

Solid Argon Vibrations

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22 January 2020



Section 1

Geometry Optimization

Lennard-Jones parameters for Argon

$\text{BE} = 99.55 \text{ cm}^{-1}$ (experimental binding energy)

$r_0 = 3.758 \text{ \AA}$ (experimental two-body equilibrium distance)

Lennard Jones potential:

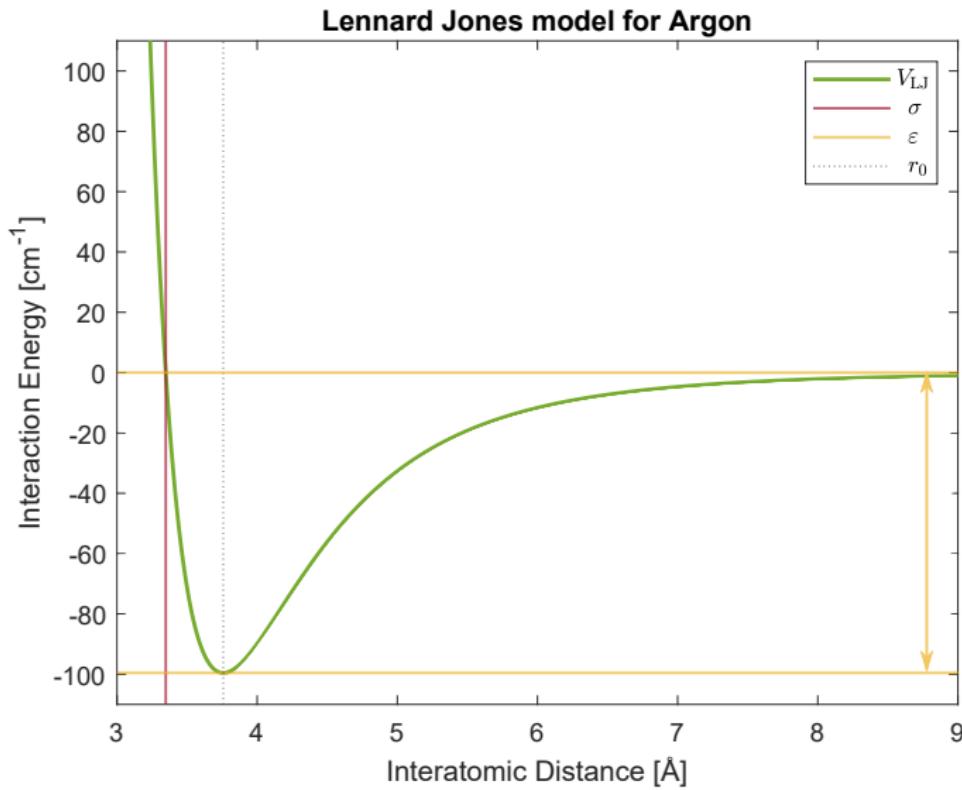
$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

We impose:

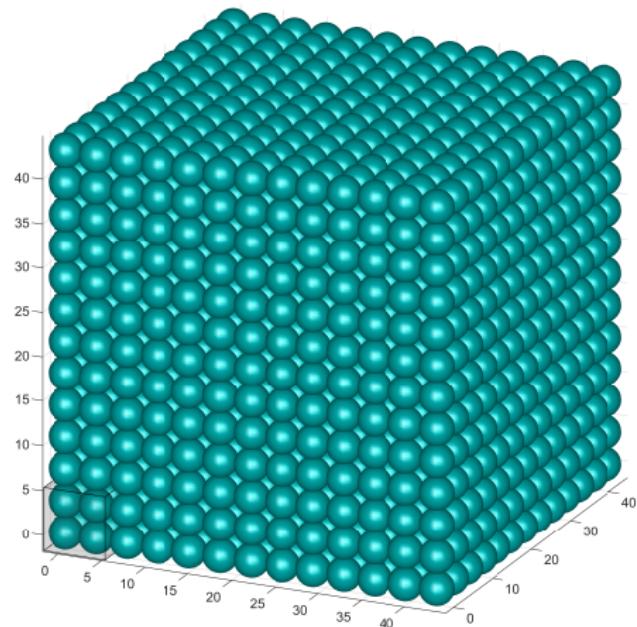
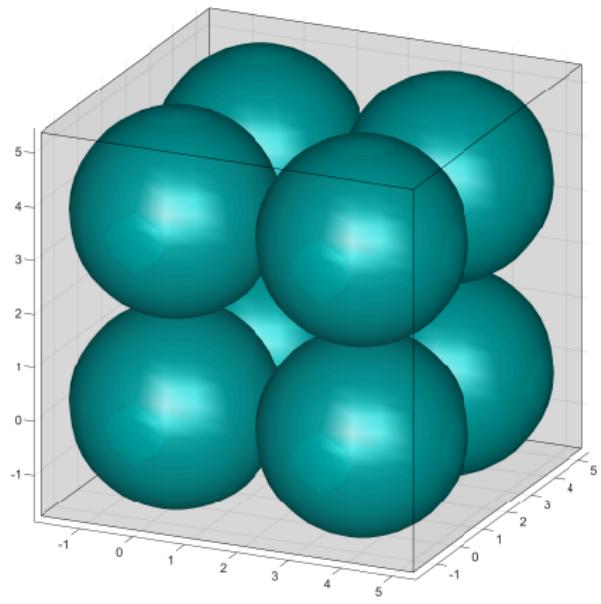
$$\frac{dV(r_0)}{dr} = 0 \implies r_0 = 2^{1/6}\sigma \implies \sigma = 3.348 \text{ \AA}$$

Also from the definition of BE: $V(\infty) - V(r_0) = \epsilon = 99.55 \text{ cm}^{-1}$

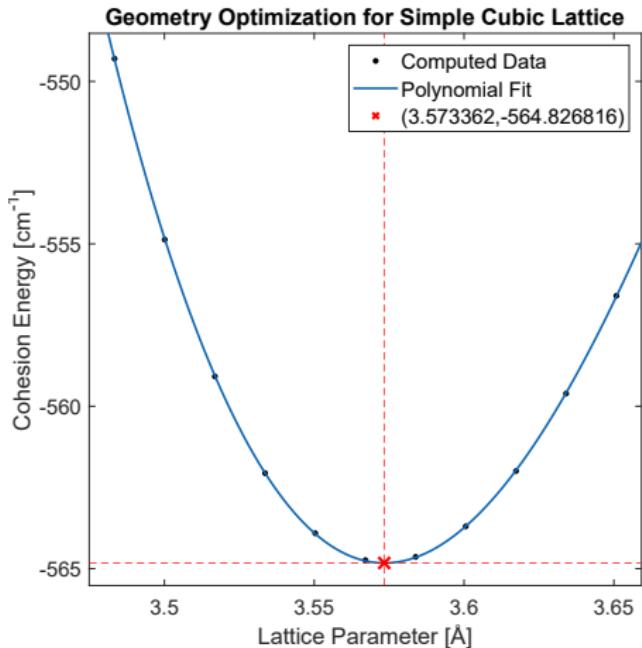
Lennard-Jones parameters for Argon



Simple Cubic Lattice

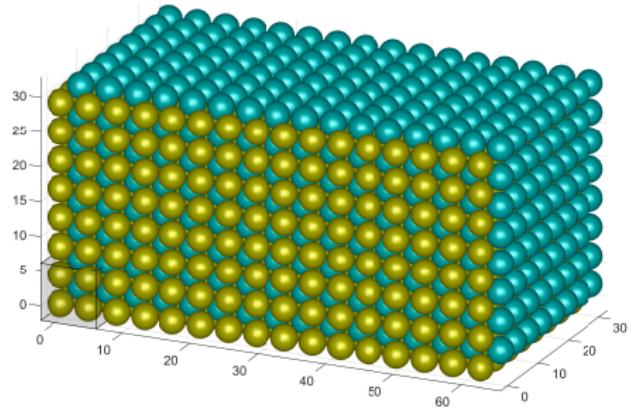
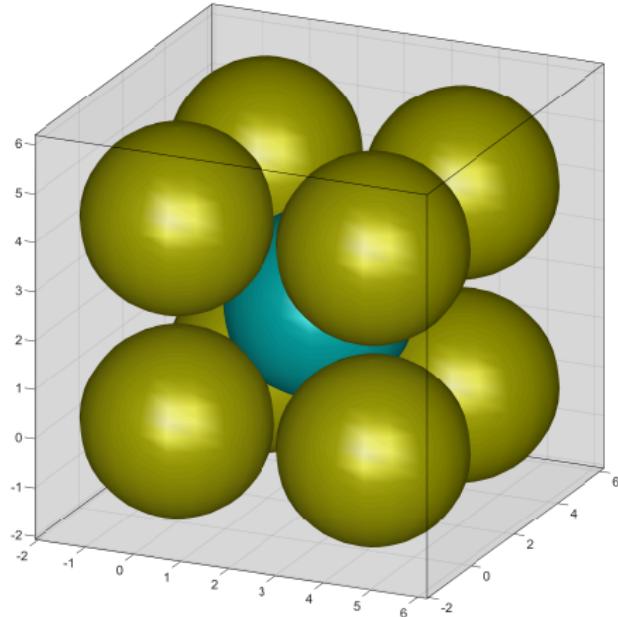


