# Phonon calculations

# References

(1) Stefano Baroni, Paolo Giannozzi, Andrea Testa, Green's-function approach to linear response in solids, Phys. Rev. Lett. 58, 1861–1864 (1987)

(2) Xavier Gonze, Perturbation expansion of variational principles at arbitrary order, Phys. Rev. A 52, 1086–1095 (1995)

(3) Andrew A. Quong, Amy Y. Liu, First-principles calculations of the thermal expansion of metals, Phys. Rev. B 56, 7767–7770 (1997)

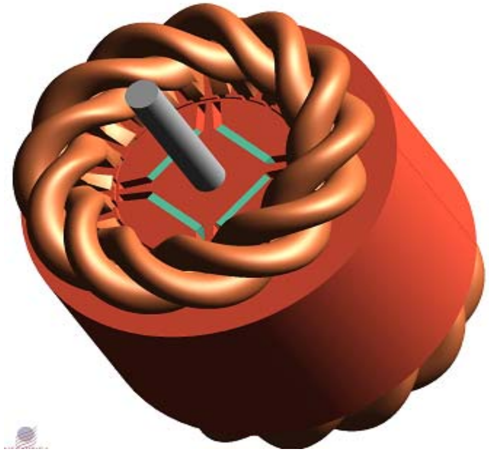
(4) Charles Kittel, Introduction to solid state physics, Wiley

(5) Krzysztof Parlinski, Calculation of phonons and thermodynamic properties of crystals by Phonon

(6) Paul Robert Tulip, PhD thesis

(7) Quantum espresso, http://www.quantum-espresso.org/

# Temperature: The ever present factor



- **Need to understand the effects of temperature on behavior.**

-**Prediction:**

**Need to know how the material will behave, expansion, heating, softening …**

- **Control:**

**Can use these behavior for control, thermostats, phase change**

- **Design**

**For new applications, need to design materials with specific properties**

**Most mechanical, electrical, magnetic and optical properties depend on temperature**

# Review of Density functional theory

## First Hohenberg-Kohn theorem: Existence

Charge density, n <=> External potential, V

$$F[\rho(\vec{r})] = \left\langle \Psi \middle| \hat{T} + \hat{V}_{e-e} \middle| \Psi \right\rangle$$

## Second Hohenberg-Kohn theorem: Variation

$$E_v[n'(\vec{r})] = F[n'(\vec{r})] + \int v_{ext}(\vec{r}) n'(\vec{r}) d\vec{r} \geq E_0$$

Schrodinger like equation ~ n

Still don’t know F

External potential $V_{ext}$ and the number of electrons completely define the problem

Wave functions completely determined from the Schrödinger Equation

System properties follow from wave functions

Energy is a functional of $V_{ext}$ and N.

## Kohn-Sham mapping:

Remove many body effects.

$$E[\{\psi_i\}] = \sum_{i=1}^{N} -\frac{1}{2} \int \psi_i^\star(\mathbf{r}) \nabla^2 \psi_i(\mathbf{r})\ d\mathbf{r} + E_H[n(\mathbf{r})] + $$

$$+ E_{xc}[n(\mathbf{r})] + \int v_{ext}(\mathbf{r}) n(\mathbf{r})\ d\mathbf{r}$$

# Ab initio calculations

**Does QM include temperature?**

$$i\hbar\frac{\partial}{\partial t}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t) = \mathcal{H}\Phi(\{\mathbf{r}_i\},\{\mathbf{R}_I\};t)$$

$$\mathcal{H} = -\sum_I \frac{\hbar^2}{2M_I}\nabla_I^2 - \sum_i \frac{\hbar^2}{2m_\mathrm{e}}\nabla_i^2 + \sum_{i<j}\frac{\mathrm{e}^2}{|\mathbf{r}_i-\mathbf{r}_j|} - \sum_{I,i}\frac{\mathrm{e}^2 Z_I}{|\mathbf{R}_I-\mathbf{r}_i|} + \sum_{I<J}\frac{\mathrm{e}^2 Z_I Z_J}{|\mathbf{R}_I-\mathbf{R}_J|}$$

Decouple nuclear and electronic contributions:

- Born Oppenheimer approximation

- Non-interacting electron cloud

- Local Density approximation

Born Oppenheimer approximation

$$\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} + \int d^3r'\, n(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|} + V_{\mathrm{xc}}[n](\mathbf{r})\right]\psi_k(\mathbf{r}) = \varepsilon_k\psi_k(\mathbf{r}).$$

# Density functional theory

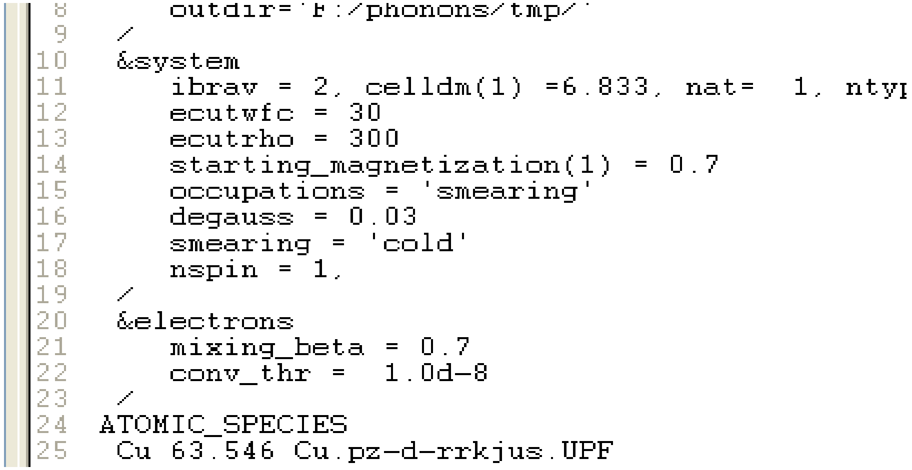
**Schrödinger equation ~ extremely complicated**

**Make assumptions to simplify**

**Completely removed any notion of temperature?**

**Not really. In practical applications of DFT**

**Electronic temperature.**



```
      outdir='F:/phonons/tmp/'
   /
   &system
      ibrav = 2, celldm(1) =6.833, nat=  1, ntyp
      ecutwfc = 30
      ecutrho = 300
      starting_magnetization(1) = 0.7
      occupations = 'smearing'
      degauss = 0.03
      smearing = 'cold'
      nspin = 1,
   /
   &electrons
      mixing_beta = 0.7
      conv_thr =  1.0d-8
   /
 ATOMIC_SPECIES
   Cu 63.546 Cu.pz-d-rrkjus.UPF
```

METAL:

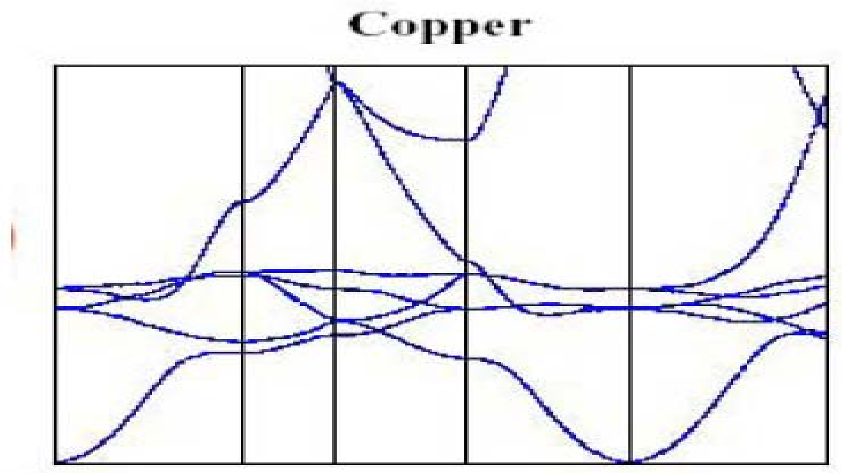
More complicated, Fermi energy, No gap,

Total charge density= sum of states + k points

Depends on where we stop.

Find fermi level and integrate below

Discontinuities



# How to include temperature?

**How does temperature manifest itself?**

- **An-harmonic terms**

  - **taken care of in MD**

  - **But time and length scales too small for practical applications … until recently**

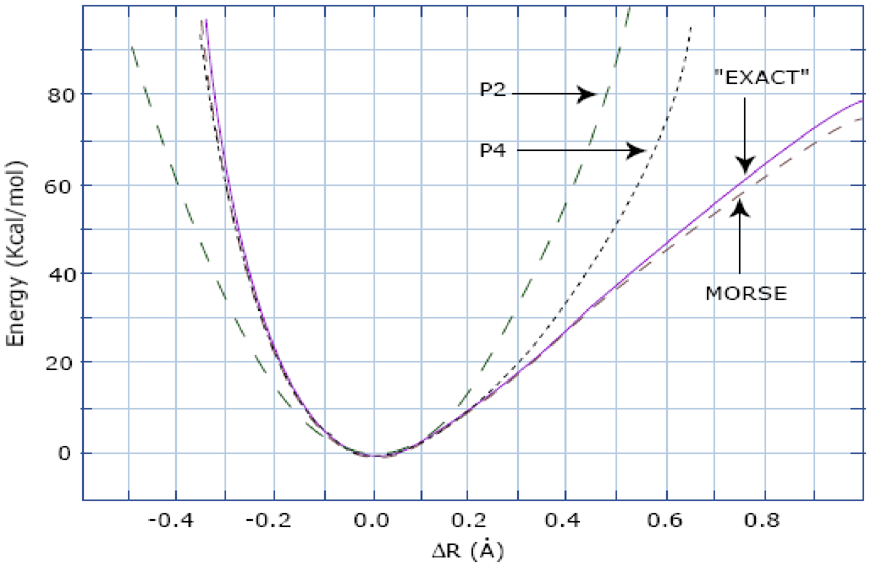
-**Perturbations in the atoms.**

  - **As the temperature increases, total energ is not only electronic energy, but includes other degrees of freedom**

**Vibrational energy.**

**Amount of vibration a measure of thermal energy**

**Link thermal and temperature dependant properties to these vibrations**



# Vibrations in molecules 1

Total energy is a function of atomic positions

$$\vec{X} = (\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M)$$

Within the Born-Oppenheimer approximation, keep the atomic positions fixed.

