QM Problems

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1 A. Solid Argon With LJ Potential

NOTE: The code and related documents are available in the GitHub repo created for this project
https://github.com/lorenzofant/QMprob2

1.1 Lattice Parameters

From the general expression of the Lennard-Jones potential

$$V(r) = 4\epsilon \left(\left(\frac{\sigma}{r}\right)^1 2 - \left(\frac{\sigma}{r}\right)^6 \right) \tag{1}$$

We can easily find the minimum finding the zero of the first derivative.

$$r_0 = 2^{\frac{1}{6}} \sigma \tag{2}$$

and, substituting it into the potential expression we find

$$V(r_0) = -\epsilon \tag{3}$$

From these two expressions we can deduce $\sigma = \frac{3.758}{2^{\frac{1}{6}}}$Åand $\epsilon = 99.55 cm^{-1}$

1.2 Crystal Structures

Knowing the expression for the Lennard-Jones potential we can derive an approximate value of the
energy of different lattice structures by numerically summing the potential energy contributions of
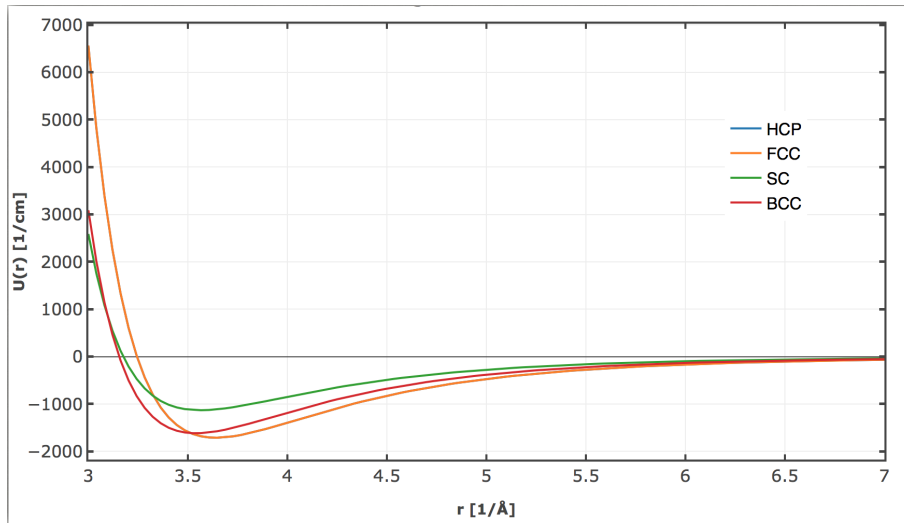the neighbours.

Figure 1: *Energy of the atoms in the lattice as a function of the lattice spacing for four possible
lattices: Simple Cubic (Blue), Face Centered (Green), Body Centered (Red), hexagonal Centered
(Light blue)*

Doing so for the 14^3 closest neighbours, we found the following values for the required structures

	spacing	energy
sc	1.066σ	-11.36ϵ
bcc	1.069σ	-16.45ϵ
fcc	1.090σ	-17.2160ϵ
hcp	1.090σ	-17.2192ϵ

We thus found that the energetically favourable configuration is the *hcp* one by a factor of 0.01% with respect to the *fcc*. This is in agreement with results found in the literature refcrystal. In the same reference it is also pointed out that despite *hcp* configuration being lower in energy, the one that more easily appears in nature is the *fcc* one. We here try to justify such a result without considering, as done in **??**, impurities.