Simple Cubic Lattice → Optimization

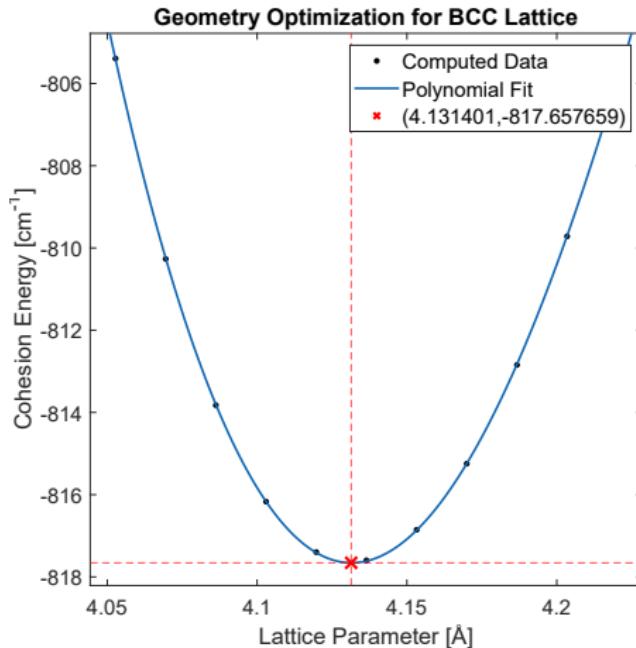


Cohesion energy versus lattice parameter for SC solid Argon modeled with Lennard-Jones potential [$\sim 10^3$ ATOMS]

Body Centered Cubic Lattice

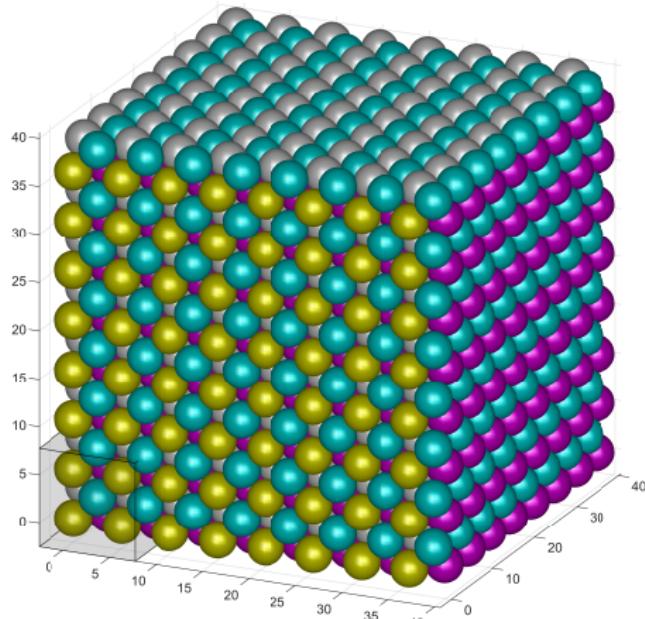
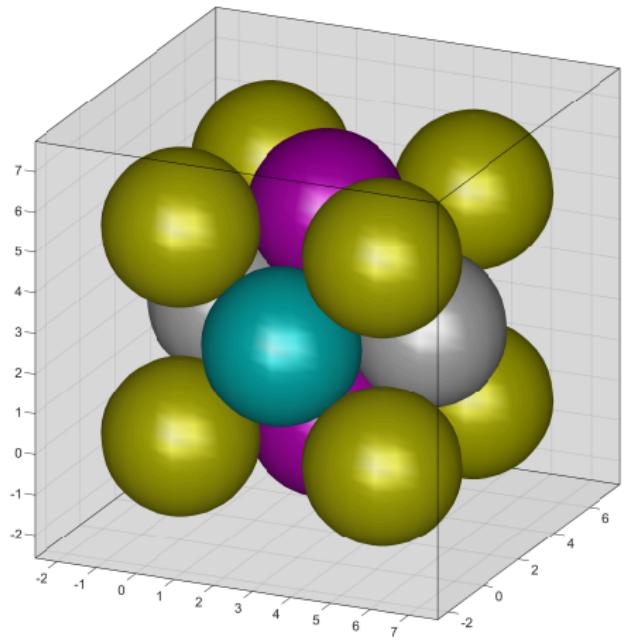


Body Centered Cubic → Optimization

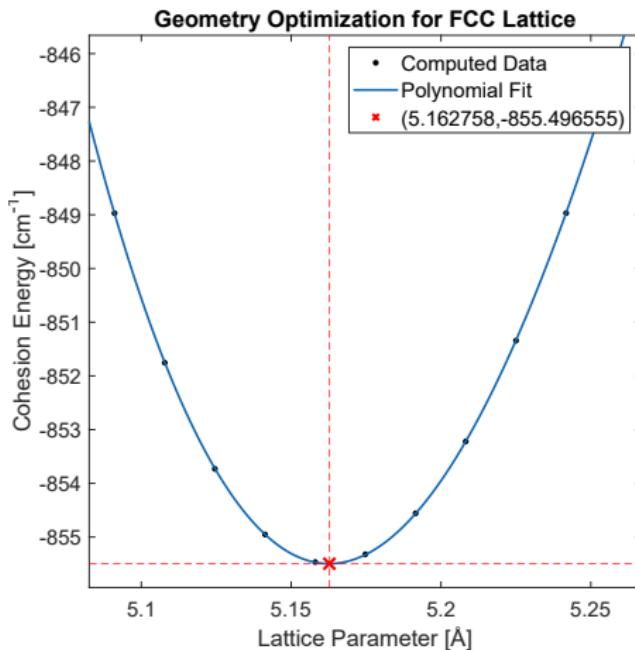


Cohesion energy versus lattice parameter for BCC solid Argon modeled with Lennard-Jones potential [$\sim 10^3$ ATOMS]

Face Centered Cubic Lattice

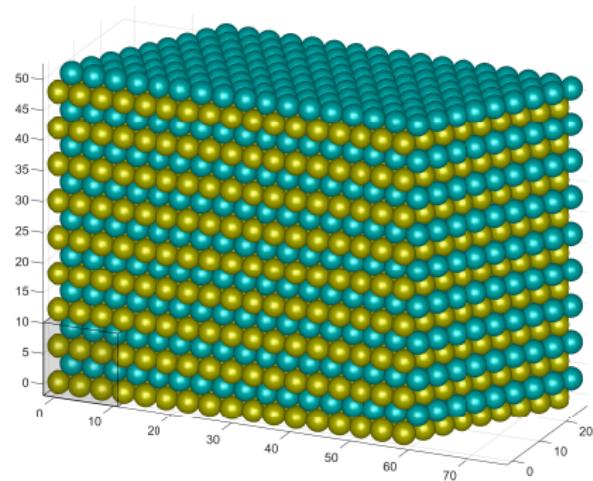
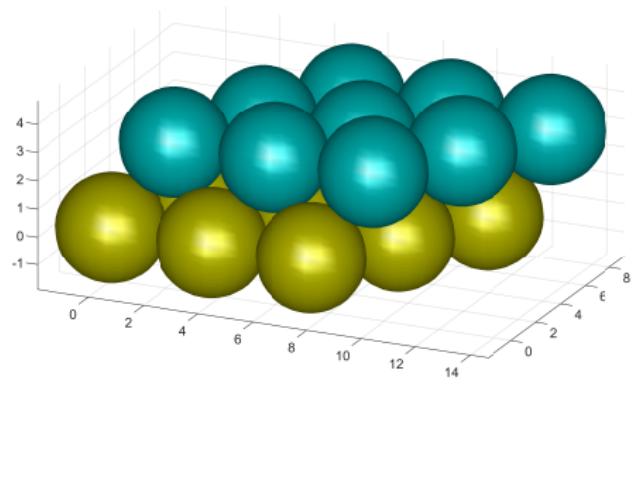