The total energy is given by:

$$E = E_e + \frac{1}{2}\sum_{k \neq l = 1}^{M} \frac{Z_k Z_l}{|\vec{R}_k - \vec{R}_l|}$$

How does one find the stable configuration of atomic positions? Minimize E

Provides a way to find perturbations from the stable configuration.

Expand

$$E(\vec{X}) \simeq E(\vec{X}^e) + \frac{1}{2}\sum_{k_1,k_2=1}^{M} \sum_{\alpha_1,\alpha_2=x,y,z} \frac{\partial^2 E(\vec{X}^e)}{\partial R_{k_1,\alpha_1}\partial R_{k_2,\alpha_2}} \times (R_{k_1,\alpha_1} - R^e_{k_1,\alpha_1})(R_{k_2,\alpha_2} - R^e_{k_2,\alpha_2}).$$

Harmonic approximation

Computing the Hessian

$$\underline{\underline{H}} = \left( \frac{\partial^2 E(\vec{X}^e)}{\partial R_{k_1,\alpha_1}\partial R_{k_2,\alpha_2}} \right)$$

# Vibrations in molecules 2

Computing the Hessian $\underline{\underline{H}} = \left( \frac{\partial^2 E(\vec{X}^e)}{\partial R_{k_1,\alpha_1} \partial R_{k_2,\alpha_2}} \right)$

GULP computes this using the BFGS scheme in the 'opti' command. Why is this necessary? Are just the forces not enough?

A simple way to compute the Hessian: Compute the energies of various small displacements of atoms

Using QM to compute these vibrations and their energies. For a small displacement, there is a restoring force acting on the atoms. Pose this as a Hamiltonian

$$\hat{H}_n = -\sum_{k=1}^{M} \frac{1}{2M_k} \nabla^2_{\vec{R}_k} + \frac{1}{2} \sum_{k_1,k_2=1}^{M} \sum_{\alpha_1,\alpha_2=x,y,z} \frac{\partial^2 E(\vec{X}^e)}{\partial R_{k_1,\alpha_1} \partial R_{k_2,\alpha_2}} \times (R_{k_1,\alpha_1} - R^e_{k_1,\alpha_1})(R_{k_2,\alpha_2} - R^e_{k_2,\alpha_2})$$

The eigenvalues of this equation $\hat{H}_n \Psi_n = E_n \Psi_n$

define the energies and modes of vibration

# Vibrations in molecules 3

Change of variables to simplify the equations $\vec{u}_k = \sqrt{M_k}(\vec{R}_k - \vec{R}_k^e),$

$$\hat{H}_n = -\sum_{k=1}^{M} \frac{1}{2}\nabla^2_{\vec{u}_k} + \frac{1}{2}\sum_{k_1,k_2=1}^{M}\ \sum_{\alpha_1,\alpha_2=x,y,z} \frac{1}{\sqrt{M_{k_1}M_{k_2}}} \frac{\partial^2 E(\vec{X}^e)}{\partial R_{k_1,\alpha_1}\partial R_{k_2,\alpha_2}} u_{k_1,\alpha_1} u_{k_2,\alpha_2}.$$

Dynamical matrix, D

Diagonalizable matrix D => $\underline{\underline{D}} = \underline{\underline{U}}^\dagger \cdot \underline{\underline{\Lambda}} \cdot \underline{\underline{U}},$

Use it to convert the equations into non-interacting terms $\hat{H}_n = \sum_k \left[ -\frac{1}{2}\frac{\partial^2}{\partial \tilde{u}_k^2} + \frac{1}{2}\Lambda_{k,k}\tilde{u}_k^2 \right],$

Can write wave function for nuclear vibrations as

$$\Psi_n(\vec{R}_1, \vec{R}_2, \ldots, \vec{R}_M) = \psi_1(\tilde{u}_1) \cdot \psi_2(\tilde{u}_2) \ldots \psi_{3M}(\tilde{u}_{3M}).$$

The nuclear vibration equation then becomes $\left[ -\frac{1}{2}\frac{d^2}{d\tilde{u}_k^2} + \frac{1}{2}\Lambda_{k,k}\tilde{u}_k^2 \right] \psi_k(\tilde{u}_k) = E_k \psi_k(\tilde{u}_k).$

Eigenvalues are $E_k = \left(m_k + \frac{1}{2}\right)\sqrt{\Lambda_{k,k}},$

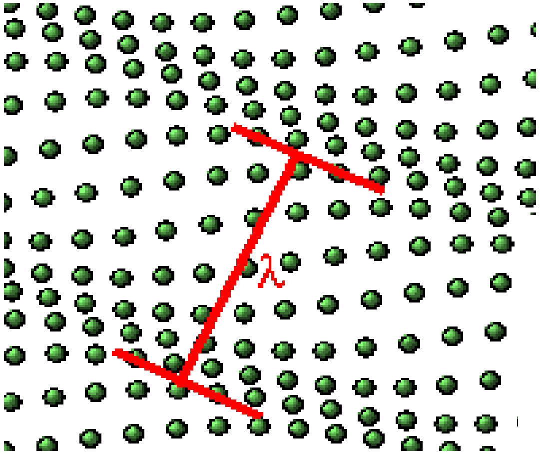
# Vibrations in infinite solids

Have an infinite number of atoms. Cannot apply previous analysis directly.

Just like we used the Block theorem (symmetry arguments) to reduce our computational domain, we utilize group symmetry arguments to reduce the infinite Hamiltonian

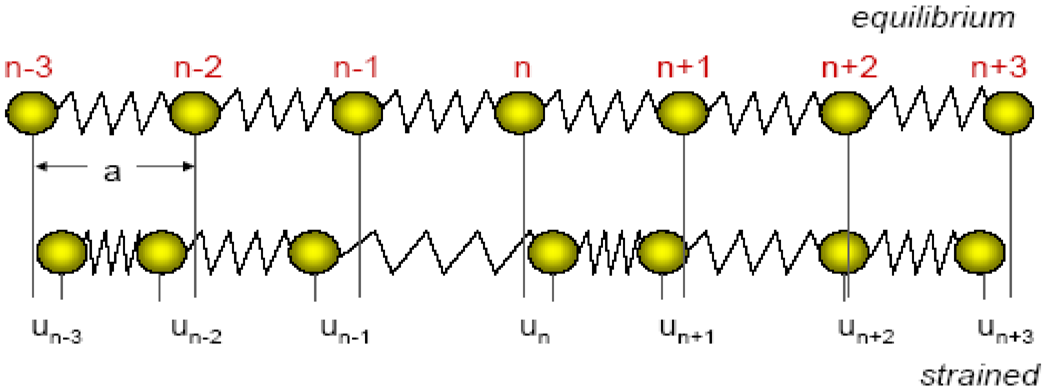
Phonons

**a phonon is a quantized mode of vibration occurring in a rigid crystal lattice**

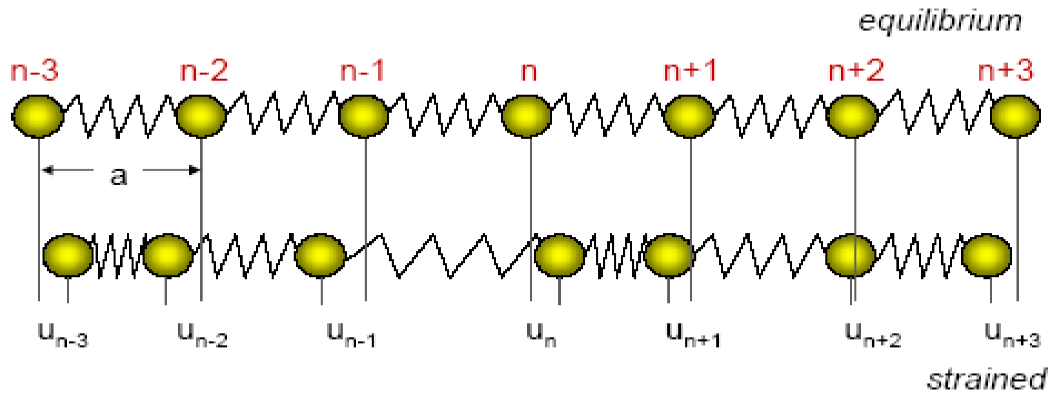


**Any vibration can be broken down into phonons: normal modes**

**Need to find the dispersion relationship**



# Phonons



$$\boxed{F[n,t] = -\left(\frac{\partial V}{\partial u[n,t]}\right)_{eq} = 0}$$

$$V(\{u[i,t]\}) = V_o + \cancel{\sum_{m=-\infty}^{\infty}\left(\frac{\partial V}{\partial u[m,t]}\right)_{\text{eq}} u[m,t]}$$

$$+\frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} u[n,t]\left(\frac{\partial^2 V}{\partial u[n,t]\,\partial u[m,t]}\right)_{\text{eq}} u[m,t]+\cdots$$

$$\Downarrow$$

$$\boxed{V(\{u[i,t]\}) = V_o+\frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} u[n,t]\left(\frac{\partial^2 V}{\partial u[n,t]\,\partial u[m,t]}\right)_{\text{eq}} u[m,t]+\cdots}$$

$$\boxed{V(\{u[i,t]\}) = V_o+\frac{1}{2}\sum_{n=-\infty}^{\infty}\sum_{m=-\infty}^{\infty} u[n,t]\widetilde{D}(n,m)u[m,t]}$$

# Phonons

Harmonic Matrix: $\widetilde{D}(n,m) = \left( \frac{\partial^2 V}{\partial u[n,t]\, \partial u[m,t]} \right)_{\text{eq}}$

$$V(\{u[i,t]\}) = V_o + \frac{1}{2} \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} u[n,t] \widetilde{D}(n,m) u[m,t]$$

Force on the jth atom

$$M \frac{d^2}{dt^2} u[j] = -\frac{\partial}{\partial u[j]} V(\{u[i]\})$$

Equations of motion

$$\boxed{M \frac{d^2}{dt^2} u[n,t] = -\sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) u[m,t]}$$