We tried instead to consider the behaviour of the energy in the minimum when some random noise is present in the lattice, displacing the positions of the atoms. We looked at the behaviour of the energy as a function of the amplitude of the noise averaging over 10^4 different realisations of the system with a Gaussian random displacement of amplitude d.
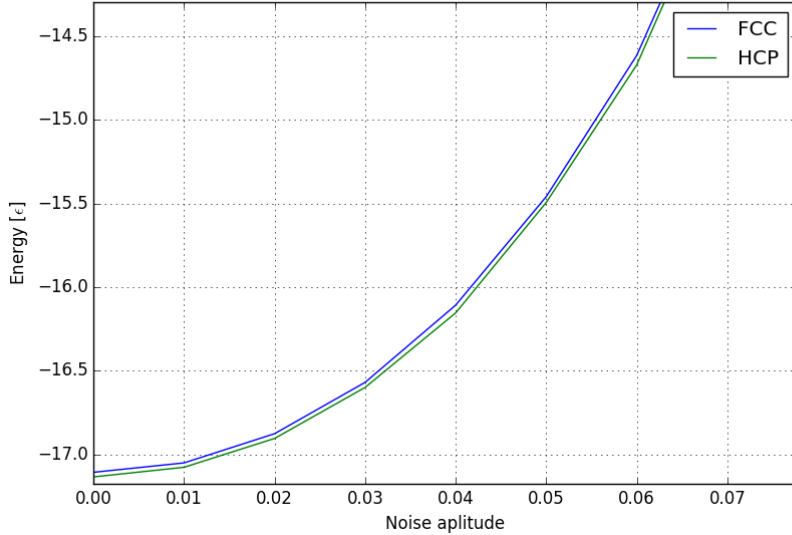

Figure 2: *Energy of the minima obtained above for FCC and HCP lattices as a function of the amplitude of a random noise displacing the atoms positions*

We can see that there is no crossing between the two energies and thus it the fact that the FCC structure is preferred in nature cannot be explained in this way. The next step would be to simulate different potential models such as Barker-Fisher-Watts (BFW) potential[**?**] and Aziz-Chen (Hartree-Fock, HFD-C) potentials[**?**] to see whether they find any results different than the one obtained using L-J potential. Even though BFW finds a new minima for the energy the HPC structure still have the minimum among the crystal structures. An improved version of this BFW known as Barker-Bobetic-Maitland-Smith (BBMS) potential[**?**] which best describes Argon behaviour can be found in the literature. as shown in the figure 3

1.3 Spectrum of the HCP

In the case of the HCP configuration we find a structure where we have two atoms per unit cell. The cell can be easily identified through the three vectors of coordinates

$$R_1 = a \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \qquad\qquad R_2 = a \begin{bmatrix} \frac{1}{2} \\ \frac{\sqrt{3}}{2} \\ 0 \end{bmatrix} \qquad\qquad R_3 = a \begin{bmatrix} 0 \\ 0 \\ 2\sqrt{\frac{2}{3}} \end{bmatrix}$$
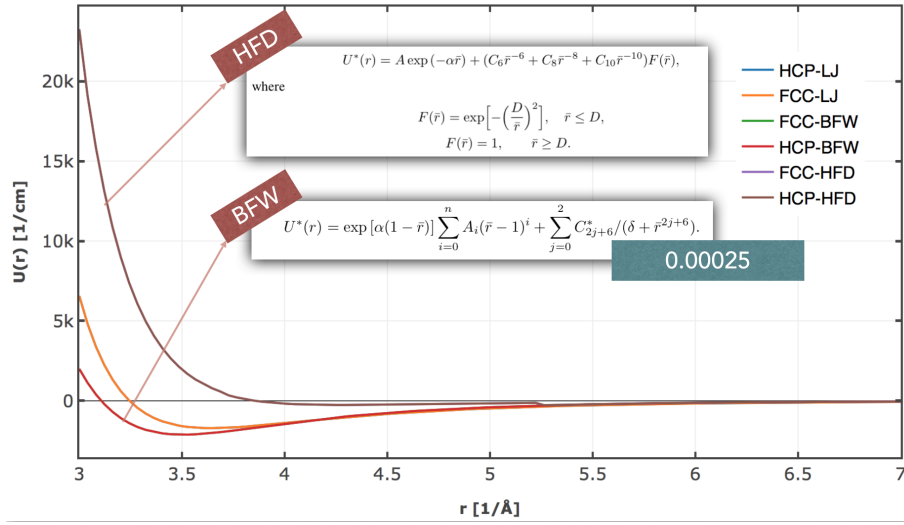
Figure 3: *Energy of the atoms in the lattice as a function of the lattice spacing for four possible lattices: Face Centered , hexagonal Centered for BFW and HFD potentials*

and that of the corresponding reciprocal lattice vectors can be constructed from those above and their coordinates are

$$G_1 = \frac{2\pi}{a} \begin{bmatrix} 0 \\ 0 \\ \sqrt{\frac{3}{2}}\pi \end{bmatrix} \qquad G_2 = \frac{2\pi}{a} \begin{bmatrix} 0 \\ \frac{2}{\sqrt{3}} \\ 0 \end{bmatrix} \qquad G_3 = \frac{2\pi}{a} \begin{bmatrix} 1 \\ -\frac{1}{\sqrt{3}} \\ 0 \end{bmatrix}$$

