamma k_b T}R_i(t) \tag{20}$$

Where γ = a friction coefficient, k_b = the boltzmann constant, T = the specified temperature and $R(t)$ is a random gaussian process satisfying:

$$\langle R(t)\rangle = 0, \quad \langle R_i(t), R_j(t')\rangle = \delta_{i,j}(t-t') \tag{21}$$

That is, $R(t)$ is uncorrelated between particles and time. In equation 20 the added terms are a friction term and a random force. These terms are thought to arise from friction and random collisions from particles in a solvent with a specific temperature. One of the main advantages of this thermostat is that having a damping term in our equation will improve numerical stability [9]. This means that we can choose a larger time step. This is of importance because we need to create a lot of sampling data to get good averages.

As is common in MD simulations, we non-dimensionalize our equations before doing the simulation. This is done by constructing three conversion factors, one each for length, energy and mass. after the simulation is done we can then convert every result back with these factors, specifically we set:

$$\overline{r} = r/\sigma, \quad \overline{E} = E/\epsilon, \quad \overline{m} = m/M, \quad \overline{t} = t/(\sigma\sqrt{M/\epsilon}) \quad \overline{T} = k_B T/\epsilon \tag{22}$$

Where σ, and M are the conversion factors for length, energy and mass respectively. We will set σ to be the lattice constant of the perovskite, ϵ the well depth of the measured potential landscape and M the average mass of the atoms in one unit cell of the perovskite.

We specifically want to find the phase transition temperature T_c. To do this we shall use theory on second order phase transitions. The theory states that we can find a phase transition by looking at discontinuities in the free energy as function of an order parameter. More specifically, we are looking at a change in order in the free energy. Phase transitions can be categorized in second order and first order phase transitions. The difference between these two is that a second order transition transitions continuously, while a first order transition changes abruptly. This can be seen in the order parameter: for a first order phase transition we expect a jump in the order parameter as function of temperature, while for second order transitions we expect a sudden jump in the derivative of the order parameter. The order parameter can take many forms, such as the magnetisation in case of the Ising model. For our model we are searching for a phase transitions where the system behaves more according to the double well potential for lower temperatures than for higher temperatures. That is, the atoms are on average in the wells of their interaction potential for low temperatures, while for high temperatures the atoms are on average at their equilibrium positions. Considering this, a first try for the order parameter could be the probability distribution function of the deviation of atoms from their equilibrium positions. For lower temperatures we then expect two peaks at the positions of the wells signaling a high probability of the atoms residing in the wells of their interaction potential. For higher temperatures we expect a single peak with zero mean. In this case the switch from two peaks to one can be considered a change in order. To find T_c our order parameter will specifically be the positions of the peaks of the probability density function. From second order phase transition theory we expect our order parameter η to follow the relation [10]:

$$\begin{cases} \eta(T) \propto |T - T_c|^c & T < T_c \\ \eta(T) = 0 & T \geq T_c \end{cases} \tag{23}$$

with c being the critical exponent. From experimental data we expect this exponent to be close to 0.25 [11].

Using above mentioned methods we will try to find if our model exhibits a phase transition like we expect and if it does, what the phase transition temperature equals. The temperature we use for our analysis is not the temperature we specify to the Langevin thermostat. Instead, we calculate the mean temperature of our system using the equipartition theorem [12]:

$$\frac{1}{2}k_B T = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{2}mv_i^2 \tag{24}$$

By using the equipartition theorem we can calculate the mean temperature of our system with the average kinetic energy. Similarly we can get an estimate for the error by calculating the variance of the kinetic energy. We also need to make sure that we only sample from the time domain after the system is equilibrated where no major temperature fluctuations occur.