Face Centered Cubic → Optimization

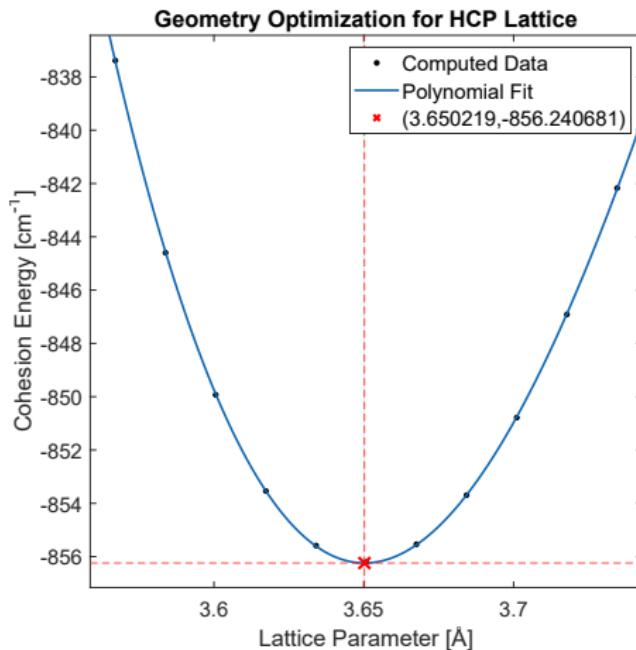


Cohesion energy versus lattice parameter for FCC solid Argon modeled with Lennard-Jones potential [$\sim 10^3$ ATOMS]

Hexagonal Closed Packed Structure

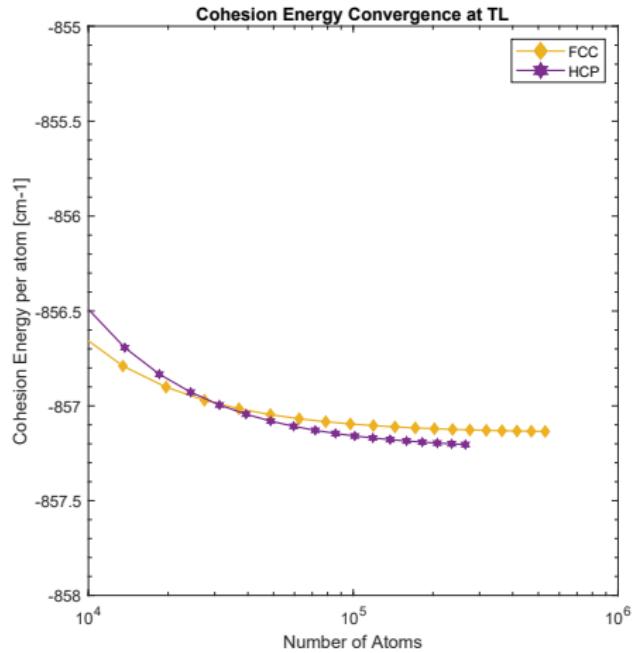
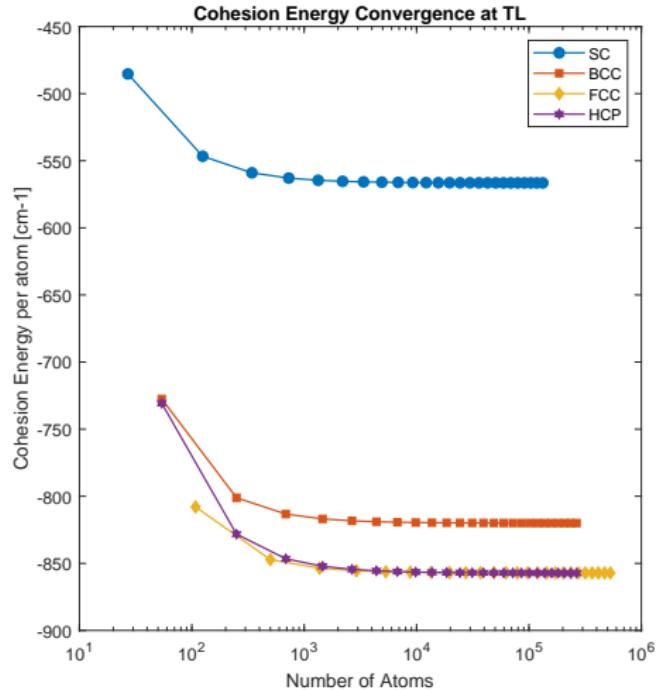


Hexagonal Closed Packed → Optimization

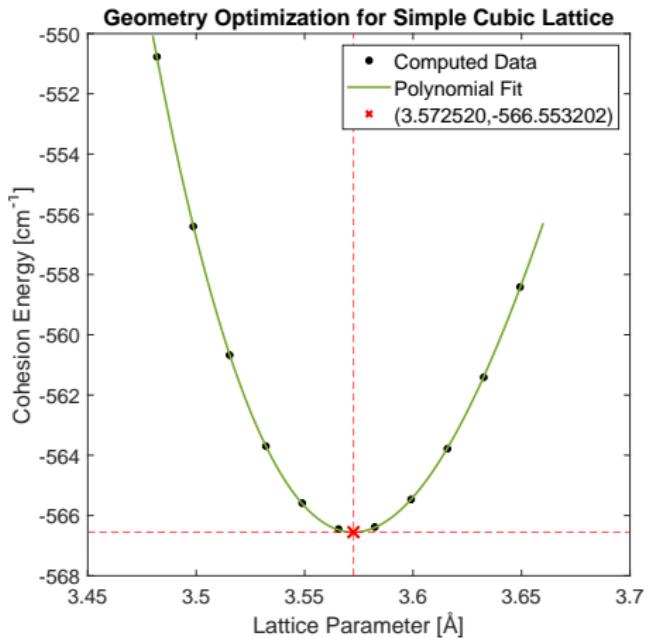


Cohesion energy versus lattice parameter for HCP solid Argon modeled with Lennard-Jones potential [$\sim 10^3$ ATOMS]

TL convergence of Cohesion Energy

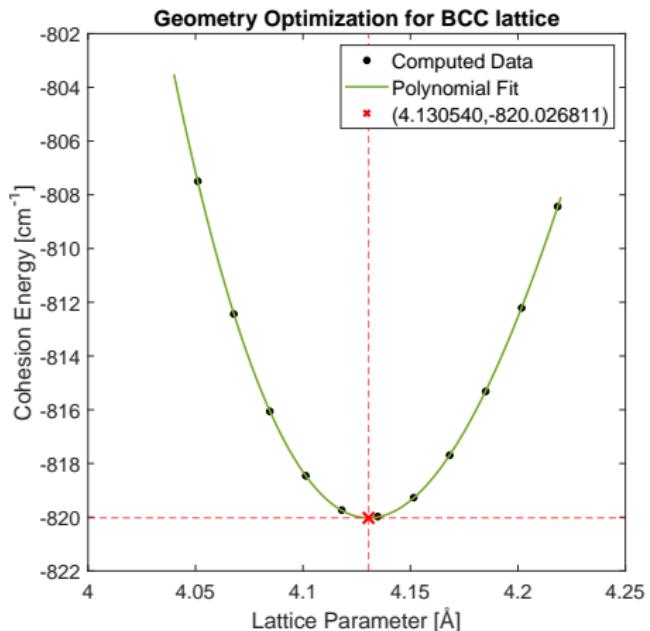


Simple Cubic Lattice → *TL* Converged Optimization



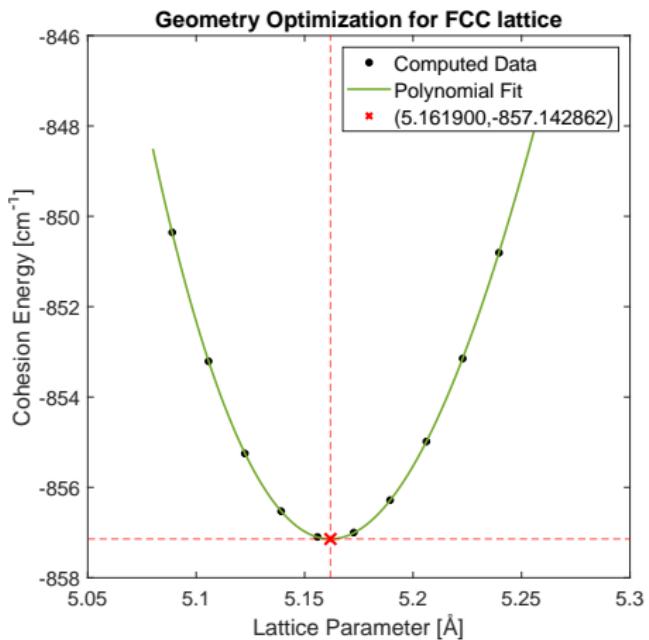
Cohesion energy versus lattice parameter for SC solid Argon modeled with Lennard-Jones potential [$\sim 10^6$ ATOMS]

