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Numerical Methods in Physics

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Phonons in rare gases

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Code directory `/home/jaer0031/Desktop/lab2-phonons/code`

Abstract

It is known that in rare gas crystals such as Ne, Ar Kr, Xe, atoms are arranged in a fcc lattice where pair of atoms interact according to Lie-Lennard-Jones potential. By making use of harmonic approximation and considering interaction only from closest neighbours, the eigensystem for phonon frequencies and polarisations are constructed from Newton's equation. With symmetric bidiagonalization and QR reduction, dispersion relations are calculated and plotted in symmetry directions as well as Gruneisen parameters. Eventually the heat capacity according to statistical mechanics is calculated with results checked in large and small temperature limit by Petit-Dulong and Debye model. Gruneisen parameters are calculated with finite difference approximations and the heat capacity with trapezoidal rule.

Contents

1	Introduction	2
2	Theory	3
2.1	Newton's equation's of motion	3
2.2	Brillouin zone	4
2.3	Plane wave solutions for fcc lattice	6
2.4	Disperssion relation	7
2.5	Gruneisen parameter	9
2.6	The heat capacity	9
2.7	Analytical estimation of the heat capacity	11
3	Code	11
3.1	Algorithm design	12
3.2	System description	12
4	Results	15
5	Conclusions	17

1 Introduction

When atoms are in solid state they are arranged with periodic structure which depends on electronic configuration of atoms and are the basis for different solid properties such as speed of sound, thermal expansion and heat capacity.

Each atom in the crystal interacts with others in a way that crystal has the smallest internal potential energy¹ when all atoms are on perfect crystal lattice. Then deviation from equilibrium position gives rise to returning force so internal energy in the crystal is stored in the oscillations. Furthermore since the returning force also depends on the configuration of other atoms then these oscillations are coupled giving rise to propagation of waves.

By assuming that return force mainly is governed by neighbour's atom electric pair interaction, then for a small oscillations one can show that waves are given as plane wave solutions (the factor $e^{i(\mathbf{k}\mathbf{r}-\omega\mathbf{t})}$) [2]. For or each wavevector \mathbf{k} the Newton's equation of motion gives three directions of oscillations and corresponding frequencies which we call normal modes.

By imposing that each mode can store only discrete sets of energies $E = (n + 1/2)\hbar\omega$ (resulting in discrete set of amplitudes) and assuming that the phonons (energy quanta) satisfy Bose-Einstein statistics then we can calculate the vibrational energy of the system for unit volume with [2]:

$$U_{vibr}(T) = \sum_{\mathbf{k},j} \left[\frac{\hbar\omega_j(\mathbf{k})}{e^{\hbar\omega_j(\mathbf{k})/k_B T} - 1} + \frac{1}{2}\hbar\omega_j(\mathbf{k}) \right] \quad (1)$$

where the summation for wavevectors \mathbf{k} is the first Brillouin zone. The specific heat capacity then comes as:

$$c_V = \frac{\partial U_{vibr}}{\partial T} = k_B \sum_{\mathbf{k},j} \frac{\hbar\omega_j(\mathbf{k})}{k_B T} \frac{1}{4 \sinh^2 \left[\frac{\hbar\omega_j(\mathbf{k})}{2k_B T} \right]} \quad (2)$$

so if we know the Brillion zone for crystal, and the dispersion relation for all points in this zone then we can theoretically predict heat capacity for different temperatures.

Also we can ask how much does the dispersion relations depend on pressure or by thermal expansion which affects lattice constant. The volume

¹Similar as with unstressed springs

dependance of the phonon frequencies are described with Gruneisen parameter deffined as:

$$\gamma_j(\mathbf{k}) = -\frac{\ln \omega_j(\mathbf{k})}{\partial \ln V} \quad (3)$$

To show it's physical meaning we *take out logarithm* and use finite difference approximation so we obtain:

$$\gamma_j(\mathbf{k}) \approx -\frac{\Delta\omega/\omega}{\Delta V/V} \quad (4)$$

where we see that it just shows how much releativly increases the frequency $\Delta\omega/\omega$ if we releativly increase the volume of crystal $\Delta V/V$, where the minus sign stands because the phonon frequencies decreases(increases) by increasing(decreasing) volume of the crystal.