Assume time harmonic solutions

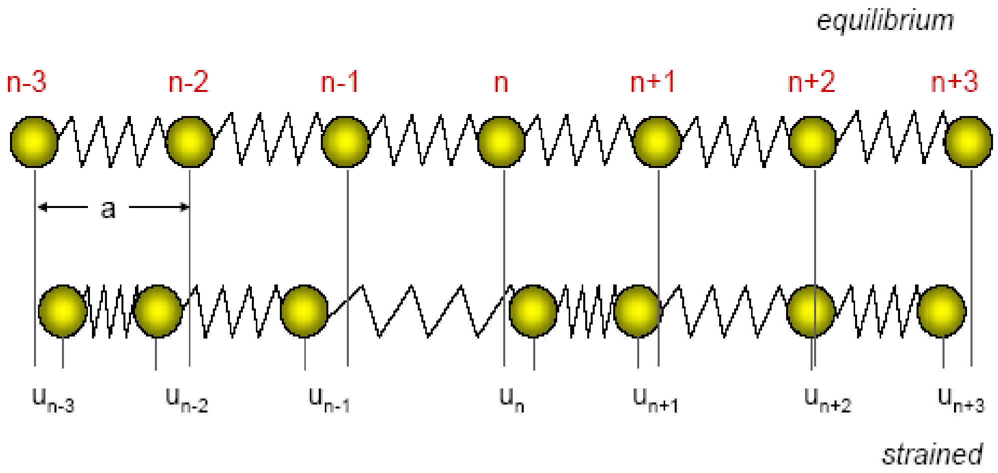
$$\boxed{M\omega^2 \tilde{U}[n] = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) \tilde{U}[m]}$$

$$\boxed{M\omega^2 = \sum_{m=-\infty}^{\infty} \widetilde{D}(n,m) e^{ika(m-n)}}$$

$$: \quad \underbrace{\sum_{p=-\infty}^{\infty} \widetilde{D}(p) e^{-ikap}}_{\text{Dynamical Matrix } D(k)}$$

$$\boxed{\omega = \sqrt{\frac{D(k)}{M}}}$$

# Phonons: Simpler example



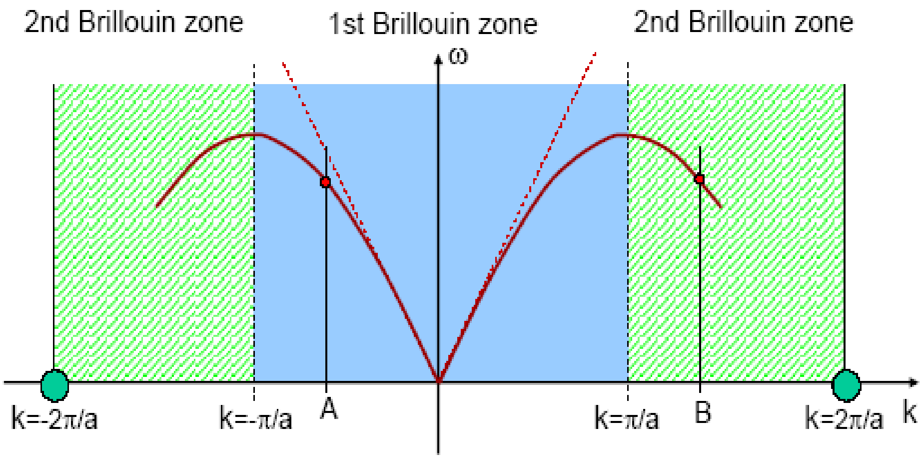
**Nearest neighbor interactions only**

$$V = \sum_{p=-\infty}^{\infty} \frac{\alpha}{2} (u[p+1] - u[p])^2$$

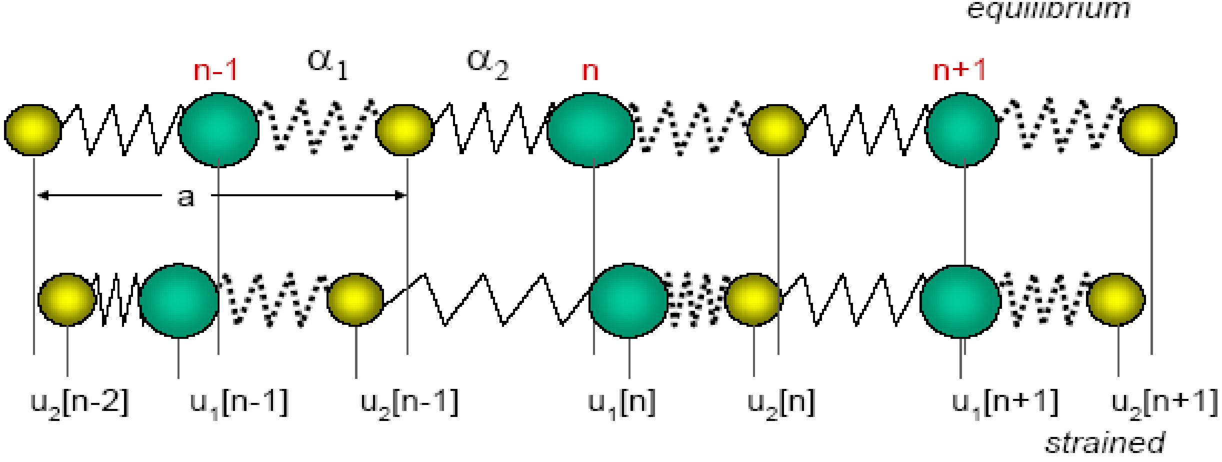
$$D(k) = 2\alpha - \alpha e^{-ika} - \alpha e^{ika}$$

$$= 2\alpha(1 - \cos ka) = 4\alpha \sin^2\left(\frac{ka}{2}\right)$$

$$\omega = 2\sqrt{\frac{\alpha}{M}}\left|\sin\left(\frac{ka}{2}\right)\right|$$

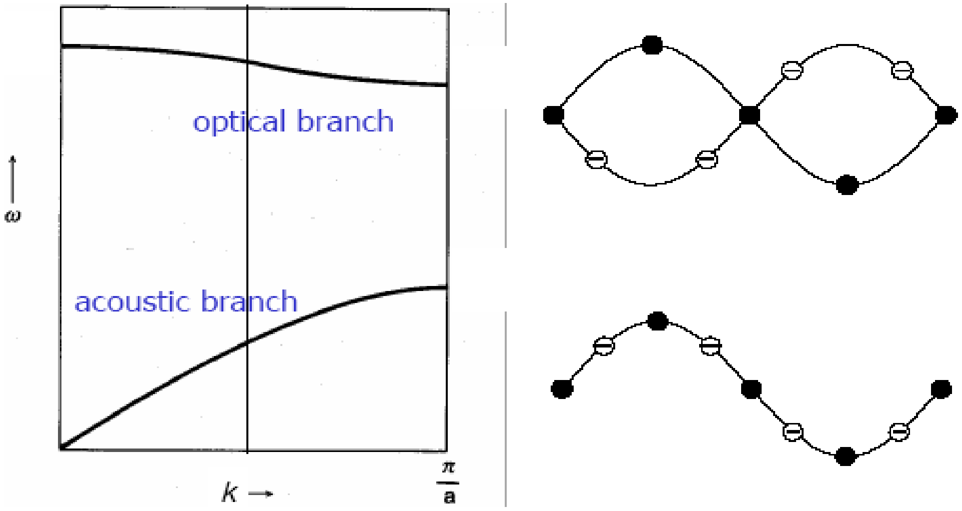


# Phonons: Another simple example



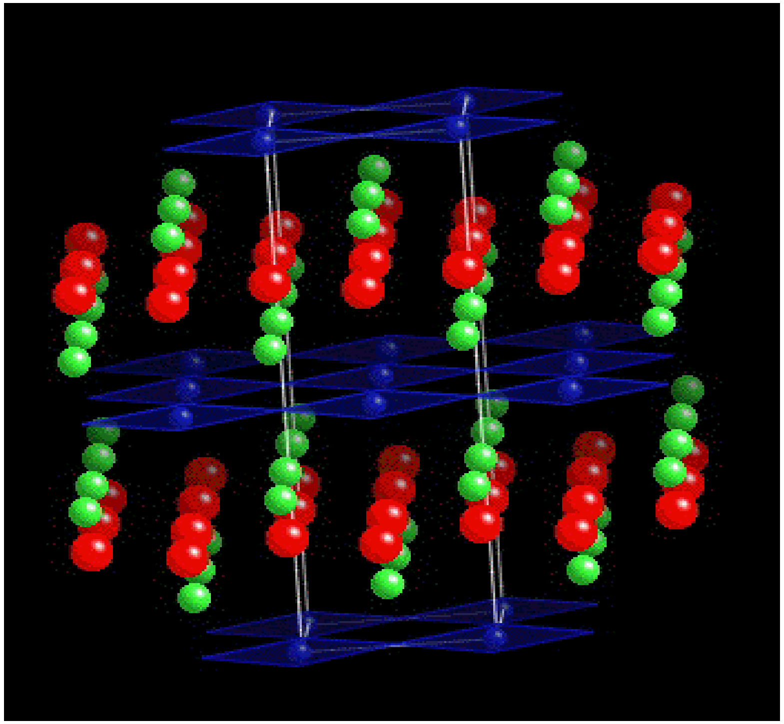
**Linear chain with Basis**

$$\omega^2 = \frac{\alpha_1+\alpha_2}{2}\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \left\{\frac{(\alpha_1+\alpha_2)^2\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2}{4} - \frac{2\alpha_1\alpha_2(1-\cos ka)}{M_1M_2}\right\}^{1/2}$$