Body Centered Cubic \rightarrow TL Converged Optimization



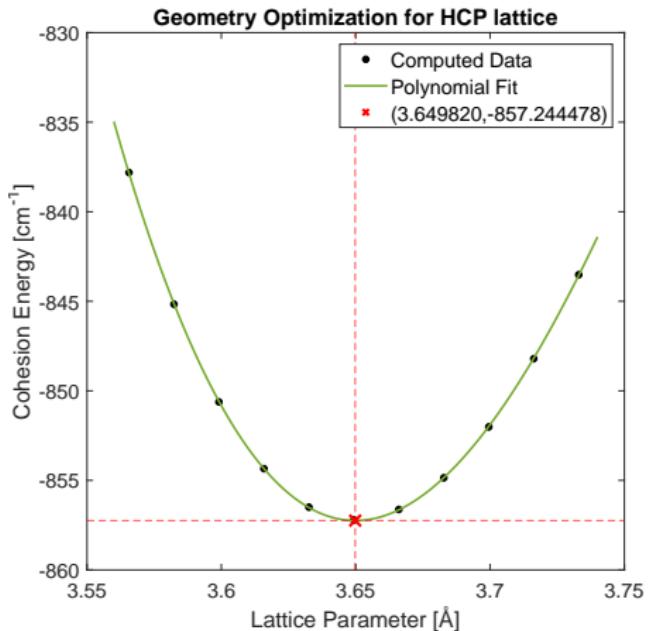
Cohesion energy versus lattice parameter for BCC solid Argon modeled with Lennard-Jones potential [$\sim 10^6$ ATOMS]

Face Centered Cubic → TL Converged Optimization



Cohesion energy versus lattice parameter for FCC solid Argon modeled with Lennard-Jones potential [$\sim 10^6$ ATOMS]

Hexagonal Closed Packed → TL Converged Optimization



Cohesion energy versus lattice parameter for HCP solid Argon modeled with Lennard-Jones potential [$\sim 10^6$ ATOMS]

Check with Literature [*Phys. Rev. B* **73**, 064112 (2006)]

	SC	BCC	FCC	HCP
<i>"Small" Supercell</i>				
a^{eq} [Å]	3.573362	4.131401	5.162758	3.650219
U^{eq} [cm $^{-1}$]	-564.8269	-817.6577	-855.4966	-856.2407
<i>"Large" Supercell</i>				
a^{eq} [Å]	3.572520	4.130540	5.161900	3.649820
U^{eq} [cm $^{-1}$]	-566.5532	-820.0268	-857.1429	-857.2445
<i>Reference Theory</i>				
a^{eq} [Å]	3.572597	4.130489	5.161733	3.649876
U^{eq} [cm $^{-1}$]	-566.5348	-820.0224	-857.1454	-857.2320

Section 2

Dynamical Matrix and Phonon Dispersions

Harmonic approximation

The harmonic approximation is based on two assumptions

- The equilibrium position of each ion is fixed on a Bravis lattice site.
- Typical excursion of each atom around these points is small compared to inter-ionic spacing.

Following these assumptions we can write the potential energy as

$$U = \frac{1}{2} \sum_{\vec{R}} \phi(\vec{R}) \approx U^{eq} + U^{harm}, \quad U^{harm} = \frac{1}{2} \sum_{\vec{R}\vec{R}', \mu\nu} u_\mu(\vec{R}) D_{\mu\nu}(\vec{R} - \vec{R}') u_\nu(\vec{R}'),$$

where:

$$D_{\mu\nu}(\vec{R} - \vec{R}') = \delta_{\vec{R}, \vec{R}'} \sum_{\vec{R}'} \phi_{\mu\nu}(\vec{R} - \vec{R}') - \phi_{\mu\nu}(\vec{R} - \vec{R}'); \quad \phi_{\mu\nu}(\vec{R}) = \frac{\partial^2 \phi(\vec{R})}{\partial R_\mu \partial R_\nu}$$

Equations of motion and Dynamical Matrix

For a system with N particles in three dimension there are $3N$ equations of motion given by:

$$M \frac{\partial^2 u_\mu(\vec{R})}{\partial t^2} = - \frac{dU^{harm}}{du_\mu(\vec{R})} = - \sum_{\vec{R}',\nu} D_{\mu\nu}(\vec{R} - \vec{R}') u_\nu(\vec{R}').$$

We seek solutions of the form

$$u_\nu(\vec{R}, t) = \epsilon_\nu e^{i(\vec{k} \cdot \vec{R} - \omega t)}, \quad M\omega^2 \epsilon_\mu = D_{\mu\nu}(\vec{k}) \epsilon'_\nu$$

where

$$D_{\mu\nu}(\vec{k}) = \sum_{\vec{R}} D_{\mu\nu}(\vec{R}) e^{i\vec{k} \cdot \vec{R}},$$

$$\omega_s(\vec{k}) = \sqrt{\frac{\lambda_s(\vec{k})}{M}},$$

being $\lambda_s(\vec{k})$ the s^{th} eigenvalue of the dynamical matrix.

Expression for the Dynamical Matrix

If there is more than one basis ion per lattice site, we generalize to:

$$D_{\mu\nu}(\vec{R} + \vec{s} - (\vec{R}' + \vec{s}')) = \delta_{\vec{s}, \vec{s}'} \delta_{\vec{R}, \vec{R}'} \sum_{\vec{R}', \vec{s}'} \phi_{\mu\nu}(\vec{R} + \vec{s} - (\vec{R}' + \vec{s}')) - \phi_{\mu\nu}(\vec{R} + \vec{s} - (\vec{R}' + \vec{s}'))$$

where \vec{s} , and \vec{s}' are the indices for basis ions.

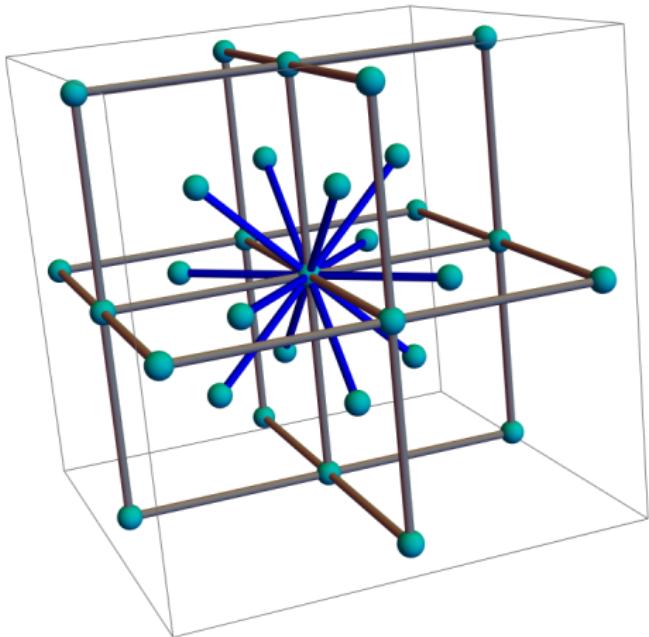
The reciprocal space Dynamical Matrix is obtained by F-transform as

$$D_{\mu\nu; \vec{s}, \vec{s}'}(\vec{k} - \vec{k}') = \sum_{\vec{R}} \sum_{\vec{R}'} e^{i\vec{k} \cdot \vec{R}} e^{i\vec{k}' \cdot \vec{R}'} D_{\mu\nu}(\vec{R} + \vec{s} - (\vec{R}' + \vec{s}')),$$

which leads to the expression:

$$D_{\mu\nu; \vec{s}, \vec{s}'}(\vec{k}) = \sum_{\vec{r}} \left[\delta_{\vec{s}, \vec{s}'} \sum_{\vec{s}''} \phi_{\mu\nu}(\vec{r} + \vec{s} - \vec{s}'') - e^{i\vec{k} \cdot \vec{r}} \phi_{\mu\nu}(\vec{r} + \vec{s} - \vec{s}') \right].$$