4 Results

We start the with results for the parameters we obtained for the potential by measuring the $CsPbBr_3$ perovskite landscape. These can be found in table 1. These parameters are then used in equation (10) to obtain the potential for the 1D atom chain. We again note that we do not have the means to determine the parameter k, so we will do an educated guess where we take the theoretical minimum allowed value as derived in equation (11):

$$k = \frac{h}{2} \tag{25}$$

determining the parameters for the phonon modes and using these in the simulation we calculate the probability density functions for multiple temperatures. We did this for an atom chain with 10000 atoms, and in dimensionless units, a time step of 0.005 for 10000 time steps. We take the averages from the time domain where the system is equilibrated, which was after 1000 time steps. The results are shown in figure 4. As can be seen for low temperatures we can distinguish two peaks which are positioned near $\pm X_0$. For higher temperatures the peaks begin to merge together to form a single peak. This seems to happen because the peaks broaden for higher temperatures and after a certain point, they overlap with each other such that only one peak can be recognized. The positions of the maxima of the PDF's are plotted for each phonon mode in figure 6. Fitting equation (23) we can obtain the phase transition temperature and the critical exponent. The results for the potential well depth h, well position X_0, transition temperature T_c and critical exponent c for each phonon mode can seen in table 1. We found that the transition temperature only depends on terms with energy, such as the parameter k or the well depth h. Moreover, we find that T_c scales linearly with these terms. This can best be seen when we vary k while keeping h constant and then plotting T_c versus k/h. This is done for the q=R2-mode and the results can be seen in 5.

Phonon mode	h [eV]	$X0$ [Å]	T_c [K]	c
R1, R3	3.74×10^{-2}	1.70	487 ±7	0.39 ±0.02
R2	2.89×10^{-2}	1.65	391 ±7	0.49 ±0.03
M1	3.49×10^{-2}	0.84	456 ±7	0.37 ±0.03

Table 1: The potential well depth h, well position X_0, Transition temperature T_c and critical exponent c for simulation of the 1D atom chain modeled after the q=R1, R2, R3 and M1 phonon modes of $CsPbBr_3$

We have found that our model does exhibit a second order phase transition analogous to the phase transition from a tetragonal to cubic phase in $CsPbBr_3$. We know that the transition is second order because there is no specific discontinuity in the order parameter at T_c, only a discontinuity in its derivative. For $k = h/2$ we also find that the phase transition temperature of the q=R2 mode is close to the value of $T_c = 388 \pm 7$ for the transition temperature of $CsPbBr_3$ found in other studies [3]. If it is supposed that $k = h/2$ is the value for which our model corresponds the most to $CsPbBr_3$, this would mean that the this mode could be responsible for the tetragonal to cubic phase transition in the perovskite. However, as mentioned before, the parameter k is not set in stone and we can not be sure of this. It is also noteworthy that the critical exponents we found deviate quite a bit from the experimentally found value of $c = 0.25$ [11], but this will be further discussed in section 5.

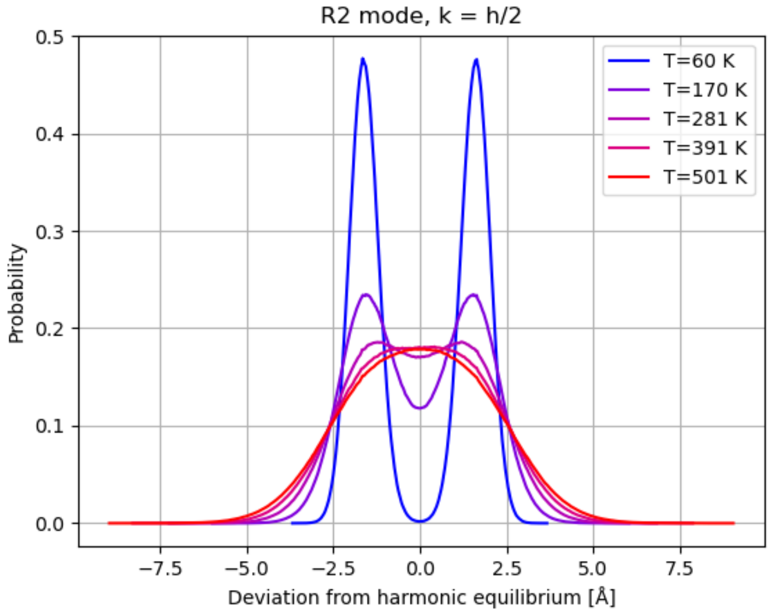


Figure 4: Probability density functions of the deviation of the atoms from their harmonic equilibria. For lower temperatures two peaks can be distinguished, which merge to form a single peak for higher temperatures. The transition temperature is the temperature at which the transition from two to one peaks happens.