In this repport I am considering how to calculate these properties for solid state of rare gases such as *Ne, Ar, Kr, Xe* which in the crystal forms face centred cubic lattice. Also it is known that between rare gase atoms pair interaction is given as Mie-Lennard-Jonnes potential:

$$\phi(r) = 2\epsilon \left[\frac{1}{2} \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (5)$$

where σ, ϵ are rare gas parameters which are given in table 1.

With this knowledge Newton's equations are written in the next section and ansatz of plane wave solutions applied which gives us eigenvalue (corresponding phonon frequency) and eigenvector (direction of oscilation) problem. To solve it standart nummerical method from GSL will be used. By ussing finite difference approximation for the derivative the Gruneisen parameter will be calculated. But to obtain heat capacity tabulated Brillion zone is going to be used to integrate the function nummerically.

2 Theory

2.1 Newton's equation's of motion

Considering only small oscillations for atom nucleus we can use the harmonic approximation which according to [2] Newton's equations in following form:

$$m\ddot{u}_\alpha^l = - \sum_{l'\beta} D_{\alpha\beta}^{ll'} u_\beta^{l'} \quad (6)$$

where D is dynamical matrix and it's expression given as:

$$D_{\alpha\beta}^{\mathbf{l}\mathbf{l}'} = \delta_{\mathbf{l}\mathbf{l}'} \sum_{\mathbf{l}''} \frac{\partial^2 \phi(\mathbf{l} - \mathbf{l}'')}{\partial x_\alpha \partial x_\beta} - \frac{\partial^2 \phi(\mathbf{l} - \mathbf{l}')}{\partial x_\alpha \partial x_\beta} \quad (7)$$

with potential ϕ where (5) will be used. Since Mie-Lennard-Jones potential decays fast or as $\propto r^{-6}$ then we are safe to say that nearest neighbour interactions are at least by $2^6 = 64$ larger than other atom interactions and that only nearest neighbour interactions are relevant to describe the oscillations in crystal.

For convince we introduce a following parameters:

$$B \stackrel{def}{=} \frac{1}{r_{nn}} \phi'(r_{nn}) = \frac{12\epsilon}{\sigma r_{nn}} \left[\left(\frac{\sigma}{r_{nn}} \right)^7 - \left(\frac{\sigma}{r_{nn}} \right)^{13} \right] \quad (8)$$

$$A \stackrel{def}{=} \phi''(r_{nn}) = \frac{12\epsilon}{\sigma^2} \left[13 \left(\frac{\sigma}{r_{nn}} \right)^{15} - 7 \left(\frac{\sigma}{r_{nn}} \right)^8 \right] \quad (9)$$

where r_{nn} is distance between two nearest neighbours at their equilibrium position. For fcc lattice that allows to rewrite equation's (7) second order derivatives as:

$$\frac{\partial^2 \phi(\mathbf{l} - \mathbf{l}'')}{\partial x_\alpha \partial x_\beta} = \frac{x_\alpha x_\beta}{x_1^2 + x_2^2 + x_3^2} [A - B] + \delta_{\alpha\beta} B \quad (10)$$

2.2 Brillouin zone

Consider one atom at center position or $\mathbf{l} = (000)$ and that atom at center interacts with it's closest neighbours. We would have defined equation of motion for center atom $\mathbf{u}^{(000)}$ if we would now the movement of neighbours so oscillations propagates as waves. Because of periodic arrangement of crystal atoms there are only certain allowed waves. We assume that these waves can be decomposed to Fourier components (plane wave solutions):

$$\mathbf{u}^{\mathbf{l}} = \mathbf{u}(\mathbf{k}, \mathbf{r}_1) = \frac{\epsilon}{\sqrt{m}} e^{i(\mathbf{k} \cdot \mathbf{r}_1 - \omega t)} \quad (11)$$

where \mathbf{r}_1 is equilibrium position for atom.