**What about 3 D structures?**

# Vibrational energy addition



$$F(V,T)=U-TS,$$

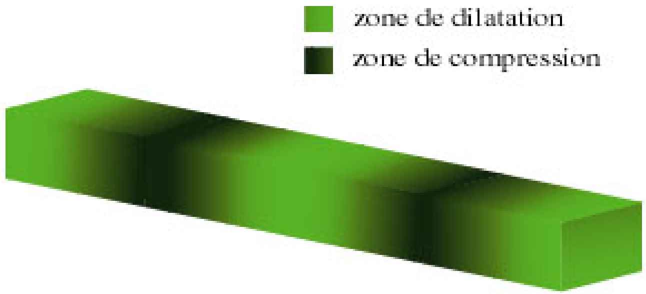
**To first order, assume that the atoms vibrate harmonically about their equilibrium positions**

$$F(V,T)=E(V)+F_{\text{vib}}(\omega,T)$$

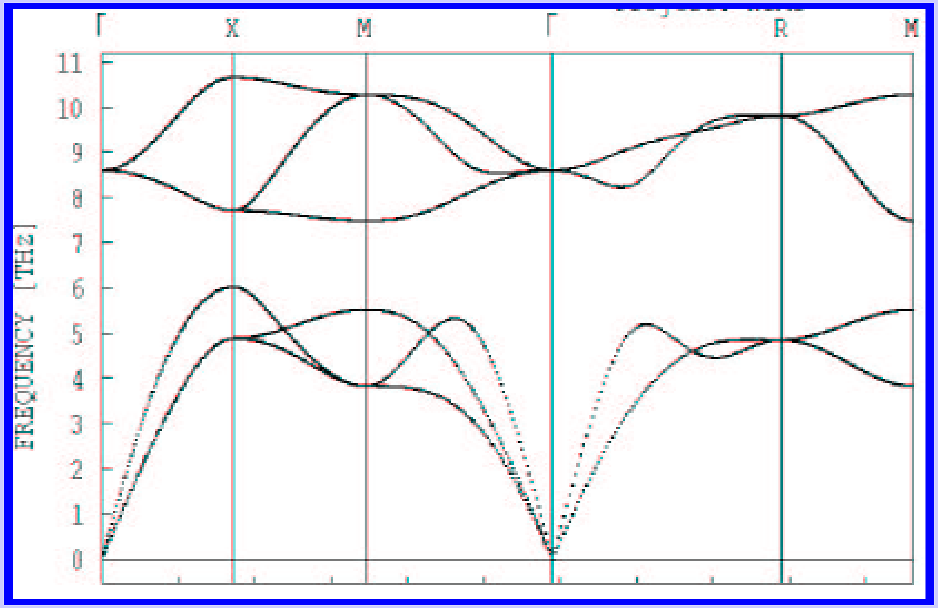
**Find all possible vibrational modes and compute the energy.**

$$\equiv E(V)+k_{\mathrm{B}}T\sum_{\mathbf{q}}\sum_{j}\ln\left\{2\sinh\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_{\mathrm{B}}T}\right)\right\},$$

$$\langle n_{k,s}\rangle=\frac{1}{\exp(\hbar\omega_{k,s}/k_BT)-1}$$



# What after Phonons?



**DOS: similar to electronic Density of states**

**Useful in inelastic neutron scattering and other characterization methods,**

**Raman spectrography**

**But more importantly:**

**MOST thermodynamic quantities depend on the phonon DOS**

# What after Phonons?

Internal energy:

$$E = \frac{1}{2} r \int_0^\infty d\omega\, g(\omega)\, (\hbar\omega)\, coth\left(\frac{\hbar\omega}{2k_BT}\right)$$

Free energy:

$$F = r k_B T \int_0^\infty d\omega\, g(\omega)\, ln\left[2 sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]$$

Entropy:

$$S = r k_B \int_0^\infty d\omega\, g(\omega) \left\{\left(\frac{\hbar\omega}{2k_BT}\right)\left[coth\left(\frac{\hbar\omega}{2k_BT}\right) - 1\right] - ln\left[1 - exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]\right\} \quad (79)$$

Heat capacity $C_v$:

$$C = r k_B \int_0^\infty d\omega\, g(\omega) \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[exp\left(\frac{\hbar\omega}{k_BT}\right) - 1\right]^2}$$

Thermal mean square displacement:

$$B_{ij}(\mu) = < U_i(\mu)\, U_j(\mu) >$$

$$B_{il}(\mu) = \frac{\hbar r}{2M_\mu} \int_0^\infty d\omega\, g_{il,\mu}(\omega)\, \frac{1}{\omega} coth\left(\frac{\hbar\omega}{2k_BT}\right)$$

**But .. Under the harmonic assumption (V = const)**

# Phonon calculations: Density functional approach

**Simple extension of DFT:**

- **The "frozen phonon" approach**
- **Similar to finite differences**
- **Perturb atom in unit cell to get specific k vector**
- **Estimate dynamical matrices**
- **Compute intensive**

**Recent developments in perturbation theory:**

**Density functional perturbation theory.**

# ‘Frozen’ phonon approach

In the T$^{th}$ unit cell given by $\vec{T}_{\vec{n}} = n_a \cdot \vec{a} + n_b \cdot \vec{b} + n_c \cdot \vec{c},$

denote the l$^{th}$ atom as $R_{l,\vec{n},\alpha}$

x,y,z

Displacement is given by $u_{l,\vec{n},\alpha} = R_{l,\vec{n},\alpha} - R^{e}_{l,\vec{n},\alpha}.$

Dynamical matrix $$\frac{1}{\sqrt{M_{l_1} M_{l_2}}} \frac{\partial^2 E_n}{\partial u_{l_1,\vec{n}_1,\alpha_1} \partial u_{l_2,\vec{n}_2,\alpha_2}}.$$

Similar to the case of electron wave functions, apply symmetry to displacements of atoms $$u^{\vec{k}}_{l,\alpha} = \sum_{\vec{n}} \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{T}_{\vec{n}}} u_{l,\vec{n},\alpha}.$$

Substitute and recompute Dynamical matrix $$\frac{1}{N} \frac{\partial^2 E(\vec{X}^e)}{\partial u^{\vec{k}*}_{l_1,\alpha_1} \partial u^{\vec{k}}_{l_2,\alpha_2}} = \sum_{\vec{n}} \frac{\partial^2 E(\vec{X}^e)}{\partial u_{l_1,\vec{n},\alpha_1} \partial u_{l_2,\vec{0},\alpha_2}} \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{T}_{\vec{n}}}$$

Reduced an infinite matrix to a series of finite matrices in k

Compute vibrational frequencies as a function of k

# ‘Frozen’ phonon approach

Calculation procedure:

- Consider a specific k
- Start with the structure with lowest total energy
- Consider all the independent displacements of the atoms specific to this k
- Calculate the change in energy and fit to the matrix

$$\frac{E}{N} = \frac{E_e}{N} + \frac{1}{2N} \sum_{l_1, l_2} \sum_{\alpha_1, \alpha_2 = x, y, z} \frac{\partial^2 E(\vec{X}^e)}{\partial u^{\vec{k}*}_{l_1, \alpha_1} \partial u^{\vec{k}}_{l_2, \alpha_2}} u^{\vec{k}*}_{l_1, \alpha_1} u^{\vec{k}}_{l_2, \alpha_2},$$

- Phonon energies computed from diagonalizing the dynamical matrix

This is not a trivial procedure, but has been automated to an extent

Can only be done for high symmetry points because of the large cell sizes to consider

# Linear Response theory

Small displacements of atoms,

The energy and potentials do not vary much (at least assumed)

Can we linearize energy variation about the minima w.r.t displacements?

Hellman-Feynman theorem

$$\frac{\mathrm{d}E_e}{\mathrm{d}\lambda_i} = \langle\Phi|\frac{\mathrm{d}\hat{H}}{\mathrm{d}\lambda_i}|\Phi\rangle = \int \rho(\vec{r})\frac{\mathrm{d}V(\vec{r})}{\mathrm{d}\lambda_i}\,\mathrm{d}\vec{r}.$$

Interested in second derivatives

$$\frac{\mathrm{d}^2E_e}{\mathrm{d}\lambda_i\mathrm{d}\lambda_j} = \int \left[\frac{\mathrm{d}\rho(\vec{r})}{\mathrm{d}\lambda_j}\frac{\mathrm{d}V(\vec{r})}{\mathrm{d}\lambda_i} + \rho(\vec{r})\frac{\mathrm{d}^2V(\vec{r})}{\mathrm{d}\lambda_i\mathrm{d}\lambda_j}\right]\mathrm{d}\vec{r}.$$

of energy. Including the nucleus - nucleus electrostatic energy

$$\frac{\mathrm{d}^2E_n}{\mathrm{d}\lambda_i\mathrm{d}\lambda_j} = \frac{\partial^2}{\partial\lambda_i\partial\lambda_j}\left[\frac{1}{2}\sum_{k\neq m=1}^{M}\frac{Z_kZ_m}{|\vec{R}_k-\vec{R}_m|}\right].$$

Displacing the nuclei will result in $\rho(\vec{r}) \to \rho(\vec{r}) + \Delta\rho(\vec{r}).$

$$V_{\mathrm{eff}}(\vec{r}) \to V_{\mathrm{eff}}(\vec{r}) + \Delta V_{\mathrm{eff}}(\vec{r})$$

Where

$$\Delta V_{\mathrm{eff}}(\vec{r}) = \Delta V_{\mathrm{n}}(\vec{r}) + \frac{1}{2}\int\frac{\Delta\rho(\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,\mathrm{d}\vec{r}\,' + \int\Delta\rho(\vec{r}\,')\cdot\frac{\delta V_{\mathrm{xc}}(\vec{r})}{\delta\rho(\vec{r}\,')}\,\mathrm{d}\vec{r}\,'.$$

and $\Delta\rho(\vec{r}) = \sum_i\left[|\psi_i(\vec{r})+\Delta\psi_i(\vec{r})|^2 - |\psi_i(\vec{r})|^2\right] \simeq 2\sum_i|\psi_i^*(\vec{r})\cdot\Delta\psi_i(\vec{r})|,$