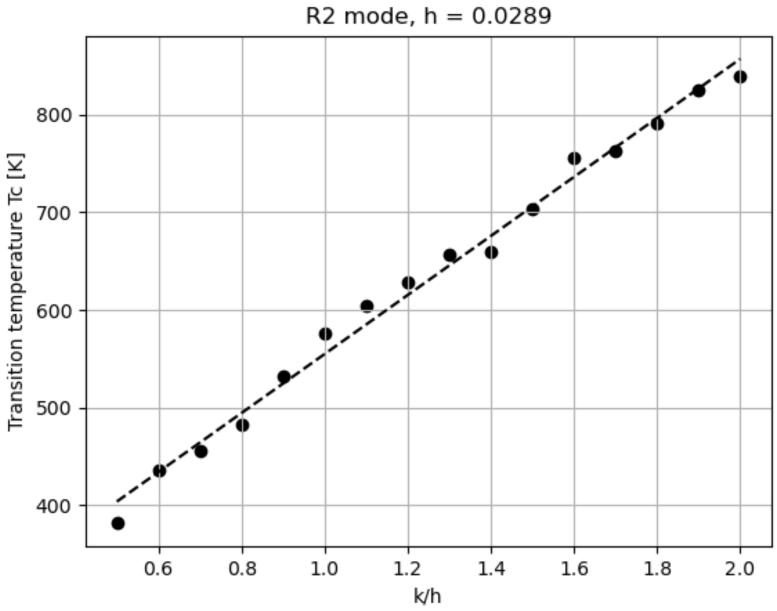
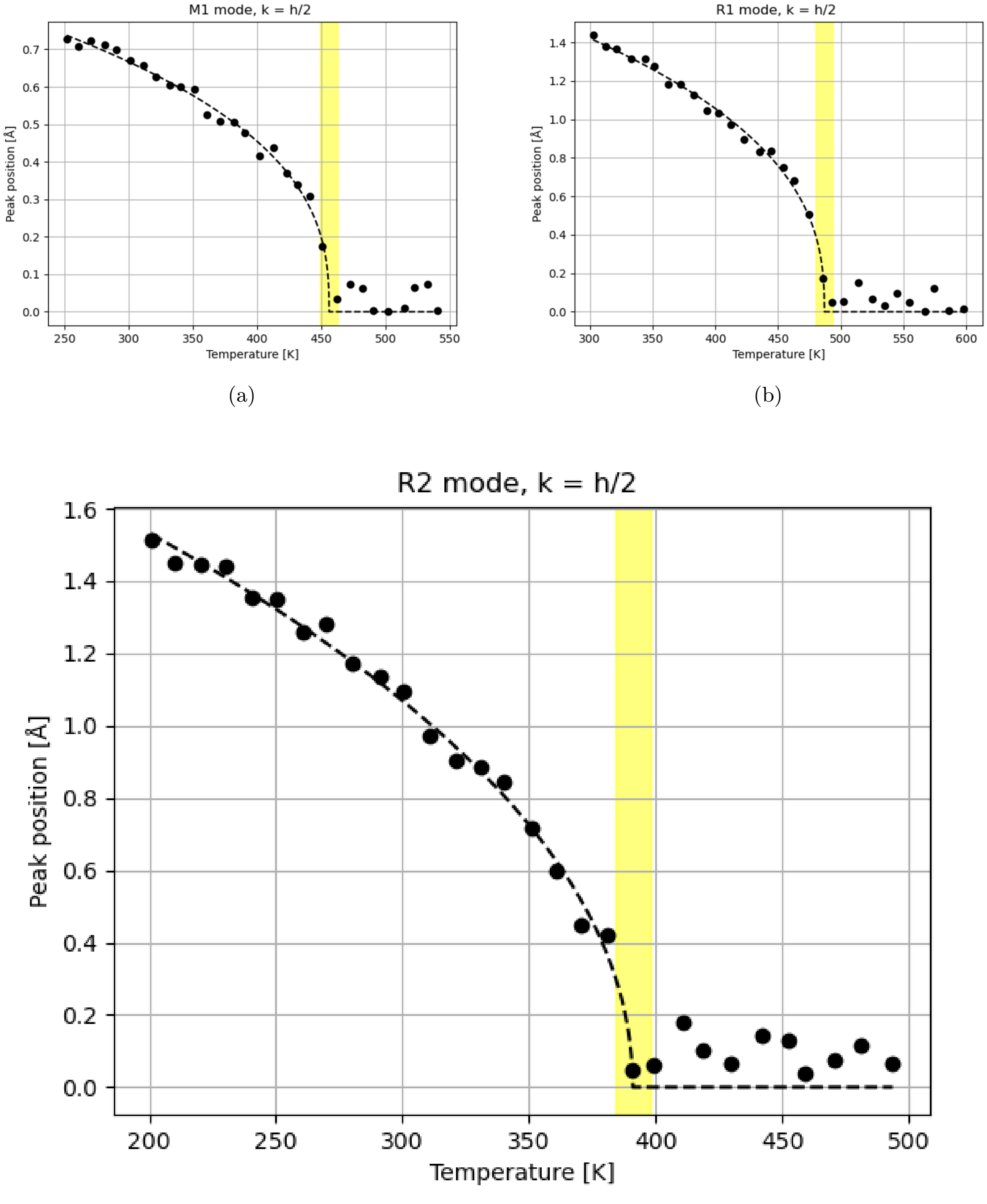