Dynamical Matrix for FCC



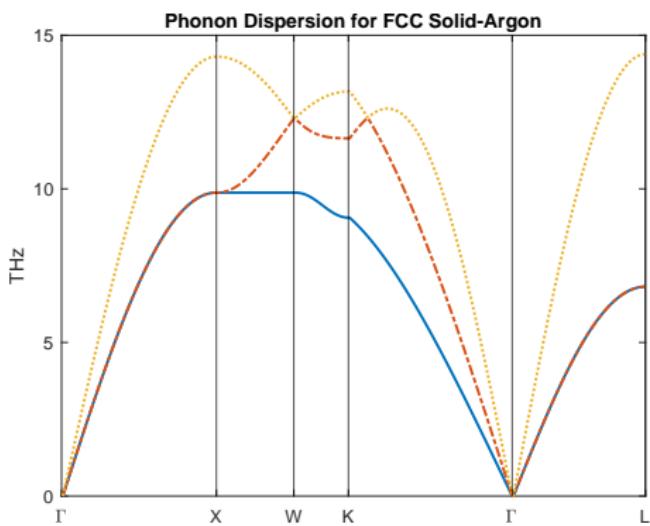
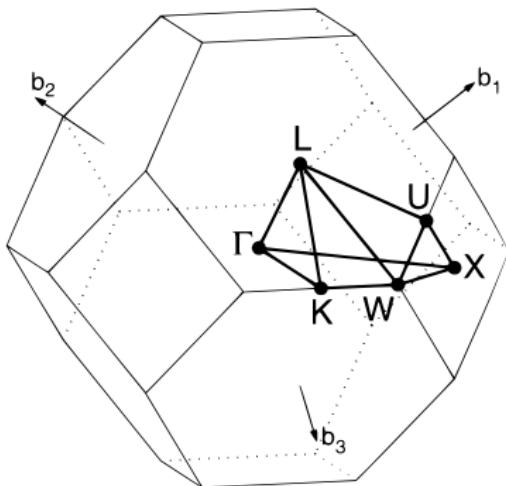
$$D_{\mu\nu}(\vec{k}) = \sum_{\vec{r}} \phi_{\mu\nu}(\vec{r}) (1 - e^{i\vec{k}\cdot\vec{r}})$$
$$= \sum_{\vec{r}} 2\phi_{\mu\nu}(\vec{r}) \sin^2\left(\frac{\vec{k}\cdot\vec{R}}{2}\right)$$

where,

$$\phi_{\mu\nu}(\vec{r}) = \frac{\partial^2 \phi(\vec{r})}{\partial r_\mu \partial r_\nu}$$
$$= \frac{\phi'(r)}{r} \delta_{\mu\nu} + \left(\frac{\phi''(r)}{r^2} - \frac{\phi'(r)}{r^3} \right) r_\mu r_\nu$$

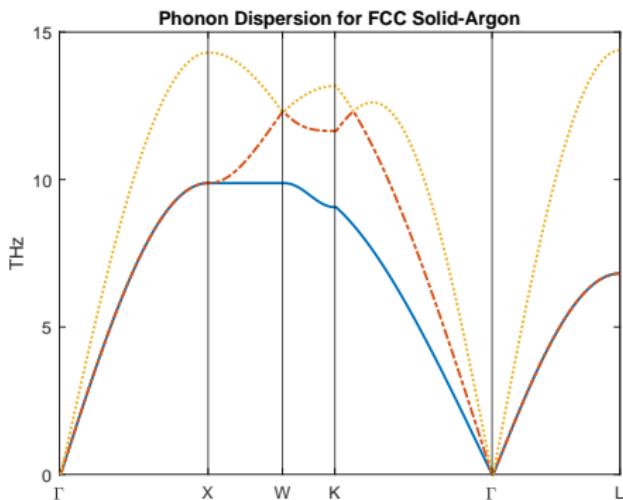
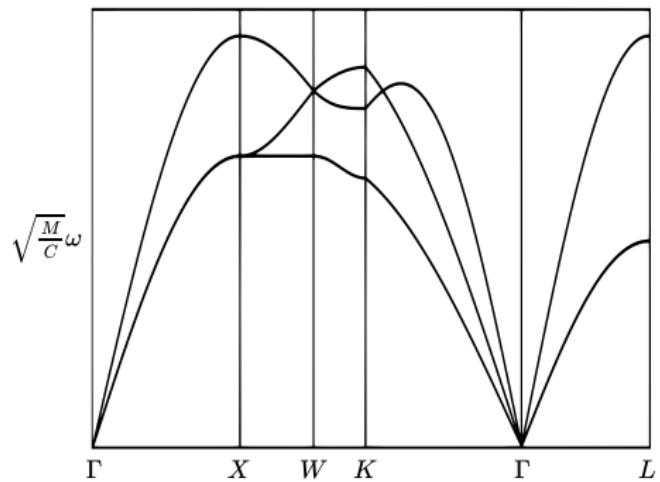
Phonon dispersion relation for FCC solid Argon

$x\mathbf{b}_1$	$x\mathbf{b}_2$	$x\mathbf{b}_3$		$x\mathbf{b}_1$	$x\mathbf{b}_2$	$x\mathbf{b}_3$	
0	0	0	Γ	$\frac{3}{8}$	$\frac{1}{4}$	$\frac{3}{8}$	U
$\frac{3}{8}$	$\frac{3}{8}$	$\frac{3}{4}$	K	$\frac{1}{2}$	$\frac{1}{4}$	$\frac{3}{4}$	W
$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	L	$\frac{1}{2}$	0	$\frac{1}{2}$	X



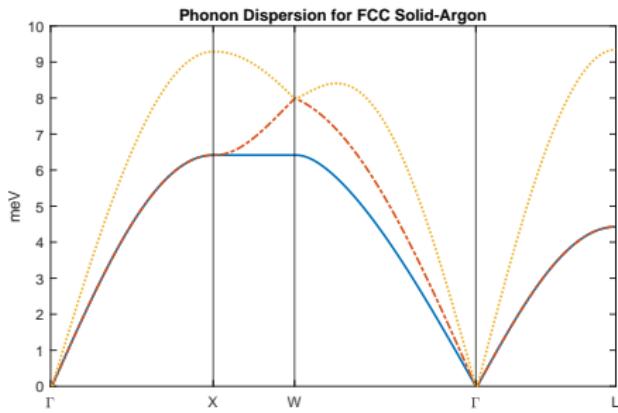
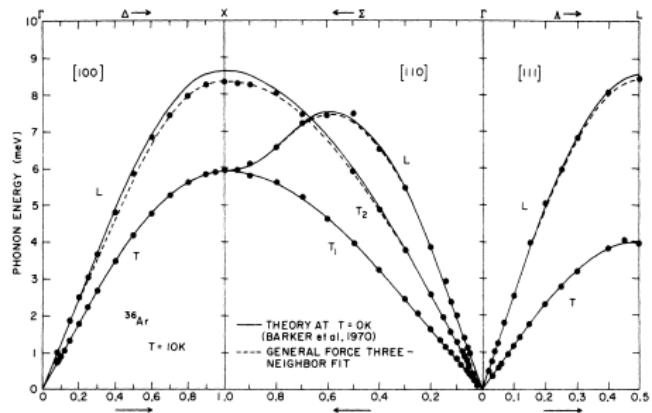
Ref. for path: *Computational Material Science* **49** 2 2010, 299-312

FCC phonons → Check with Literature [Lattice Dynamics]



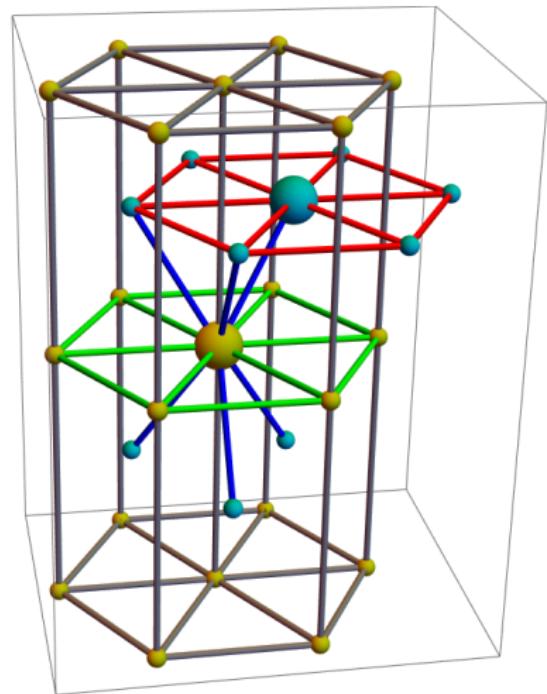
Ref. <http://lampx.tugraz.at/~hadley/ss1/phonons/fcc/fcc3.php>