This may now be solved self consistently

# Density functional perturbation theory

**Density functional perturbation theory (DFPT) is a particularly powerful and flexible theoretical technique that allows calculation of system responses to perturbation within the density functional framework,**

$$X(\lambda) = X^{(0)} + \lambda X^{(1)} + \lambda^2 X^{(2)} + \ldots$$

Basic premise

Variations upto first order term obtained by solving the *Sternheimer* equation

$$(H_{KS}^{(0)} - \epsilon_n^{(0)})|\psi_n^{(1)}\rangle = -(H_{KS}^{(1)} - \epsilon_n^{(1)})|\psi_n^{(0)}\rangle$$

Where the first order KS Hamiltonian

$$H_{KS}^{(1)} = T^{(1)} + v_{ext}^{(1)}(\mathbf{r}) + e^2 \int \frac{n^{(1)}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + \int \frac{\delta v_{xc}}{\delta n(\mathbf{r}')} n^{(1)}(\mathbf{r}') d\mathbf{r}'.$$

Hence, first order energy is …

$$\epsilon_n^{(1)} = \langle\psi_n^{(0)}|H_{KS}^{(1)}|\psi_n^{(0)}\rangle.$$

… and first order change in the wave function

$$\psi_n^{(1)}\rangle = \sum_{m \neq n} C_{nm}^{(1)}|\psi_m^{(0)}\rangle$$

$$C_{nm}^{(1)} = \frac{\langle\psi_m^{(0)}|H_{KS}^{(1)}|\psi_n^{(0)}\rangle}{\epsilon_n^{(0)} - \epsilon_m^{(0)}}.$$

First order electron density is

$$n^{(1)}(\mathbf{r}) = \sum_{n=1}^{N} \psi_n^{(0)\star}(\mathbf{r})\psi_n^{(1)}(\mathbf{r}) + \psi_n^{(1)\star}(\mathbf{r})\psi_n^{(0)}(\mathbf{r})$$

**Self Consistent Perturbed Equations**

The computational cost of solving this system of linear equations is comparable to that required to solve the zeroth order Kohn-Sham equations

# Density functional perturbation theory

Energy can be written as

$$E_{tot}(\Delta\tau) = E_{tot}^{(0)} + \sum_{a\kappa\alpha}\sum_{b\kappa'\beta}\frac{1}{2}\left(\frac{\partial^2 E_{tot}}{\partial\tau^a_{\kappa\alpha}\partial\tau^b_{\kappa'\beta}}\right)\Delta\tau^a_{\kappa\alpha}\Delta\tau^b_{\kappa'\beta} + \dots$$

Force, truncated to two orders

$$F^{ab}_{\kappa\alpha} = -\sum_{\kappa',\beta} C_{\kappa\alpha,\kappa'\beta}(a,b)\Delta\tau^b_{\kappa'\beta}$$

**FFT**

$$\tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \frac{1}{N}\sum_{ab} C_{\kappa\alpha,\kappa'\beta}(a,b)e^{-i\mathbf{q}\cdot(\mathbf{R}_a-\mathbf{R}_b)}$$

**The dynamical matrix**

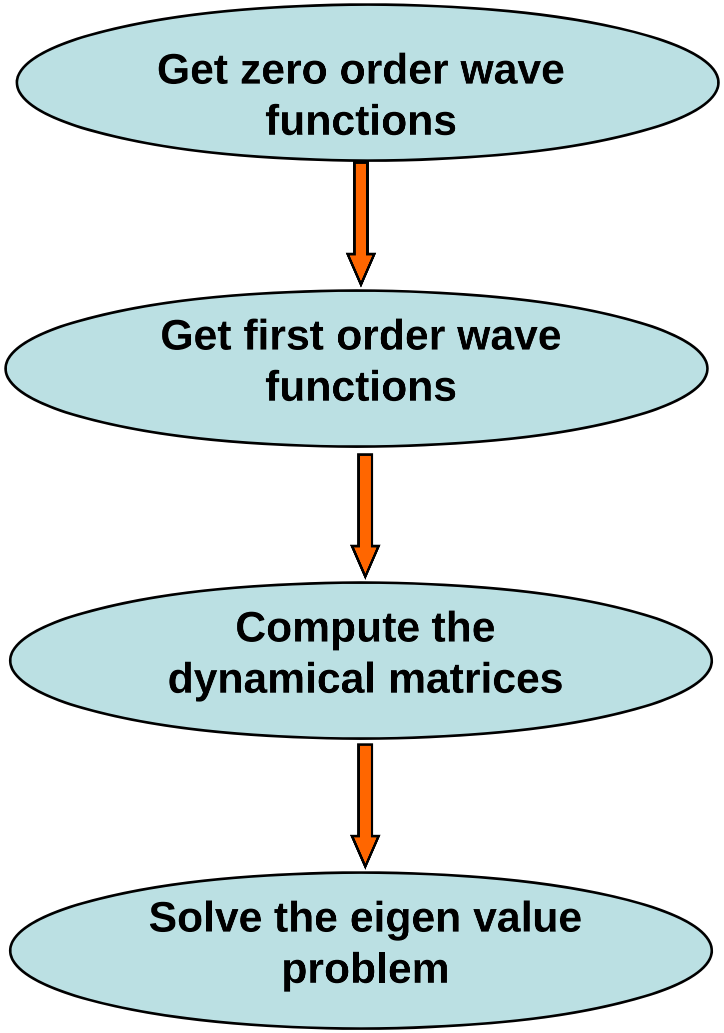
$$\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q}) = \tilde{C}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})/(M_\kappa M_{\kappa'})^{1/2}.$$

$$\sum_{\kappa',\beta}\tilde{D}_{\kappa\alpha,\kappa'\beta}(\mathbf{q})e_{m\mathbf{q}}(\kappa',\beta) = \omega^2_{m\mathbf{q}}e_{m\mathbf{q}}(\kappa\alpha)$$

**Phonon dispersion relation**

Applicable to arbitrary k vectors

# Numerical details



**Get zero order wave functions**

**SCF calculation, PW.x**

**‘2n+1’ theorem**

**Get first order wave functions**

**nSCF calculation, PW.x**

**Compute the dynamical matrices**

**In momentum space, PH.x**

**Solve the eigen value problem**

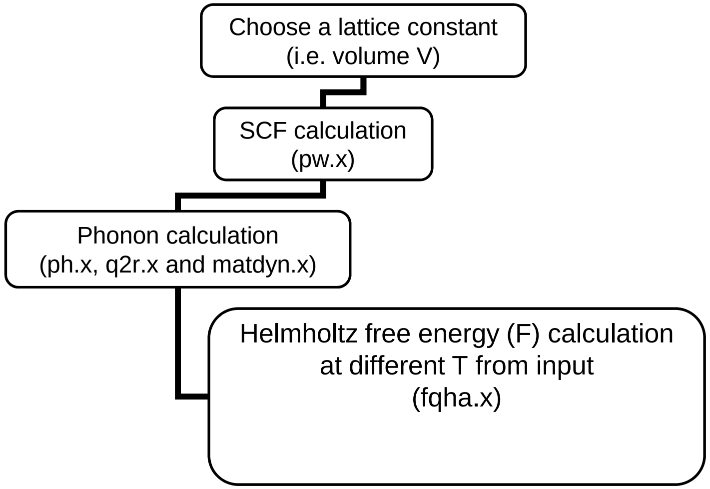
# Illustrative example

Find the bulk modulus of Cu at 300 K

Instead of free energy must use Helmholtz free energy

$$F(T,V) = E_{LDA}(V) + k_B T \sum_{\mathrm{q}j} \ln\{2 \sinh \frac{h\varpi_{\mathrm{q}j}(V)}{4\pi k_B T}\}$$

where the first term is the energy of the static lattice at a given volume V and the second term includes the phonon frequency. $w_{\mathbf{q}j}(V)$ indicates the frequency of the jth phonon band at the point **q** in the Brillioum zone.



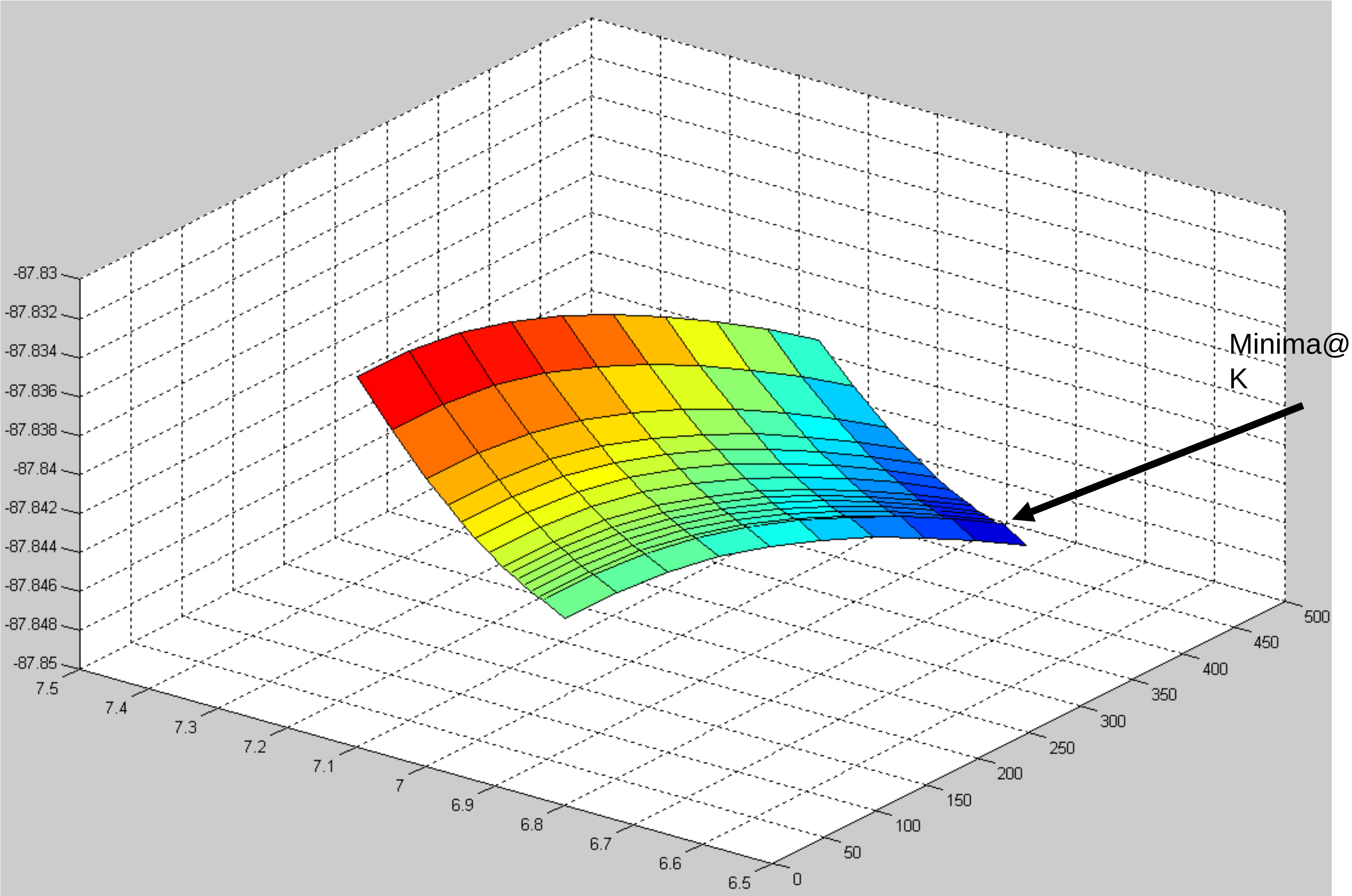
Choose a lattice constant
(i.e. volume V)