Figure 5: Transition temperature against the on site potential parameter k for the q=R2 phonon mode.



(a)

(b)

(c)

Figure 6: Peak positions of the probability density functions of the deviation of the atoms from their harmonic equilibria against the Temperature. The dotted line is a fit of equation (23). The yellow area indicates the phase transition temperature.

5 Discussion

We would first like to discuss the quartic approximation of the perovskite potential landscape. As can be seen in figure 3, the wells of the perovskite potential landscape are less wide than that of the approximation. Although not proven, we would argue that this does not change the value for the transition temperature in our model. The reason we would argue this is that the energy to overcome the potential hill to go from one well to the other is the same. However, the shape of the potential does affect the shape of the probability density functions shown in 4. To get out of the well of the perovskite potential one has to travel a steeper slope than for the quartic approximation. At lower temperatures this would mean that for our approximated model, the probability density function is wider than what one would expect if the perovskite potential was to be implemented. Furthermore, because the slope at the top of the potential hill is less for the perovskite potential, we would expect the widths of the peaks of the PDF to grow more rapidly if one were to increase the temperature. This could explain the difference between our found critical exponents and the exponent found in experiments $c = 0.25$. If we were to use a potential which resembles the perovskite potential landscape more closely, then we would expect the peak positions to close in on zero less for temperatures far below the transition temperature. For temperatures approaching the transition temperature we expect the peak positions to suddenly close in on zero more rapidly. This would be equivalent to a lower critical exponent in equation (23). To test if this theory is correct we would propose that in future research one could use a potential which resembles the perovskite potential more closely. This could be done by adding higher order polynomial terms for example.

Another reason for the deviation of our critical exponent could simply be that the critical exponent is different for a one dimensional system. This is the case for multiple other models and order parameters, such as the Ising model. Similarly, in our model we only study one particular phonon mode of the perovskite $CsPbBr_3$, while the experimental data is obtained by measuring on the perovskite $MAPbI_3$. Not only are these perovskites different from each other, which could potentially lead to different critical exponents, but the measurement was also done on the perovskite instead of just one phonon mode of a perovskite, which could also lead to different results. Because the real system is a collection of many interacting phonon modes we would not necessarily expect the results of our model to coincide with real measurements of a perovskite.