As usual periodic boundary conditions for deviations in the crystal are used:

$$\mathbf{u}(\mathbf{k}, \mathbf{r}_1) = \mathbf{u}(\mathbf{r}_1 + N_i \mathbf{t}_i, \mathbf{k}) \quad (12)$$

The plane wave solution ansatz from this condition then gives:

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{g}_1 + \frac{m_2}{N_2} \mathbf{g}_2 + \frac{m_3}{N_3} \mathbf{g}_3 \quad (13)$$

where m_i are integers and $\mathbf{g}_i \mathbf{r}_j = 2\pi \delta_{ij}$. Now we see that any wave in crystal can be expressed with its fundamental components in following way (or as Fourier transform):

$$\mathbf{U}(\mathbf{r}_1) = \sum_{\mathbf{k}} \mathbf{u}_0(\mathbf{k}) e^{i\mathbf{r}_1 \mathbf{k}} \quad (14)$$

where summation is for all allowed wavevectors \mathbf{k} given by . We can rewrite the sum in the following way because of periodicity of exponent:

$$\mathbf{U}(\mathbf{r}_1) = \sum_{\mathbf{k}}^{B.Z.} \left(\sum_{\mathbf{g}_n} \mathbf{u}_0(\mathbf{k} + \mathbf{g}_n) \right) e^{i\mathbf{r}_1 \mathbf{k}} \quad (15)$$

where we see that we can restrict the \mathbf{k} to be in the Brillion deffined with (13) where $-N_1/2 < m_1 < N_1$. For fcc lattice the Brillion zone is shown in figure 1.

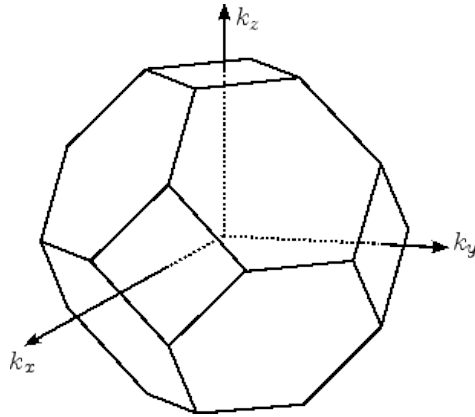


Figure 1: The Brillouin zone for fcc lattice [3].

2.3 Plane wave solutions for fcc lattice

When one puts the plane wave ansatz (11) in Newton's equation (6) a following expression is obtained:

$$\begin{aligned}
\omega^2 \epsilon_x = & \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(k_x a) \cos(k_y a) - 4 \cos(k_x a) \cos(k_z a)] \right. \\
& + \frac{B}{m} [4 - 4 \cos(k_y a) \cos(k_z a)] \left. \right\} \epsilon_x \\
& + \frac{1}{2m} [A - B] [(4 \sin(k_x a)) \sin(k_y a)] \epsilon_y \\
& + \frac{1}{2m} [A - B] [4 \sin(k_x a) \sin(k_z a)] \epsilon_z
\end{aligned} \tag{16}$$

where $\mathbf{r}_1 = \mathbf{a}\mathbf{l}$ and $2a$ corresponds to the length of a side in the conventional unit cell which for fcc lattice can be expressed from distance of two nearest neighbours r_{nn} as:

$$r_{nn} = \sqrt{2}a \tag{17}$$

To obtain similar equations for other components we can observe that Brillouin zone (in figure 1) as well as crystal looks the same for x , y , z directions. For example let's consider way of constructing equation for ϵ_y , from ϵ_x . If we look at the crystal from y direction then new z axis corresponds to y but new x axis to z direction. The transformations for which equations are covariant are given as permutations:

$$\begin{array}{lll}
x \rightarrow y & y \rightarrow z & z \rightarrow x
\end{array} \tag{18}$$

$$\begin{array}{lll}
x \rightarrow z & y \rightarrow x & z \rightarrow y
\end{array} \tag{19}$$

The corresponding equations explicitly then:

$$\begin{aligned}
\omega^2 \epsilon_y &= \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(k_y a) \cos(k_z a) - 4 \cos(k_y a) \cos(k_x a)] \right. \\
&\quad + \frac{B}{m} [4 - 4 \cos(k_z a) \cos(k_x a)] \left. \right\} \epsilon_y \\
&\quad + \frac{1}{2m} [A - B] [(4 \sin(k_y a)) \sin(k_z a)] \epsilon_z + \frac{1}{2m} [A - B] [4 \sin(k_y a) \sin(k_x a)] \epsilon_x \\
\omega^2 \epsilon_z &= \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(k_z a) \cos(k_x a) - 4 \cos(k_z a) \cos(k_y a)] \right. \\
&\quad + \frac{B}{m} [4 - 4 \cos(k_x a) \cos(k_y a)] \left. \right\} \epsilon_z \\
&\quad + \frac{1}{2m} [A - B] [(4 \sin(k_z a)) \sin(k_x a)] \epsilon_x + \frac{1}{2m} [A - B] [4 \sin(k_z a) \sin(k_y a)] \epsilon_y
\end{aligned} \tag{20}$$