SCF calculation
(pw.x)

Phonon calculation
(ph.x, q2r.x and matdyn.x)

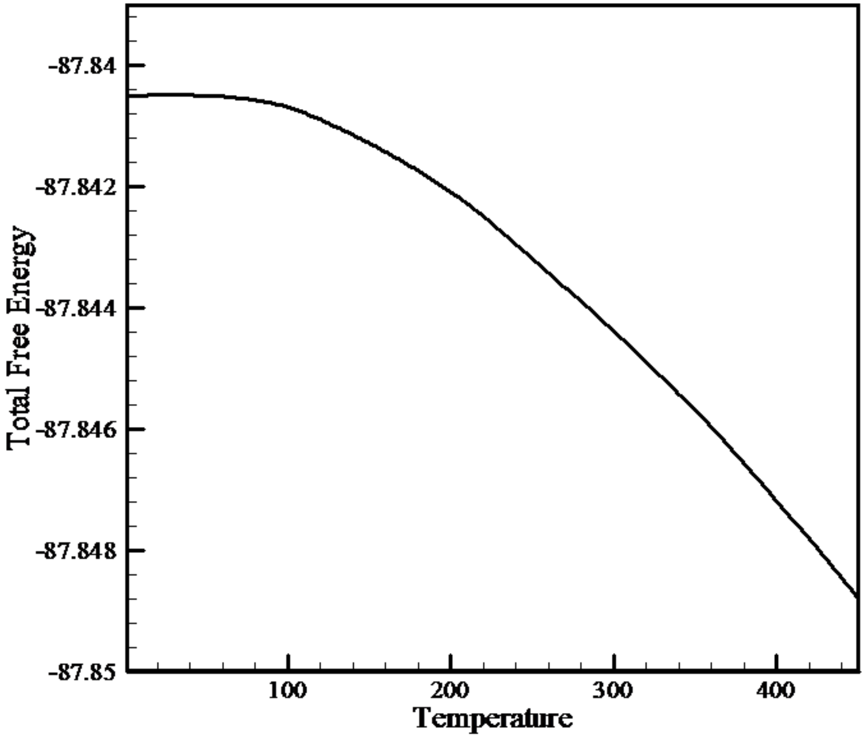
Helmholtz free energy (F) calculation
at different T from input
(fqha.x)