While the second atom in the cell is placed in
$$R_1 = a \begin{bmatrix} n_1 + \frac{n_2+1}{2} \\ \frac{\sqrt{3}(n_2+\frac{1}{3})}{2} \\ (2n_3 + 1)\sqrt{\frac{2}{3}} \end{bmatrix}$$

To evaluate the spectrum of the phonon dispersion one can evaluate, in the harmonic approximation, the equation

$$\omega^2 u_{i,\alpha,g} = \sum_{m,\beta,f} \frac{1}{M} \frac{\partial^2 V(r)}{\partial r_{i,\alpha,g} \partial r_{m,\beta,f}} e^{i\underline{q}\underline{r}_{im}} u_{m,\beta,f} \tag{4}$$

where the approximation on the solution $s_{i,\alpha} = e^{i(\underline{q}\underline{r}_i - \omega)} u_\alpha$ was applied assuming the harmonic nature of the system. The indices α, β can assume values between x, y, z, the indices i, m along the cells in the lattice and g, f along the atoms inside the unit cell. We can now define

$$\Phi_{\alpha\beta}^{imgf}(r) := \frac{\partial^2 V(r)}{\partial r_{i,\alpha,g} \partial r_{m,\beta,f}} \tag{5}$$

where the expression for the second derivative of the potential reads

$$\frac{\partial^2 V(r)}{\partial r_{i,\alpha,g} \partial r_{m,\beta,f}} = \sum_{jh} \left[\frac{\partial^2 v(r_{ij})}{\partial r_{ij}^2} \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^2} + \frac{\partial v(r_{ij})}{\partial r_{ij}} \left(\frac{\delta_{\alpha\beta}}{r_{ij}} - \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^3} \right) \right] (\delta_{gf}\delta_{im} - \delta_{fh}\delta_{jm})$$

and from here the dynamical matrix

$$D_{\alpha\beta}^{g,f} = \frac{1}{M} \sum_j \left[\frac{\partial^2 v(r_{ij})}{\partial r_{ij}^2} \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^2} + \frac{\partial v(r_{ij})}{\partial r_{ij}} \left(\frac{\delta_{\alpha\beta}}{r_{ij}} - \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^3} \right) \right] \left(\delta_{gf}(1 - e^{i\underline{q}\underline{r}_{ij}}) \bar{\delta}_{f,g} e^{i\underline{q}\underline{r}} \right)$$
$$\tag{6}$$

The diagonalization of the former thus brings to the dispersion relation of the phonons. The calculated phonon dispersion is given in the figure 4
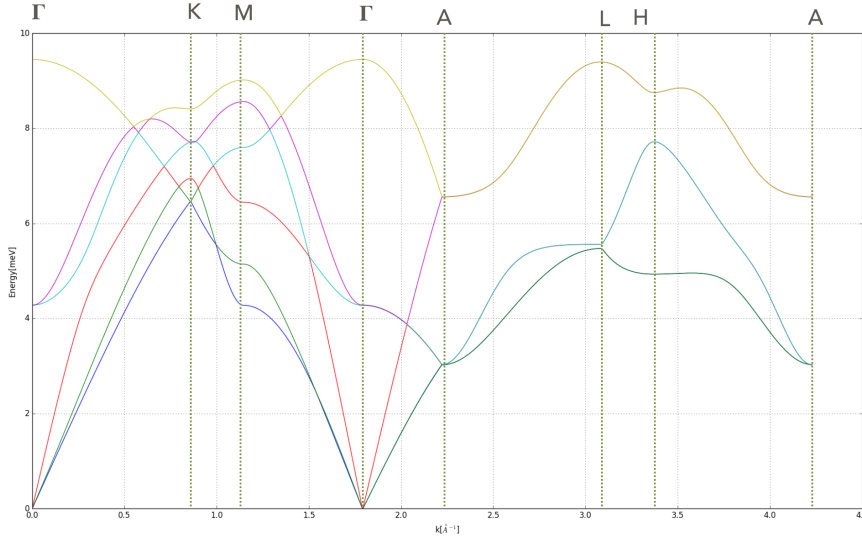
Figure 4: *Phon dispersion of HCP structure*