FCC phonons → Check with Literature [Exp. Data for Ar]



Ref. *Phys. Rev. B* **10** 3647, 1974

Dynamical Matrix for HCP



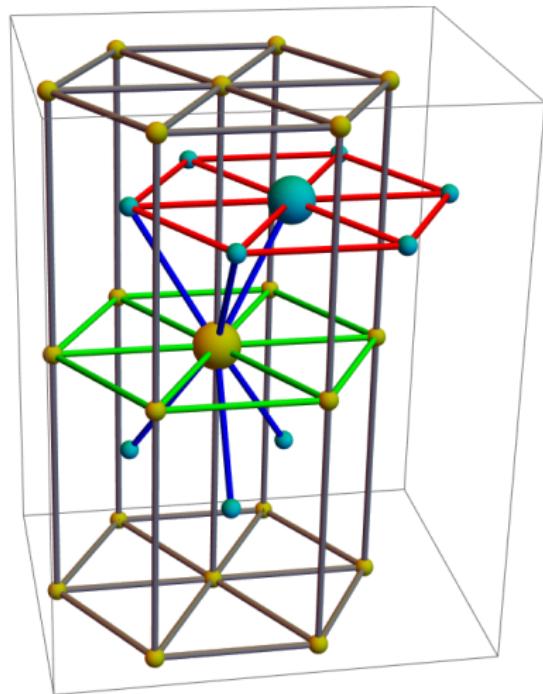
$$D_{\mu\nu; \vec{s}_A, \vec{s}'_A}(\vec{k}) = \sum_{\vec{r}} 2\phi_{\mu\nu}(\vec{r}) \sin^2\left(\frac{\vec{k} \cdot \vec{R}}{2}\right)$$

$$+ \sum_{\vec{r}'} \phi_{\mu\nu}(\vec{r}' - \vec{s}_B)$$

$$D_{\mu\nu; \vec{s}_B, \vec{s}'_B}(\vec{k}) = \sum_{\vec{r}} 2\phi_{\mu\nu}(\vec{r}) \sin^2\left(\frac{\vec{k} \cdot \vec{R}}{2}\right)$$

$$+ \sum_{\vec{r}'} \phi_{\mu\nu}(\vec{r}' + \vec{s}_B)$$

Dynamical Matrix for HCP



$$D_{\mu\nu; \vec{s}_A, \vec{s}_B}(\vec{k}) = \sum_{\vec{r}} -e^{i\vec{k}\cdot\vec{r}} \phi_{\mu\nu}(\vec{r} - \vec{s}_B)$$

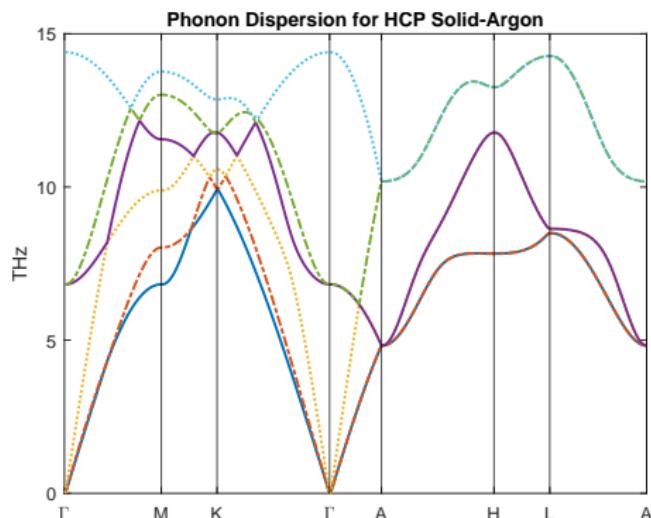
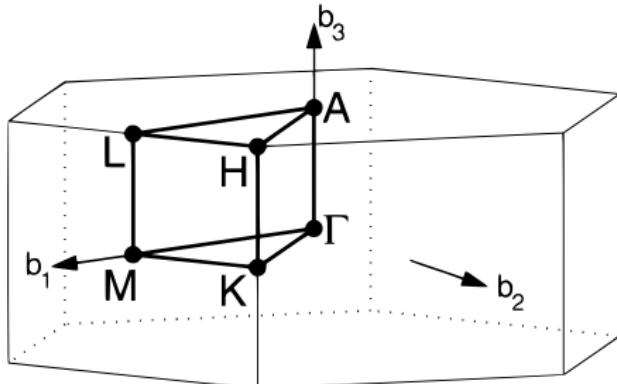
$$D_{\mu\nu; \vec{s}_B, \vec{s}_A}(\vec{k}) = \sum_{\vec{r}} -e^{i\vec{k}\cdot\vec{r}} \phi_{\mu\nu}(\vec{r} + \vec{s}_B)$$

$$\phi_{\mu\nu}(\vec{r}) = \frac{\partial^2 \phi(\vec{r})}{\partial r_\mu \partial r_\nu}$$

$$= \frac{\phi'(r)}{r} \delta_{\mu\nu} + \left(\frac{\phi''(r)}{r^2} - \frac{\phi'(r)}{r^3} \right) r_\mu r_\nu$$

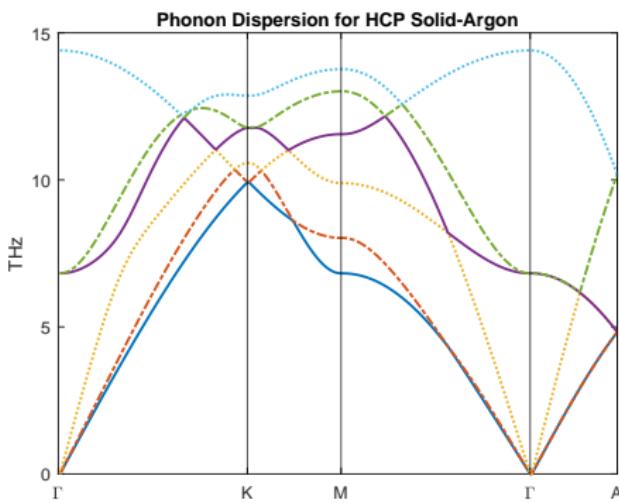
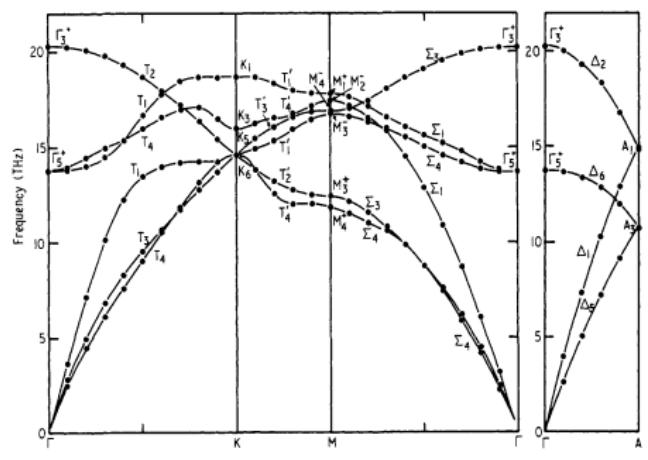
Phonon dispersion relation for HCP solid Argon

$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$		$\times \mathbf{b}_1$	$\times \mathbf{b}_2$	$\times \mathbf{b}_3$	
0	0	0	Γ	$\frac{1}{3}$	$\frac{1}{3}$	0	K
0	0	$\frac{1}{2}$	A	$\frac{1}{2}$	0	$\frac{1}{2}$	L
$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{2}$	H	$\frac{1}{2}$	0	0	M