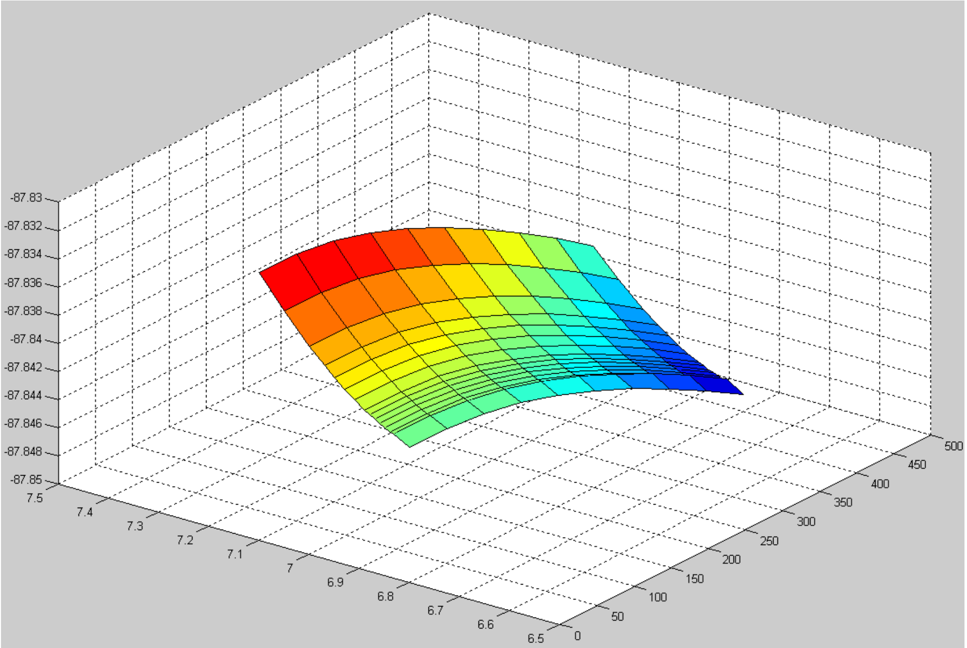
# Total Helmholtz energy



Minima@300 K

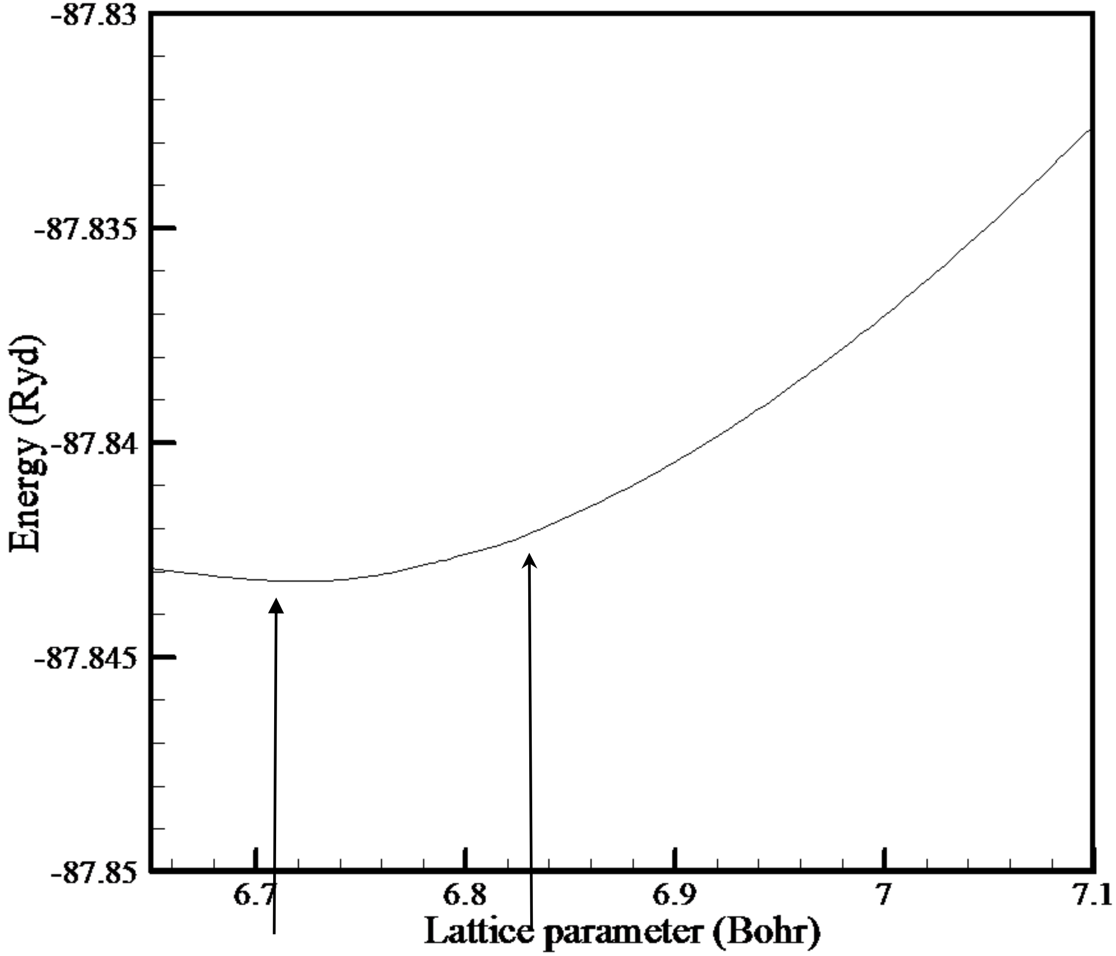
# Total minimum Helmholtz energy



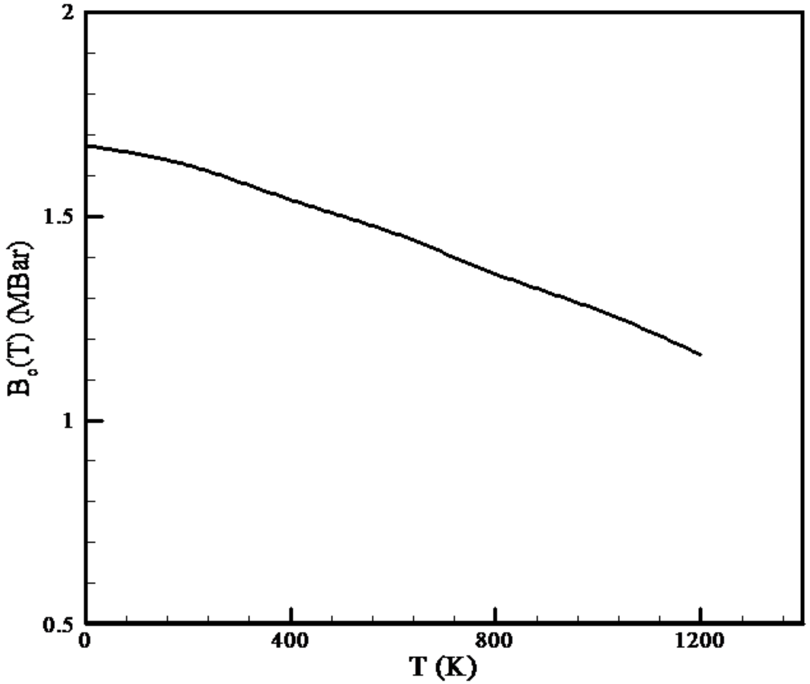


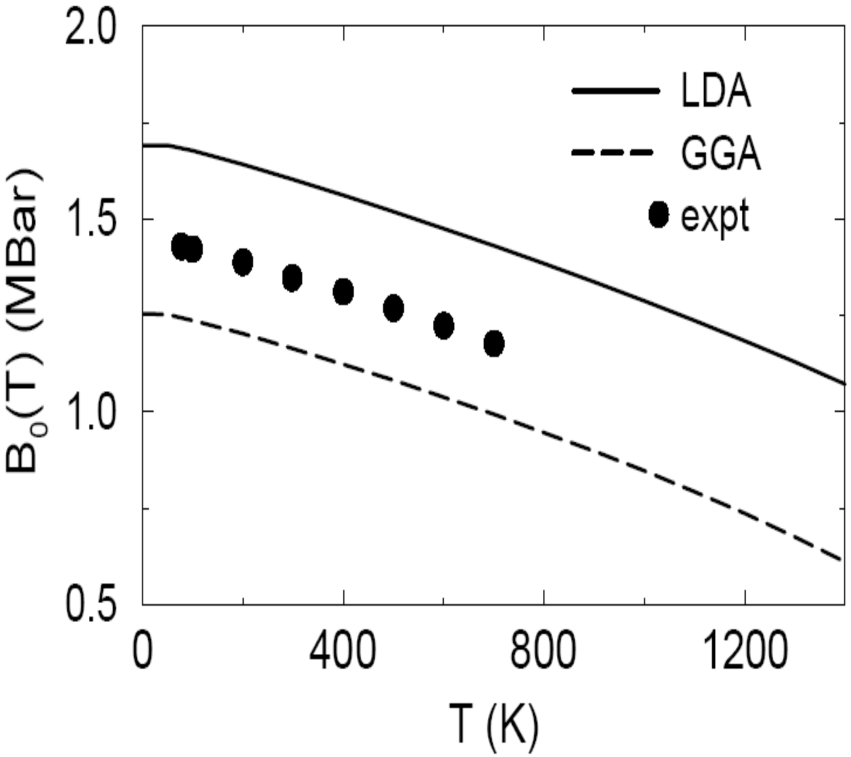
# Numerical Examples

**Copper: Variation of E (0 K) with lattice parameter**

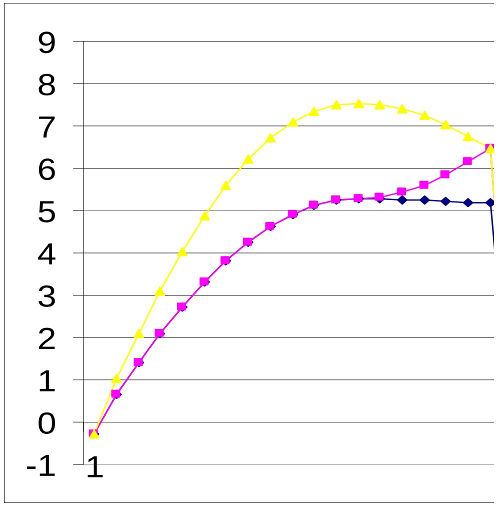


# Bulk Modulus

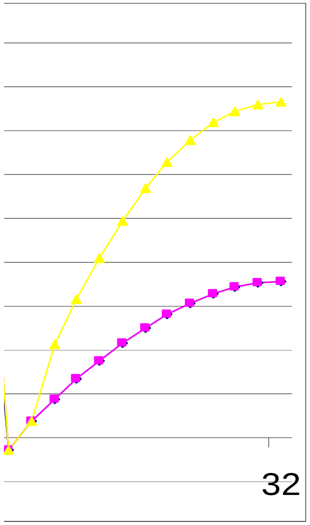


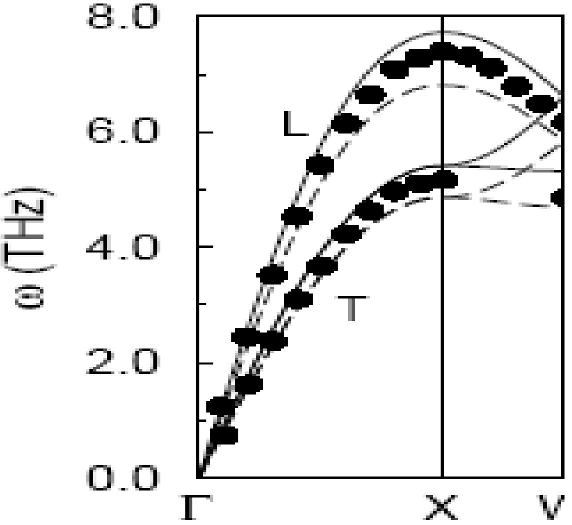


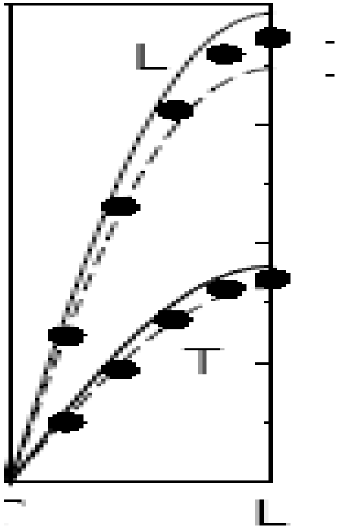
# Phonon dispersion relationships



All values match with LDA by **arXiv:cond-mat/0109020 v1 3 Sep 2001**

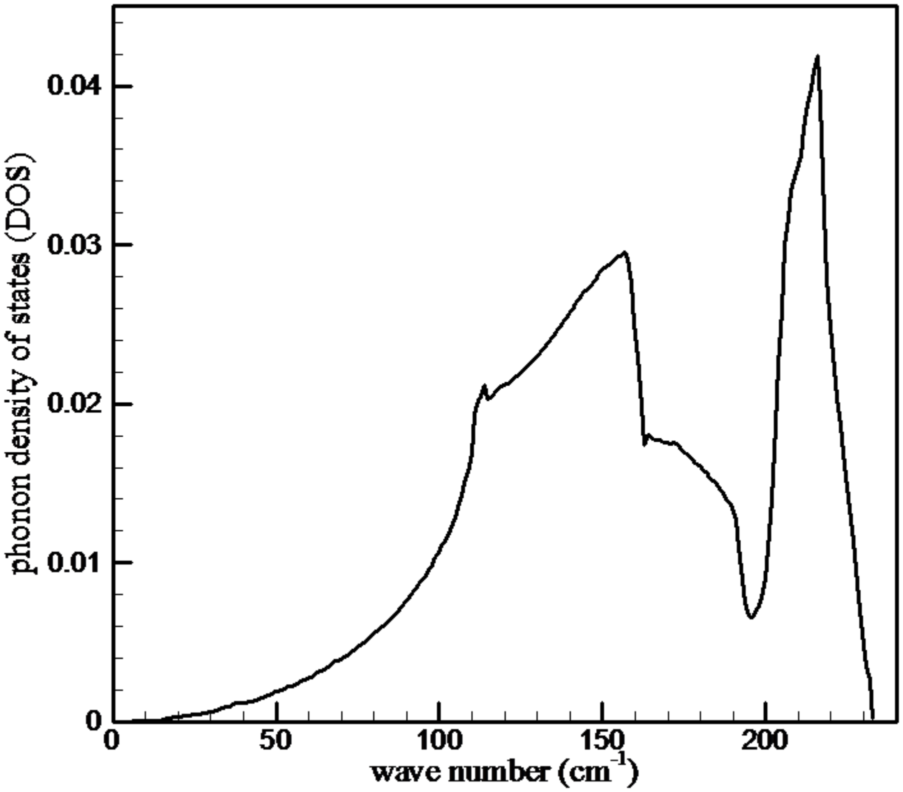




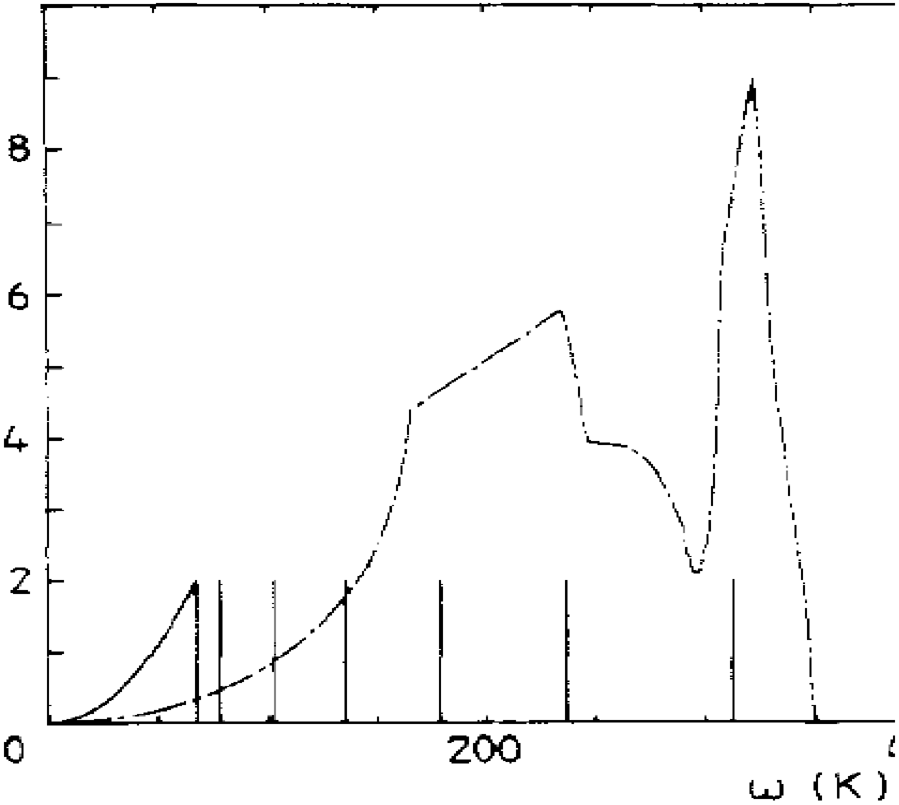