1.4 Spectrum of the FCC

In the case of the FCC configuration the cell contains only one atom and can be identified through the three vectors of coordinates

$$R_1 = a \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ 0 \end{bmatrix} \qquad R_2 = a \begin{bmatrix} \frac{1}{\sqrt{2}} \\ 0 \\ \frac{1}{\sqrt{2}} \end{bmatrix} \qquad R_3 = a \begin{bmatrix} 0 \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

and that of the corresponding reciprocal lattice vectors can be constructed from those above and their coordinates are

$$G_1 = \frac{2\pi}{a} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \end{bmatrix} \qquad G_2 = \frac{2\pi}{a} \begin{bmatrix} \frac{1}{\sqrt{2}} \\ -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix} \qquad G_3 = \frac{2\pi}{a} \begin{bmatrix} -\frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \\ \frac{1}{\sqrt{2}} \end{bmatrix}$$

We can now define

$$\Phi_{\alpha\beta}^{im}(r) := \frac{\partial^2 V(r)}{\partial r_{i,\alpha} \partial r_{m,\beta}} \tag{7}$$

where the expression for the second derivative of the potential reads

$$\frac{\partial^2 V(r)}{\partial r_{i,\alpha,g} \partial r_{m,\beta,f}} = \sum_j \left[\frac{\partial^2 v(r_{ij})}{\partial r_{ij}^2} \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^2} + \frac{\partial v(r_{ij})}{\partial r_{ij}} \left(\frac{\delta_{\alpha\beta}}{r_i j} - \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^3} \right) \right] (\delta_{in} - \delta_{jn})$$

and from here the dynamical matrix

$$D_{\alpha\beta} = \frac{1}{M} \sum_j \left[\frac{\partial^2 v(r_{ij})}{\partial r_{ij}^2} \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^2} + \frac{\partial v(r_{ij})}{\partial r_{ij}} \left(\frac{\delta_{\alpha\beta}}{r_i j} - \frac{(r_{ij})_\alpha (r_{ij})_\beta}{r_{ij}^3} \right) \right] \left(1 - e^{iq r_{ij}} \right) \tag{8}$$

The diagonalization of the former thus brings to the dispersion relation of the phonons. The calculated phonon dispersion is given in the figure 5

2 Calculation of Elastic Constants

The elastic stiffness tensor is defined in the limit of small de- formations. In this regime, there is a linear relationship between the deformation and the stress, as expressed by the generalised Hooke's law:

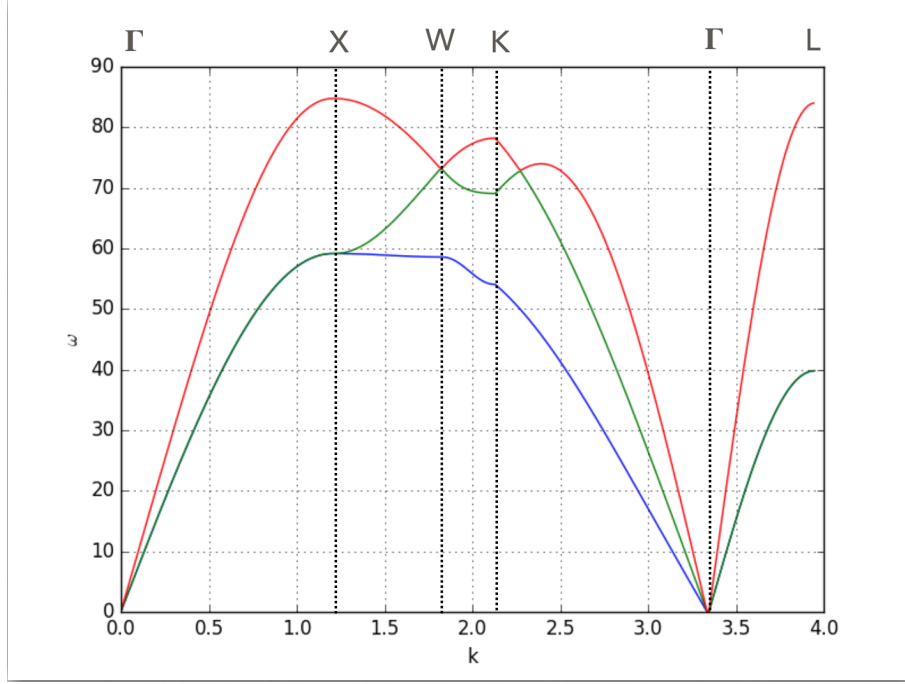$$\sigma_{\alpha\beta} = C_{\alpha\beta\mu\nu} \epsilon_{\mu\nu} \tag{9}$$

Figure 5: *Phon dispersion of FCC structure*

where the implicit sum convention is used and where α, β, μ, ν represent the Cartesian coordinates, ϵ is the strain tensor, σ is the stress tensor and C is the stiffness tensor, a fourth-rank tensor. The strain tensor elements give the change in an element of length when the body is deformed. For small deformations, strain tensor elements are equal to

$$\epsilon_{\alpha\beta} = \frac{1}{2} \left(\frac{\delta d_\alpha}{\delta r_\beta^0} + \frac{\delta d_\beta}{\delta r_\alpha^0} \right) \tag{10}$$

where $d = r - r0$ is the displacement of point r from its reference state $r0$ It can be easily shown that ϵ and σ are symmetric tensors. The Voigt notation is commonly used to represent symmetric tensors by reducing their order and simplify notations. Pairs of indices α, β are written as singlets, with xx = 1, yy = 2, zz = 3, yz = 4, xz = 5 and xy = 6. Using this representation, ϵ and σ can be written as vectors with six components and C as a 6 by 6 matrix. The generalised Hooke's law is then written:

$$\sigma_i = C_{ij}\epsilon_j \tag{11}$$

using implicit sum convention with j = 1 to 6 and $\epsilon_4 = 2\epsilon_{yz}, \epsilon_5 = 2\epsilon_{xz} and \epsilon_6 = 2\epsilon_{xy}$

2.1 Numerical calculation of Elastic Constants

From Sound Velocities

Using the phonon dispersion of the FCC Argon, one is able to find the elastic constants using the following equations:

velocity ω/k of a longitudinal wave in the [100] direction is $v_s = (C_{11}/\rho)^{1/2}$

velocity ω/k of a transverse wave in the [100] direction is $v_s = (C_{44}/\rho)^{1/2}$

velocity ω/k of a longitudinal wave in the [110] direction is $v_s = ((C_{11} + C_{12} + 2C_{44})/\rho)^{1/2}$

The calculated values are then compared with values from literature

Sound Speed [m/s]	Elastic Constants[GPa]	Litterature values
$V_{s1} = 1786$	$C_{11} = 3.2$	$C_{11} = 2.3$
$V_{s2} = 1350$	$C_{44} = 1.8$	$C_{44} = 1.5$
$V_{s3} = 2081$	$C_{12} = 1.8$	$C_{12} = 1.2$

From the Second derivative

Calculation of elastic constants are carried out again using the application of an appropriate strain on the lattice and calculating the optimised energy and taking the second derivative of the same. The values are tabulated in the table below.

Stress/strain [GPa]	From sound speed [GPa]	Litterature values
$C_{11} = 2.6$	$C_{11} = 3.2$	$C_{11} = 2.3$
$C_{44} = 1.5$	$C_{44} = 1.8$	$C_{44} = 1.5$
$C_{12} = 1.1$	$C_{12} = 1.8$	$C_{12} = 1.2$