We can rewrite equations above in matrix form:

$$\mathbf{D} \epsilon = \omega^2 \epsilon \tag{21}$$

where the matrix $\mathbf{D} = \mathbf{D}(\mathbf{k})$ is called dynamical matrix, but $\omega_\alpha(\mathbf{k})$ normal mode (phonon) frequencies for each direction of oscillation $\epsilon_\alpha(\mathbf{k})$ if wave vector \mathbf{k} . So we see that in order to obtain phonon frequencies one needs to compute dynamical matrix $D(\mathbf{k})$ for specific \mathbf{k} and crystal parameters A, B, m, r_{nn}, a and then solve the eigenvalue problem for $\omega^2(\mathbf{k})$ which would give necessary modes.

2.4 Dispersion relation

To further simplify the equations we introduce dimensionless wavevector variable as:

$$\mathbf{k} = \mathbf{q}\pi/a \tag{22}$$

which makes Brillouin zone unchanged when crystal parameter r_{nn} is changed. Also this variable is reciprocal variable to \mathbf{l} because $\mathbf{l}\mathbf{q} = \mathbf{r}_1\mathbf{k}$. The substitu-

	Ne	Ar	Kr	Xe
$\sigma(A)$	3.035	3.709	3.966	4.318
$\epsilon(10^{-20}J)$	0.0721	0.236	0.325	0.458
$r_{nn}(A)$	3.1562	3.7477	3.9922	4.3346
$m(10^{-25}kg)$	0.335092	0.66335	1.3915	2.18017

Table 1: The parameters for rare gas crystals [1]

tion it in the dynamical matrix $D = D(\mathbf{k}) = D(\mathbf{k})$ results in:

$$\begin{aligned}
\omega^2 \epsilon_x &= \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(q_x \pi) \cos(k_y a) - 4 \cos(q_x \pi) \cos(q_z \pi)] \right. \\
&\quad + \frac{B}{m} [4 - 4 \cos(q_y \pi) \cos(q_z \pi)] \left. \right\} \epsilon_x \\
&\quad + \frac{1}{2m} [A - B] [(4 \sin(q_x \pi)) \sin(q_y \pi)] \epsilon_y + \frac{1}{2m} [A - B] [4 \sin(q_x \pi) \sin(q_z \pi)] \epsilon_z \\
\omega^2 \epsilon_y &= \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(q_y \pi) \cos(q_z \pi) - 4 \cos(q_y \pi) \cos(q_x \pi)] \right. \\
&\quad + \frac{B}{m} [4 - 4 \cos(q_z \pi) \cos(q_x \pi)] \left. \right\} \epsilon_y \\
&\quad + \frac{1}{2m} [A - B] [(4 \sin(q_y \pi)) \sin(q_z \pi)] \epsilon_z + \frac{1}{2m} [A - B] [4 \sin(q_y \pi) \sin(q_x \pi)] \epsilon_x \\
\omega^2 \epsilon_z &= \left\{ \frac{1}{2m} [A + B] [8 - 4 \cos(q_z \pi) \cos(q_x \pi) - 4 \cos(q_z \pi) \cos(q_y \pi)] \right. \\
&\quad + \frac{B}{m} [4 - 4 \cos(q_x \pi) \cos(q_y \pi)] \left. \right\} \epsilon_z \\
&\quad + \frac{1}{2m} [A - B] [(4 \sin(q_z \pi)) \sin(q_x \pi)] \epsilon_x + \frac{1}{2m} [A - B] [4 \sin(q_z \pi) \sin(q_y \pi)] \epsilon_y
\end{aligned} \tag{23}$$

Solving the eigenproblem for a vector \mathbf{q} gives us three eigenvalues for $\omega^2(\mathbf{q})$. If eigenvalue is positive then it corresponds to phonon frequency on the other hand if it is negative then the oscillations in the corresponding direction decays exponentially with time so it is reasonable for calculation of dispersion relation to set it then $\omega^2(\mathbf{q}) = 0$.