# Phonon Density of States (P-DOS)

**Used q2r.x and matdyne.x to get density of states**



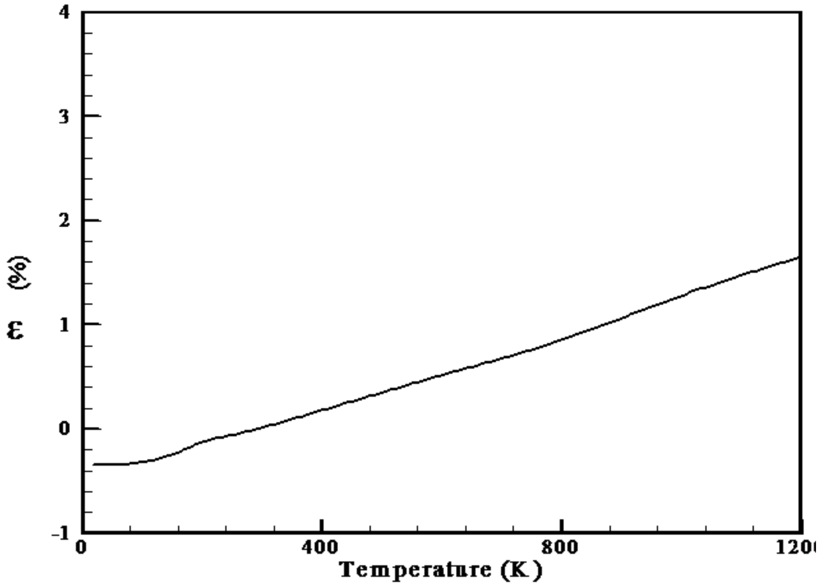
Phonon Frequencies in Copper at 49 and 298°K*

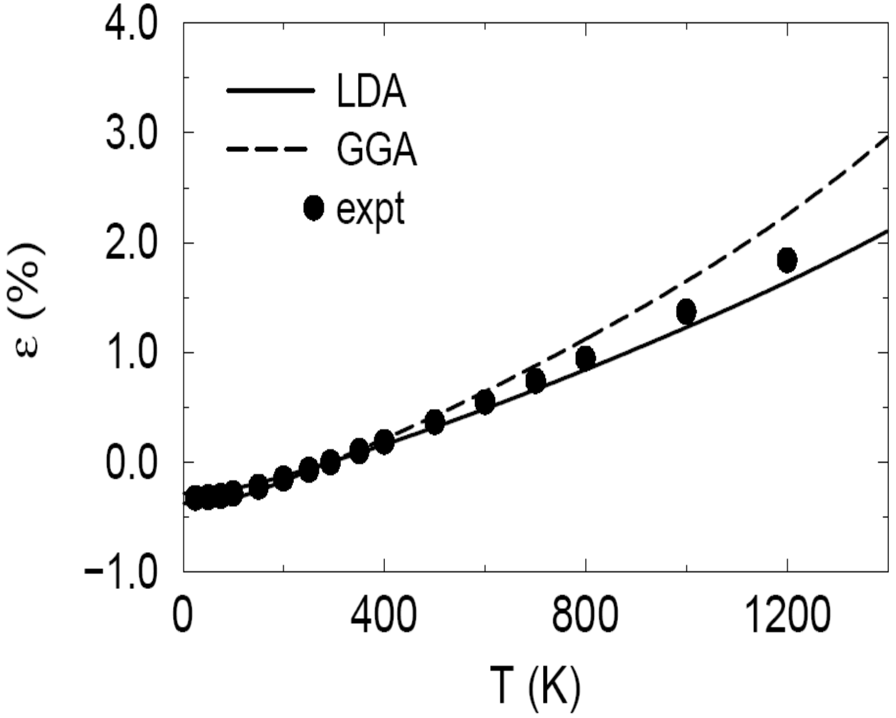


**Phys Rev, 164, 1967**

# Thermal expansion

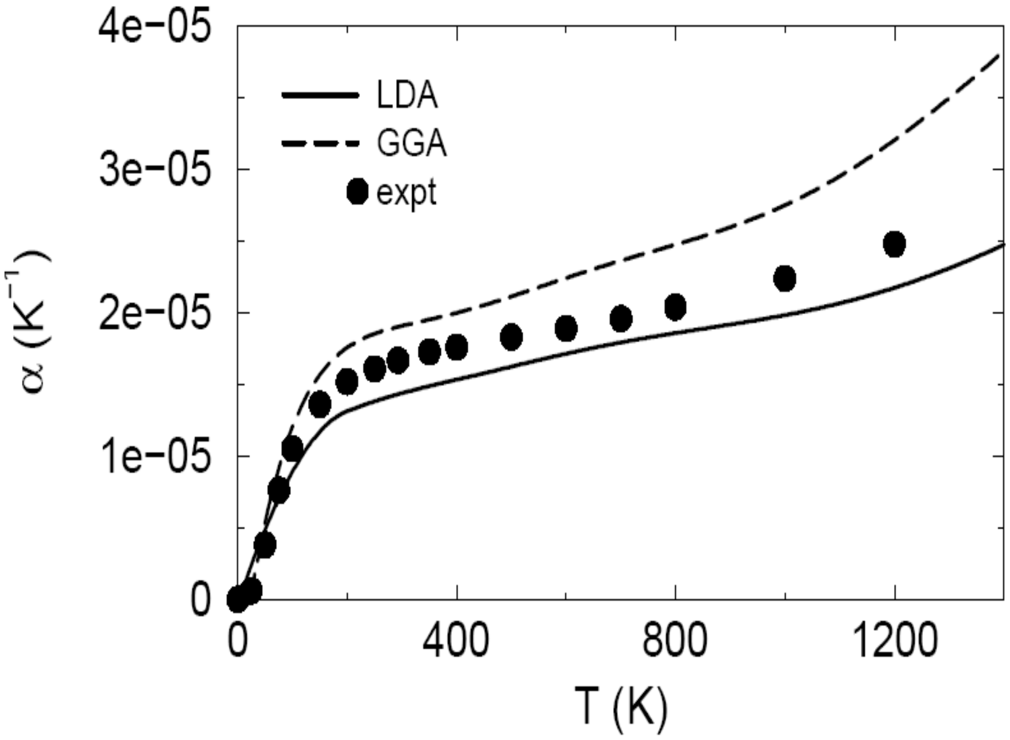
$$\epsilon(T) = \frac{a_0(T) - a_0(T_c)}{a_0(T_c)},$$

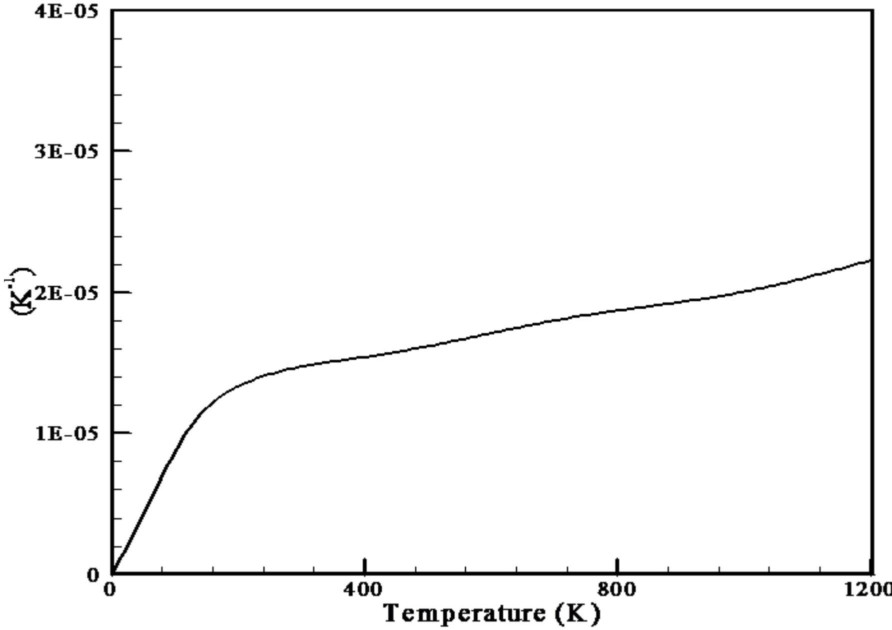




# Linear expansion

$$\alpha(T) = \frac{1}{a_0(T_c)}\left(\frac{da_0(T)}{dT}\right).$$





# Specific heat

$$C_V^{\mathrm{ph}}(T) = \sum_{\mathbf{q}\lambda} C_v(\mathbf{q}\lambda) = k_B \sum_{\mathbf{q}\lambda} \left( \frac{\hbar\omega_{\mathbf{q}\lambda}(a_0(T))}{2k_B T} \right)^2 \sinh^{-2}\left( \frac{\hbar\omega_{\mathbf{q}\lambda}(a_0(T))}{2k_B T} \right).$$