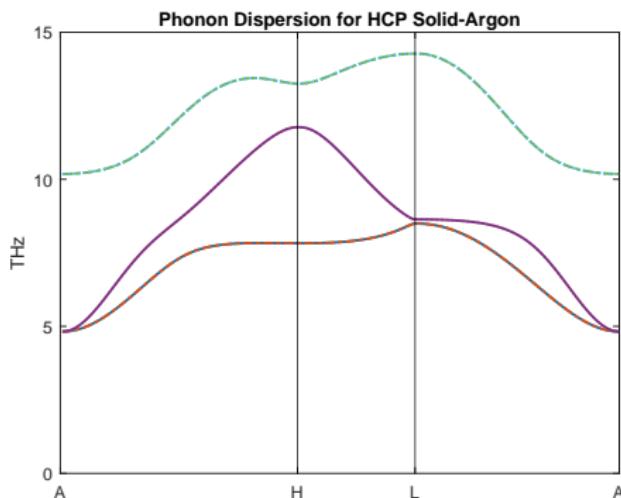
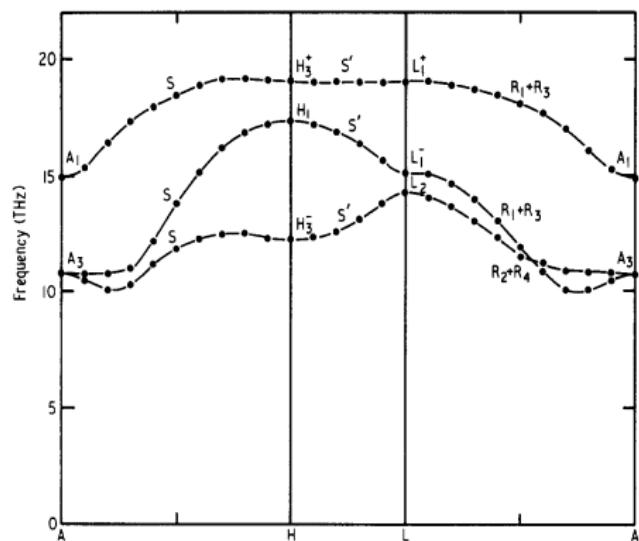
Ref. for path: *Computational Material Science* **49** 2 2010, 299-312

HCP phonons → Check with Literature [Exp. Data for Be]



Ref. *Journal of Physics F: Metal Physics* **6** 157 1976, 157-166

HCP phonons → Check with Literature [Exp. Data for Be]

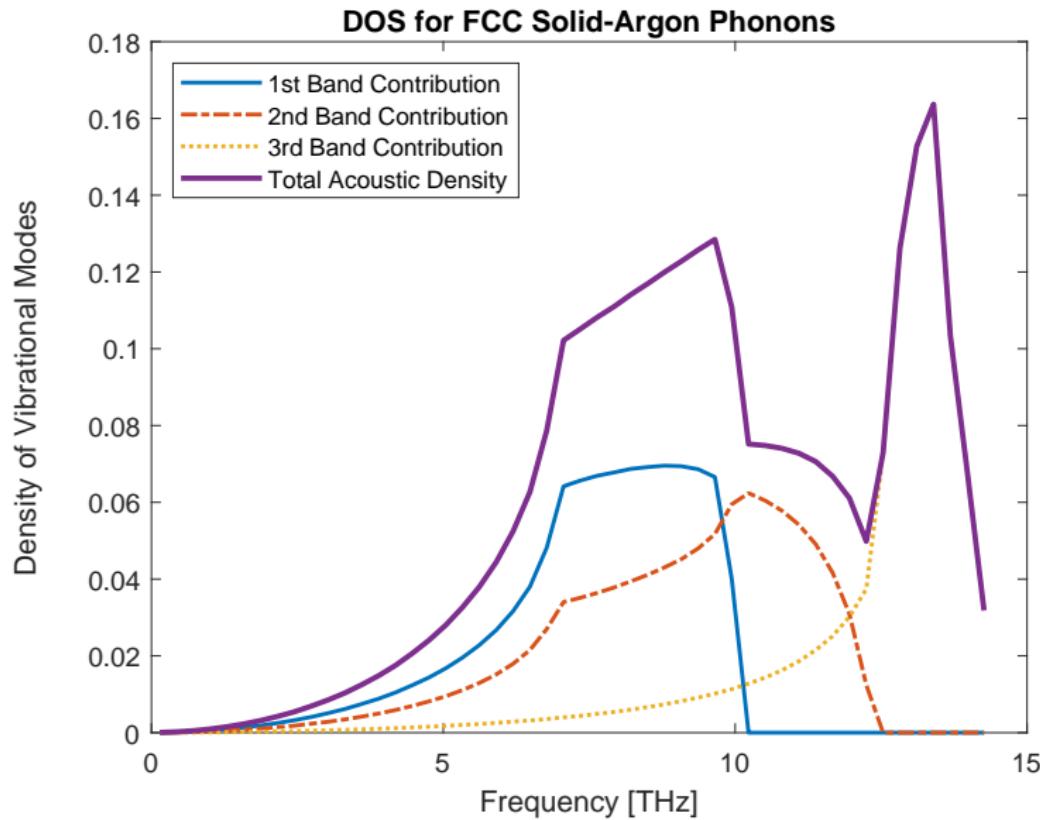


Ref. *Journal of Physics F: Metal Physics* **6** 157 1976, 157-166

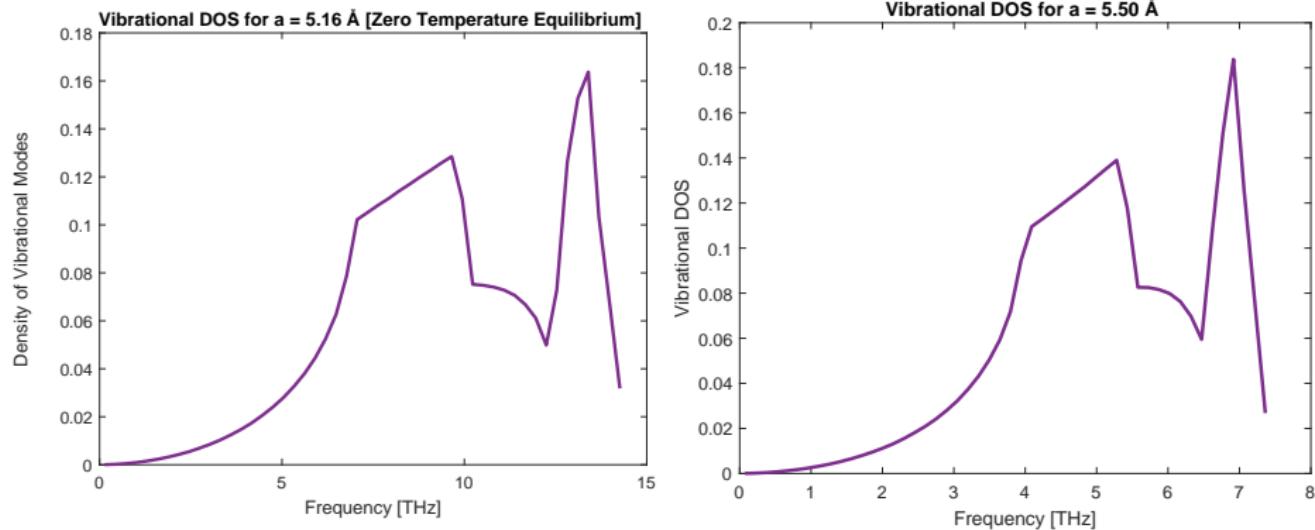
Section 3

Density of States for FCC phonons

Density of States for FCC phonons at optimized geometry



DOS's shape is independent on lattice parameter!



⇒ Inexpensive k-space sums at different volumes... thermodynamics? :)

Section 4

Thermal Expansion

Quasi-Harmonic approximation in crystals

- Harmonic approximation does not predict thermal expansion: equilibrium lattice parameter is temperature independent.
- **Quasi-Harmonic approximation:** harmonic approx. is assumed to hold for some values of the lattice parameter around equilibrium, so treating crystal volume as a parameter which phonon frequencies depend on. [Ref. Dove, M. T. *Introduction to Lattice Dynamics*, Cambridge University Press]
- Within this approximation scheme is possible to build thermodynamic potentials and so look for temperature dependent equilibrium. We will then address thermal expansion of fcc solid Argon.

Free Energy Minimization

The quantum theory of harmonic crystal at finite temperature gives:

$$U_{lattice}(a, T) = U^{eq}(a) + \frac{1}{2} \sum_{\vec{k}, s} \hbar \omega_s(\vec{k}, a) + \sum_{\vec{k}, s} \frac{\hbar \omega_s(\vec{k}, a)}{e^{\frac{-\hbar \omega_s(\vec{k}, a)}{k_B T}} - 1} ,$$

where $\frac{1}{2} \sum_{\vec{k}, s} \hbar \omega_s(\vec{k}, a)$ is the zero-point vibrational energy.

The corresponding Helmholtz Free Energy is:

$$F_{lattice}(a, T) = U^{eq}(a) + \frac{1}{2} \sum_{\vec{k}, s} \hbar \omega_s(\vec{k}, a) + k_B T \sum_{\vec{k}, s} \ln \left[1 - e^{\frac{-\hbar \omega_s(\vec{k}, a)}{k_B T}} \right] .$$

The thermal equilibrium volume is then determined by minimizing the latter expression with respect to the lattice parameter, fixing the temperature to some given values.