To get the dispersion relations for specific rare gas atoms we need to specify the parameters which are in (5) and the mass of atom m which are given in table 1.

2.5 Gruneisen parameter

The volume of crystal element can be calculated as:

$$V = a^3 = 2^{3/2} r_{nn} \quad (24)$$

so the Gruneisen parameter in (3) after applying chain rule becomes:

$$\gamma_j(\mathbf{q}) = -\frac{r_{nn}}{3\omega_j(\mathbf{q})} \frac{\partial \omega_j(\mathbf{q})}{\partial r_{nn}} \quad (25)$$

Nummerically I use finite difference approximation for the derivative so it becomes (keeping in mind the dependance on (j, \mathbf{q})):

$$\gamma \approx -\frac{r_{nn}}{3\omega(r_{nn})} \frac{\omega(r_{nn} + h) - \omega(r_{nn} - h)}{2h} \quad (26)$$

where $\omega(r_{nn})$ in the calculation I approximate as²:

$$\omega(r_{nn}) = \frac{\omega(r_{nn} + h) + \omega(r_{nn} - h)}{2} \quad (27)$$

2.6 The heat capacity

To calculate the heat capacity which is defined in (2) we firstly consider macroscopically large crystal so discrete \mathbf{k} vectors lie closely spaced and we can use:

$$\sum_{\mathbf{k}} \rightarrow \frac{V}{(2\pi)^3} \int d\mathbf{k} \quad (28)$$

which gives:

$$\frac{C_V}{V} = \frac{1}{(2\pi)^2} \int d\mathbf{k} k_B \left[\frac{\hbar \omega_j(\mathbf{k})}{k_B T} \right]^2 \frac{1}{4 \sinh^2 \left[\frac{\hbar \omega_j(\mathbf{k})}{2k_B T} \right]} \stackrel{def}{=} \frac{1}{(2\pi)^3} \int d\mathbf{k} f_j(\mathbf{q}(\mathbf{k})) \quad (29)$$

where the integration is for first Brillouin zone. Since the equations of motion was written applying the symmetry of the Brillouin zone then we expect that that the same symmetry holds with calculated parameters ω .

²For finite differences used above the error decreases as $O(h^2)$ and also the error for quantity below is with $O(h^2)$ which we see after doing Taylor expansion

For example we see from the dynamical matrix (23) that the $\det(\omega^2 I - D(\mathbf{q}))$ remains unchanged with given ω under following transformations:

$$\mathbf{q} \rightarrow -\mathbf{q} \quad (30)$$

$$q_x \rightarrow q_y \quad q_y \rightarrow q_z \quad q_z \rightarrow q_x \quad (31)$$

$$q_x \rightarrow q_z \quad q_y \rightarrow q_x \quad q_z \rightarrow q_y \quad (32)$$

where the inversion holds because of even functions in dynamical matrix. The other two transformations holds because the determinant is invariant under permutations of rows, also the $\omega^2 I$ is invariant under permutations therefore the $\det(\omega^2 I - D(\mathbf{q}))$ is invariant under row permutations of matrix $D(\mathbf{q})$. Since we obtain permuted dynamical matrix $D(\mathbf{q})$ with the last two transformations above then we have shown that $\omega^2(\mathbf{q})$ is invariant under these given transformations. In similar way one can show that determinant remains invariant to 48 transformations (including identity) [3] only 1/48 part of Brillouin zone is interesting which is shown in figure:

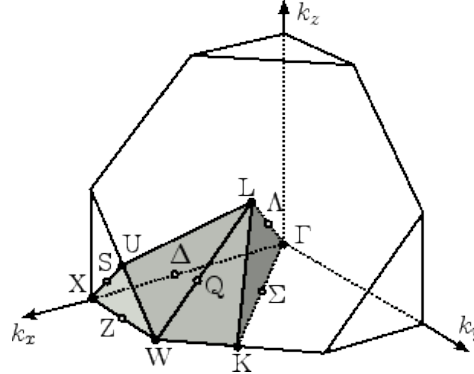


Figure 2: The interesting part of Brillouin zone from which with symmetry operations one gets back full Brillouin zone for fcc lattice [3].

