

The influence of long range strain fields on phonon frequencies

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Abstract

The document outlines a theoretical framework for an ab initio based method for studying the influence of long range strain fields on phonon frequencies, dispersions, and density of states. For long range strain fields which vary slowly with position, we can make a 'local homogeneous strain' approximation, and apply the Gruneisen tensor obtained via DFT to linear elasticity theory and even analytical scattering theories (i.e. Fermi's Golden Rule). This allows us to extract first order physical mechanisms of the influence of long range strain fields on phonons. This methodology would be able to treat cases that can not be computed exclusively with a DFT simulation due to supercell size restrictions.

1 Outline of theory

1.1 Strain and the Gruneisen tensor

We define the phonon Gruneisen tensor following Wallace (Eq. 11.74) [2]

$$\gamma_{ij}(\mathbf{k}, s) = -\frac{\partial \ln \omega(\mathbf{k}, s)}{\partial \epsilon_{ij}}, \quad (1)$$

where $\omega(\mathbf{k}, s)$ are the phonon frequency at wave vector \mathbf{k} and polarization s . ϵ_{ij} are the components of the symmetric strain tensor as defined by Nye (pg. 98) [1]. If a unit volume within the material is displaced by u_i then the change in u_i with x_j is

$$e_{ij} = \frac{du_i}{dx_j}; \quad (2)$$

which I call deformations, to distinguish them from strain which has a symmetric tensor. e_{ij} is not necessarily symmetric. The strain tensor is by definition symmetric and is defined as,

$$\epsilon_{ij} = \frac{1}{2}(e_{ij} + e_{ji}). \quad (3)$$

The antisymmetric portion of $[e_{ij}]$ is the rotation

$$\eta_{ij} = -\frac{1}{2}(e_{ij} - e_{ji}) = -\eta_{ji} \quad (4)$$

and is by definition antisymmetric. I believe we would only consider a rotation to change phonon frequencies through the anisotropy of the phonon dispersion (different frequencies and group velocities in different directions) not through anharmonicity and third order force constants. I know this is rigorously true for cubic materials not sure about other symmetries. Thus, for PbTe we will only consider ϵ_{ij} . A change in volume is described by the trace of ϵ_{ij} , $Tr(\epsilon_{ij})$ or in Einstein notation ϵ_{kk} . When considering only hydrostatic strains we can write, from Eq. 1

$$\gamma_V(\mathbf{k}, s) = -\frac{V}{\omega(\mathbf{k}, s)} \frac{d\omega(\mathbf{k}, s)}{dV}, \quad (5)$$

where the subscript 'V' indicates that we are only considering a change in volume. As we will discuss later, when applied to dislocations, there is zero strain in one dimension along the line of the dislocation, and the strain state contains shear components, thus we will need to use γ_{ij} . The strains required to construct γ_{ij} are shown in 1. The part I haven't figured out yet is how to define the phonons for all of the cases shown in 1 in a consistent way, since these strain are symmetry breaking. Even if this becomes a more fundamental problem, a simple phonon density of states output would be very useful and a lot could be learned. Maybe this is a good place to start.

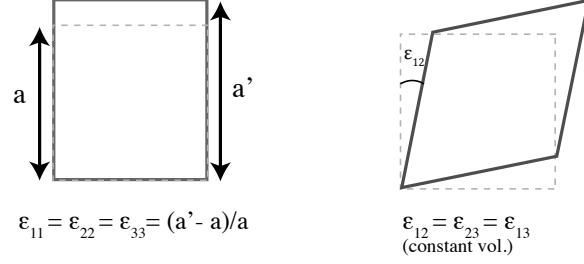


Figure 1: Illustrations of ϵ_{ij} . The simulations for positive and negative $\epsilon_{11} = \epsilon_{22} = \epsilon_{33}$ will be distinct, where the simulations for positive and negative $\epsilon_{12} = \epsilon_{23} = \epsilon_{13}$ will be identical, except for a rotation of the lattice.

1.2 Long range strain approximation

At low strain we can rewrite

$$\omega(\mathbf{k}, s) = \omega_0(\mathbf{k}, s) (1 - \gamma_{ij}(\mathbf{k}, s) \epsilon_{ij}) . \quad (6)$$

Now we say that the strain induced is a long-ranged, slowly varying strain fields and are a function of position \mathbf{r} such that

$$\omega(\mathbf{k}, s, \mathbf{r}) = \omega_0(\mathbf{k}, s) (1 - \gamma_{ij}(\mathbf{k}, s) \epsilon_{ij}(\mathbf{r})) . \quad (7)$$

Thus, we can perform a volumetric average of the phonon frequencies

$$\omega(\mathbf{k}, s) = \frac{\omega_0(\mathbf{k}, s)}{V} \int (1 - \gamma_{ij}(\mathbf{k}, s) \epsilon_{ij}(\mathbf{r})) d^3\mathbf{r} . \quad (8)$$

In order to compute this, γ_{ij} and ϵ_{ij} need have a consistent definition of axes. So when computing $\gamma_{ij}(\mathbf{k}, s)$ for a cubic system such as PbTe, the cubic space group should be used rather than the primitive unit cell. Now, if we consider the case of positive shear strain, ϵ_{12} , and assume that γ_{12} is positive meaning the phonon frequency shifts down for the \mathbf{k}, s we care about. Now, imagine we apply the same shear strain but negative, these two strain states are identical (except for a rotation of the crystal) so the phonon frequency shift is the same. Thus, since $d\epsilon_{12}$ is negative in this case γ_{12} is negative as well. Consequently, if phonon frequencies shift down with increased shear strain (as they are expected too thermodynamically, at least on average), then the product $\gamma_{12}\epsilon_{12}$ will always be positive, since γ_{12} and ϵ_{12} show change sign together. The same is not true for $\gamma_{11}\epsilon_{11}$. Thus, if we have a system with equal amounts of positive and negative hydrostatic and shear strain, the hydrostatic strain is not expected to reduce the average phonon frequency while the shear strain is.

References

- [1] John Nye. *Physical Properties of Crystals: Their Representation by Tensors and Matrices*. Clarendon Press, 1985.
- [2] Duane C. Wallace. *Thermodynamics of Crystals*. 1972.