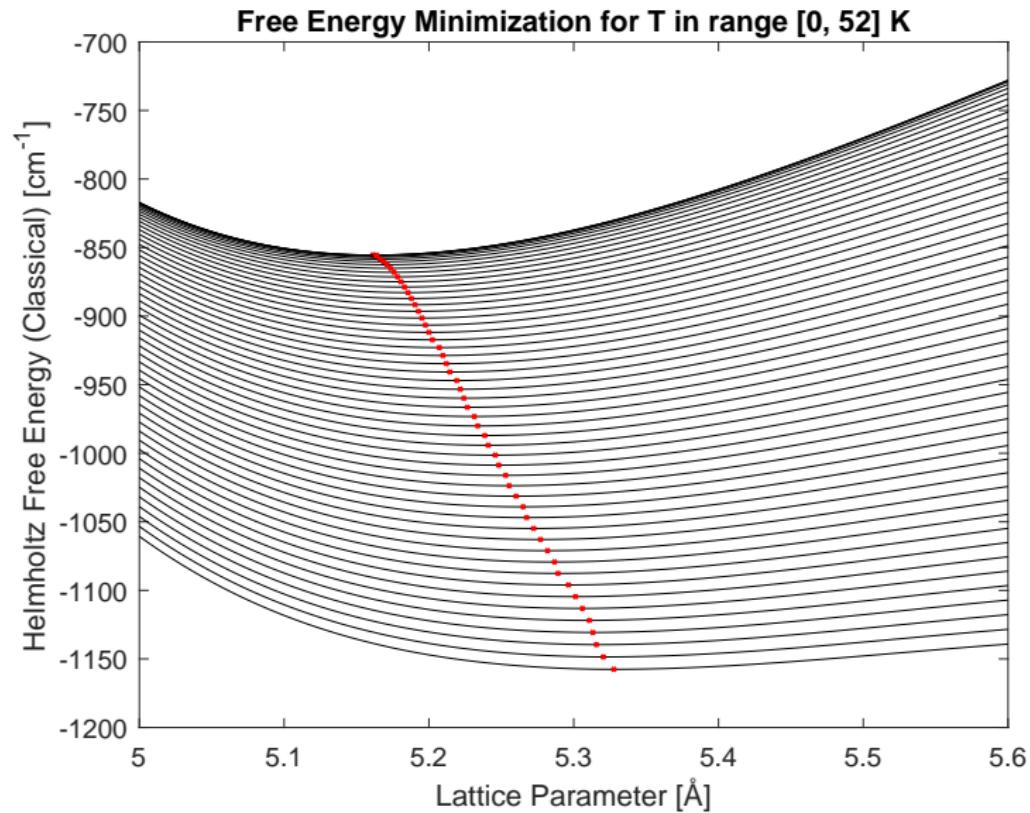
Classical Free Energy

We actually discarded the zero-point energy, in order to better match with previous results for $T = 0$ equilibrium volume, thus defining a classical approximation for the Free Energy:

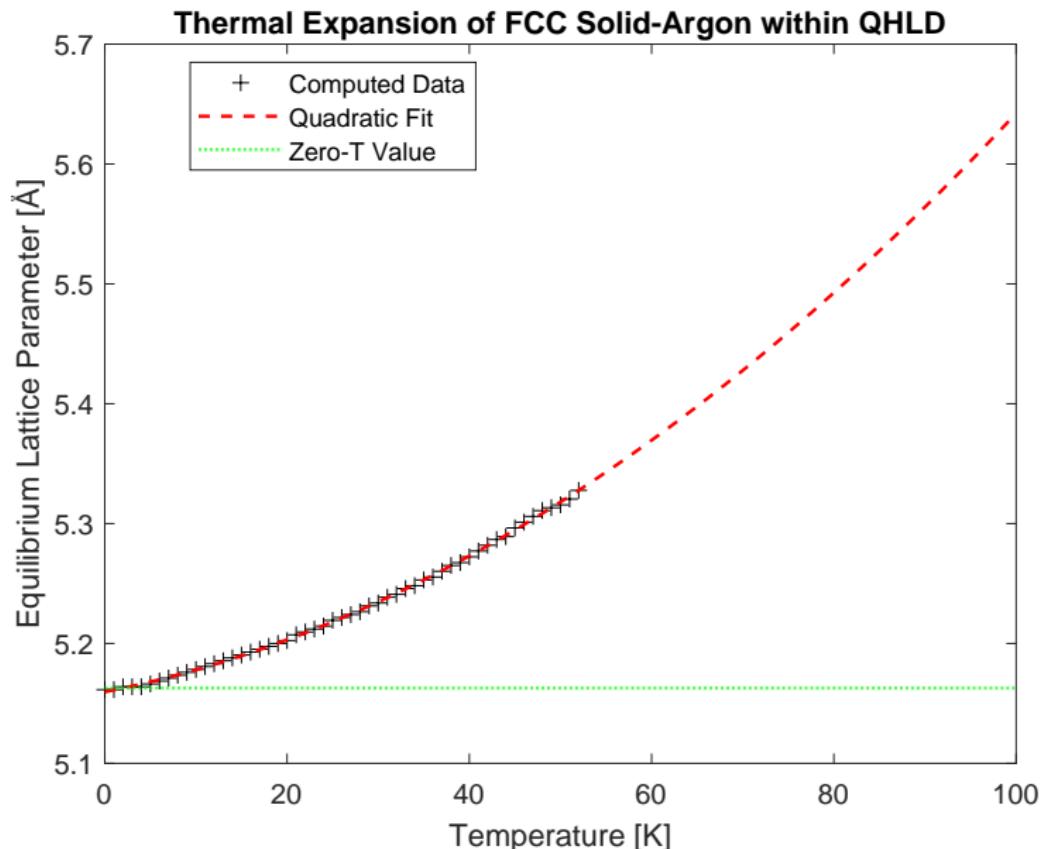
$$F_{lattice}(a, T) \simeq F_{classical}(a, T) = U^{eq}(a) + k_B T \sum_{\vec{k}, s} \ln \left[1 - e^{\frac{-\hbar \omega_s(\vec{k}, a)}{k_B T}} \right],$$

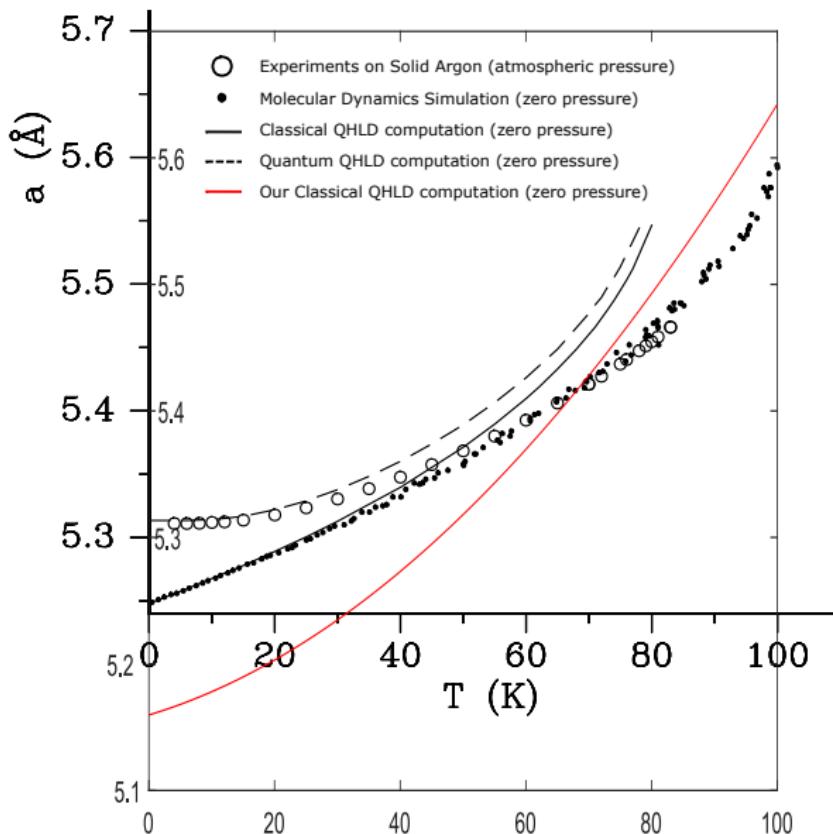
$$\lim_{T \rightarrow 0} \min F_{classical}(a, T) = \min U^{eq}(a).$$

Free Energy Minima at different Temperatures



Thermal expansion of Solid Argon





Thanks for your attention!