In order to do the integral numerically we discretize it with $\Delta \mathbf{k}$ small enough to account the variations of integrated function $f_j(\mathbf{q})$. We use already tabulated 1/48 part of Brillouin zone from file `qv.txt` where $\Delta q = \frac{4}{1000}$ so $\Delta \mathbf{k} = \frac{4}{1000} \left(\frac{\pi}{a}\right)^3$. To account the boundary terms properly³ and that we

³Similarly as in one dimensional trapezoidal rule we set boundary value weights equal to 1/2

are only integrating 1/48 part of Brillion zone then the heat capacity is callculated nummerically as follows:

$$\frac{C_V}{V} = \frac{1}{(2\pi)^3} \frac{4}{1000} \left(\frac{\pi}{a}\right)^3 \sum_{\mathbf{q},j} W(\mathbf{q}) f_j(\mathbf{q}) \quad (33)$$

where $W(\mathbf{q})$ are weights.

2.7 Analytical estimation of the heat capacity

According to [2] the Einstein model replaces all different phonon frequencies by average frequency ω_e . If we denote by N_a the number of atoms and put the average frequency in the expression (2) then for large temperatures we would get:

$$C_V = 3N_a k_B T \quad k_B T \gg \hbar \omega_e \quad (34)$$

which is Dulong and Petit value. The number of atoms for fcc lattice are four times more than number of cells $N_a = 4N$ since each cell is made by 4 basis atoms. The volume for each cell is given as $(2a)^3$ so the number of cells is $N = V/(2a)^3$. Using this relation and that $r_{nn} = \sqrt{2}a$ we can express specific heat capacity as:

$$\frac{C_V}{V} = \frac{3 \cdot 5 k_B}{2\sqrt{2} r_{nn}^3} \quad (35)$$

The Debye model [2] is however more realistic and gives also heat capacity for low temperatures:

$$C_V(T) = \frac{12}{5} \pi^4 N k_B \frac{T^3}{T_D^3} \quad (36)$$

The message from expression above is that the heat capacity should be proportional to T^3 for small enough temperatures.

3 Code

The program's source code directory is:

`/home/jaer0031/Desktop/lab2-phonons/code`

which includes three files `phonons.c`, `frequencies.c` and `Makefile`. For compiling the source to the binary called `phonons` execute `make` from the source directory.

The program utilises GSL library to solve the eigensystem by symmetric bidiagonalization and QR reduction with functions `gsl_eigen_symm` and `gsl_eigen_symmv` [4].

3.1 Algorithm design

Starting from arbitrary input in the command line program firstly tries to parse it to the defined variables in `main`. After that program switches to the calculation depending on value of value of subcommand.

If the subcommand has value `omega` then frequency calculation starts. Firstly the calculation of parameters A and B are performed according to (8) which defines the eigensystem (23). To calculate the eigenvalues of it GSL functions `gsl_eigen_symmv` or `gsl_eigen_symm` are used depending on if eigenvectors are needed. After the eigenvalues are calculated they are sorted with `gsl_eigen_symmv_sort` and printed out to `stdout`.

On the other hand if subcommand has a value `gamma` then two sets of frequencies are computed with $r_{nn} \rightarrow r_{nn} \pm h$ the same way as above only eigenvalues are stored in arrays. Then applying (26) Gruneisen parameters are calculated and printed out to `stdout`.

And eventually if subcommand has a value `cv` then heat capacity calculation is started. Firstly the tabulated Brillouin zone is extracted from the file `qvekt`. Then for each wavevector \mathbf{q} frequency calculation is performed as above and eigenvalues stored. With application of (33) then heat capacity temperature dependance can be efficiently calculated and printed out to `stdout`.

3.2 System description

```
void frequencies(double A, double B,
                double m, double *q, double *omega, double *eps)
type function
input the mass of atom  $m$ , dimensionless wavevector  $\mathbf{q}$ , and constants  $A, B$ 
        defined in (8)
output phonon frequencies  $\omega_i$  and corresponding polarisations  $\epsilon_{ij} = eps[j +$ 
         $3i]$ 
```

purpose Solve eigensystem (23)

```
void calculate_AB(double sigma, double eps, double rnn,
    double *A, double *B)
```

type function

input parameters of Mie-Lennard-Jonnes potential (5)

output parameters defined in (8)