As discussed before, our model did exhibit a phase transition analogous to the phase transition of the tetragonal to cubic phase of $CsPbBr_3$. For $k = h/2$ and for the q=R2 mode the temperature at which this occurred is similar to the the expected value for the transition temperature of $CsPbBr_3$ of 388 ± 7 [3]. As mentioned before however, we would not necessarily expect the results of our model and a complete perovskite to be similar. The fact that the results are similar could then be explained in multiple ways. One explanation would be that the phonon mode for which the data was similar is a "dominant" phonon mode. That is to say, the q=R2-mode is mostly responsible for the phase transition in $CsPbBr_3$. This does seem unlikely however, as this can only be correctly concluded if we assume that our model is correct, but as previously mentioned, our system is as of yet incomplete because of the unspecified parameter k. It seems more likely that we just had a lucky guess for this parameter.

The guess for parameter k had to be made because our model described in equation (10) has three parameters of which we are only able to determine two. To determine all three parameters we would need extra information about the phonon mode of the perovskite we are interested in. We did not have the time to look for a way to find this extra bit of information. If one were to research the model further we would argue that this would be the first thing one should look at. Furthermore, we would propose that a possible method is by looking at other properties such as the power spectral density of the velocities of the atoms and to compare this to the phonon mode of the perovskite. Another possibility to get extra information about the system is by calculating the potential landscape of the perovskite as discussed in section 2, but for a different kind of movement. This can then possibly be compared to an analogous movement of the one dimensional model to obtain k. What this movement should exactly be is up for debate however. For example we could try to explore the situation where the system is equilibrated except for one atom as discussed in section 2. We would argue that the corresponding movement in the perovskite of which we should measure the potential landscape is to rotate just one of the octahedra in the perovskite, but proper analysis has to be done to see if this actually holds true.

One could also look if a different potential can be constructed such that we still have a similar potential landscape and similar behaviour of the system but such that the potential is only specified by two parameters. We would argue that obtaining the correct behaviour of the atoms in the 1D chain could be achieved by satisfying two criteria. The first being that the potential landscape of the system and the perovskite should be similar and the second being that if the system is equilibrated except for one atom, the interaction potential for this atom should only have one minimum as discussed in section 2. We have shown how our model achieves these criteria, but it could be possible that there are multiple other model which could achieve them as well. If such a model were only to have two parameters it should be possible to compare results of the model to properties of a perovskite, something we were not able to do.

Because of these issues we note that until further research is done, our model is to be used as a toy model. This means that for now the specific results of our research should not be used for any real system, however as we have shown, our system can replicate phase transitions in a similar manner to phase transitions from a perovskite. With further research the model could be expanded or similar models could be constructed which could lead to a better understanding of phase transitions in perovskites and the roles certain phonon modes play in these transitions.

6 Conclusion

We have constructed a simplified model which exhibits phase transitions analogous to the transition from a tetragonal to cubic phase of $CsPbBr_3$. Because we have not found a way to couple the on site potential term k for our potential to the phonon modes of the perovskite, we can not compare our results directly to the properties of $CsPbBr_3$. We have found that for $k = h/2$ the transition temperature of our model for the q=R2 phonon mode is closest to the value for the perovskite [3], but as of now we can not be certain of this being simply a coincedence or not, because of the previously mentioned unspecified parameter k. The critical exponents found for the different phonon modes are slightly higher than the expected value of $c = 0.25$ [11], but this could be attributed to the quartic approximation made of the potential landscape of the perovskite, or that the dimensions of the systems are different and the fact that in a real perovskite we are dealing with many interacting phonon modes as opposed to just a single phonon mode in our simplified model. We conclude that the model is to be used as a toy model. It could help to lead to a better understanding of phase transitions, but we note that a direct link from the results of our model to an actual perovskite should not be drawn as of yet. Further research should be done to conclude if the model can be actually applied to a perovskite.

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