purpose intermediate calculation before the **frequencies** function is used

```
void gas_parameters(char * substance,
    double *sigma, double *eps, double *rnn, double *m)
```

type function

input name of the substance for example Ne, Ar, Xe, Kr

output the rare gas parameters

purpose be a dictionary for table 1

```
void read_cv(int argc, char *argv[], double *T1, double *T2, int *npoints)
```

type function

input unprocessed command line arguments

output temperature interval and number of points. If only temperature have been passed then **npoints=1**

purpose input error handling and interpretation

```
void read_qs(int argc, char *argv[],
    double *qx1, double *qy1, double *qz1,
    double *qx2, double *qy2, double *qz2, int *npoints)
```

type function

input unprocessed command line arguments

output wavevector interval and number of points. If only one wavevector have been passed then **npoints=1**

purpose input error handling and interpretation

```
void calculate_gammas(double sigma, double eps, double rnn,
    double m, double *q, double *gamma)
```

type function

input rare gas parameters σ , ϵ , r_{nn} , m and wavevector \mathbf{q}

output Gruinesen parameters γ_j from equation (26)

purpose calculate Gruneisen parameters

void read_qvekt(double *q,double *W, int *N)
type function
input file with name **qvekt** in programm execution directory
output W_j and $q_{ij} = q[i + 3j]$
purpose read Brillouin zone file

void calculate_omegas(double A, double B, double m,
 double *q_arr,double *omega_arr, int N)
type function
input gas parameters A , B , m and wavevectors $q_{ij} = q[i + 3j]$
output for each wavevector q_i returns $\omega_{ij} = \omega[i + 3j]$
purpose calculates phonon frequencies for an array by using **frquency** function

double cv(double T, double rnn,double *omega_arr, double *W, int N)
type function
input Temperature T , distance between neighbours r_{nn} , calculated frequencies $\omega_{ij} = \omega[i + 3j]$ and weights W_j .
output specific heat capacity c_v
purpose calculates heat capacity with formula (33)

phonons (substance) omega q_x1 q_y1 q_z1 [q_x2 q_y2 q_z2 [npoints]]
type program subcommand
input substance **Ne**, **Ar**, **Kr**, **Xe** and wavevector interval or single wavector
output calculated frequencies for each wavevector in the form $q_x q_y q_z \omega_1 \omega_2 \omega_3$ at **stdout**
purpose calculate the dispersion curves, for example for figure 3

phonons (substance) gamma q_x1 q_y1 q_z1 [q_x2 q_y2 q_z2 [npoints]]
type program subcommand
input substance **Ne**, **Ar**, **Kr**, **Xe** and wavevector interval or single wavector
output calculated Gruneisen parameters for each wavevector in the form $q_x q_y q_z \gamma_1 \gamma_2 \gamma_3$ at **stdout**
purpose calculate the Gruneisen parameters, for example for figure 6

phonons (substance) T_1 [T_2 [npoints]]
type program subcommand
input substance **Ne**, **Ar**, **Kr**, **Xe** and temperature interval or single temperature
output calculated specific heat capacities in form $T c_V$ at **stdout**
purpose calculates heat capacities for example for figure 4 and figure 5

4 Results

By the slow neutron scattering it is possible to measure the dispersion relations to the main symmetry directions [6]. That allows us to check with experiment if the used approximations for specific heat model aren't too rough. Since we expect that all fcc lattices share the same qualitative behaviour then qualitative agreement for *Ne* calculated in here with Al [2] and Cu [5] dispersion relations supports our used physical assumptions - harmonic and local interaction approximations. Specifically for *Ne* the dispersion relation is shown in 3, where for 100 and 111 lower branches are degenerate and corresponds to transverse polarisations since the Brillouin zone in figure 1 in these directions remains unchanged by rotation of $\pi/2$. Another expected behaviour is that for endpoints of 100 and 110 calculated frequencies coincide since these points has the same relation to Brillouin zone elements shown in figure 2. In similar way since Brillouin zone is symmetric to reflection for plane 111 then the same symmetry should be found on dispersion relations which indeed are there.

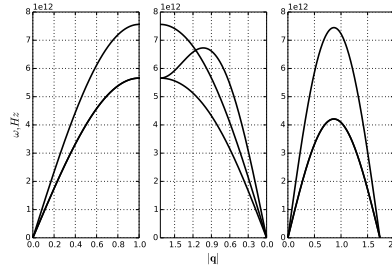


Figure 3: Calculated dispersion relation for *Ne* in three symmetry directions starting from the left 100, 110, 111. The lower branches for 100 and 111 are degenerate, which from rotational symmetry of the Brillouin zone corresponds to transverse polarisations. The qualitative agreement is also apparent with [5] where Cu parameters are determined

The calculation (2) for specific heat capacities gives temperature dependence shown in figure 4. In order to see if the calculation is done correctly we firstly compare the classical limit value of heat capacity (35) with numerical calculation shown in table 2 where we see good agreement. Since for small values of \mathbf{q} dispersion relation in any direction has a good linear approximation (for example for *Ne* in figure 3) then for small temperatures

we are able to use Debye model which gives $\propto T^3$ dependance as in (36). Comparison with numerics in figure 5 gives good agreement until turning point again supporting implementation of (2).

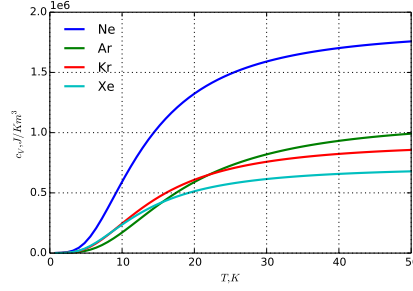


Figure 4: Heat capacity temperature dependance for different kinds of rare gas solids.

	Theoretical (35)	Calculation
Ne	1863410	1863047
Ar	1112820	1112808
Kr	920625	920619
Xe	719237	719234

Table 2: Heat capacities for Large temperatures.

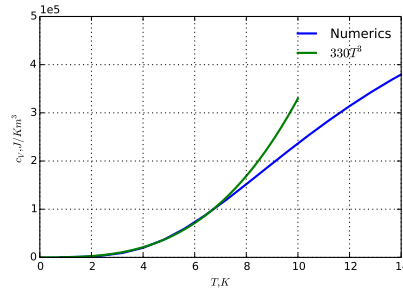


Figure 5: Heat capacity for Ne at low temperatures. We see that there is correspondence with experimental T^3 as in (36)

Experimentally it is also possible to measure heat capacities and dispersion relations under high pressure [5] which changes lattice constant a . A

convenient parameter for the changes in dispersion relation is defined in (3) and for Ne (where other rare gas elements has similar behaviour) is shown in 6. First thing we that degenerate states will remain degenerate under pressure since crystal symmetry remains. Next we observe that frequencies in dispersion relation will increase, but the proportion will change. Specifically longitudinal modes will increase faster. Due to lift of all frequencies for dispersion relation then each factor $\frac{\hbar\omega_i}{k_B T}$ in (2) will increase so to *compensate* it temperature should also increase, so applying pressure to the crystal heat capacity decreases at all temperatures.

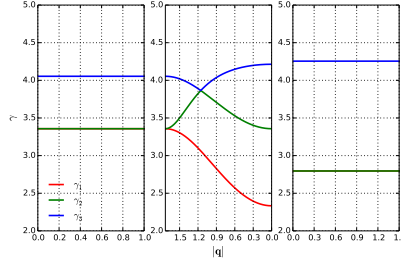


Figure 6: Calculated Gruneisen parameters for Ne starting from the left 100, 110, 111. The lower branches for 100 and 111 are degenerate.

5 Conclusions

In this report classical formulation of lattice vibrations with Mie-Lennard-Jones potential were used to obtain dispersion relations for rare gas solids where for Neon calculation expected symmetries is shown supporting numerical result.

The qualitative correspondence for dispersion relations with other fcc crystals in literature's experimental data, gives us confidence that harmonic and local approximations are good enough to give valuable description for process.

By imposition that each frequency mode can store only discrete sets of energies, the heat capacity temperature dependance of rare gas crystals were calculated and showed good agreement with classical prediction for large temperatures. For small temperatures the experimentaly observable $\propto T^3$ law was present in numerical calculation so again supporting physical model.

To even more improve the accuracy of the obtained numerical results next shell of neighbour atom interaction could be added for calculation. Also to take into account thermal expansion effect which contributes to heat capacity, because volume is kept constant then one needs to go beyond harmonic approximation.

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