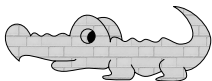


# Thermal expansion of graphene beyond the quasiharmonic approximation

Jonathan Lloyd-Williams



UNIVERSITY OF  
CAMBRIDGE

Electronic Structure Discussion Group  
Cambridge – 6th April 2016

# Introduction

- ▶ The physical properties of graphene make it a good candidate material for the next generation of electronic devices and heat management systems.
- ▶ Knowledge of the lattice parameter as a function of temperature is required for such applications.
- ▶ Experimental measurements are inconclusive and there is significant discrepancy between different theoretical calculations.

# The thermodynamics of deformation (i)

- ▶ The fundamental thermodynamic relation for deformed bodies is

$$d\mathcal{U} = TdS + \Omega\sigma_{ij}d\epsilon_{ij} ,$$

where  $\mathcal{U}$  is the internal energy,  $T$  is the temperature,  $S$  is the entropy,  $\Omega$  is the volume,  $\sigma$  is the stress tensor, and  $\epsilon$  is the strain tensor.

- ▶ The differential Gibbs free energy  $d\mathcal{G}$  of a system subject to fixed external stress  $\sigma^{\text{ext}}$  is

$$d\mathcal{G} = d\mathcal{F} - \Omega\sigma_{ij}^{\text{ext}}d\epsilon_{ij} ,$$

where  $\mathcal{F}$  is the Helmholtz free energy.

- ▶ At constant temperature, the equilibrium configuration of the system is found by minimising the Gibbs free energy with respect to variations in strain.

## The thermodynamics of deformation (ii)

- ▶ Within the Born-Oppenheimer approximation, the Helmholtz free energy is a sum of electronic and vibrational terms.
- ▶ Using the definition of the stress tensor, we have

$$d\mathcal{F}^{\text{elec}} = \Omega \sigma_{ij}^{\text{elec}} d\epsilon_{ij},$$

where  $\sigma^{\text{elec}}$  is the electronic contribution to the internal stress, and

$$d\mathcal{F}^{\text{vib}} = \Omega \sigma_{ij}^{\text{vib}} d\epsilon_{ij},$$

where  $\sigma^{\text{vib}}$  is the vibrational contribution to the internal stress.

- ▶ Therefore, equilibrium is reached when the internal and external stresses balance,

$$\sigma^{\text{elec}} + \sigma^{\text{vib}} = \sigma^{\text{ext}}.$$

# The quasiharmonic approximation

- ▶ The vibrational free energy in the harmonic approximation is given by

$$\mathcal{F}^{\text{vib}} = \frac{1}{2} \sum_{n,\mathbf{k}} \omega_{n\mathbf{k}} + \frac{1}{\beta} \sum_{n,\mathbf{k}} \ln \left( 1 - e^{-\beta \omega_{n\mathbf{k}}} \right),$$

where  $\beta$  is the inverse temperature and  $\omega_{n\mathbf{k}}$  is the frequency of the phonon with branch index  $n$  at wave vector  $\mathbf{k}$ .

- ▶ In a perfectly harmonic crystal, the phonon frequencies are independent of volume, so thermal expansion is an intrinsically anharmonic phenomenon.
- ▶ In the quasiharmonic approximation, we assume that the harmonic approximation holds at all volumes.

## Thermal expansion tensor (i)

- ▶ In general, thermal expansion is described by a tensor  $\alpha$  whose components are given by

$$\alpha_{ij} = \left( \frac{\partial \epsilon_{ij}}{\partial T} \right)_{\sigma} .$$

- ▶ This can be rewritten as

$$\alpha_{ij} = - \left( \frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_T \left( \frac{\partial \sigma_{kl}}{\partial T} \right)_{\epsilon} ,$$

where

$$S_{ijkl} = \left( \frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \right)_T$$

are the components of the so-called elastic compliance tensor.

## Thermal expansion tensor (ii)

- ▶ Within the harmonic approximation, it can be shown that

$$\left( \frac{\partial \sigma_{kl}}{\partial T} \right)_{\epsilon} = \sum_{n, \mathbf{k}} \frac{c_{n\mathbf{k}}}{\omega_{n\mathbf{k}}} \left( \frac{\partial \omega_{n\mathbf{k}}}{\partial \epsilon_{kl}} \right),$$

where  $c_{n\mathbf{k}}$  is the contribution of the phonon with branch index  $n$  at wave vector  $\mathbf{k}$  to the specific heat.

- ▶ Therefore, we can write the components of  $\alpha$  as

$$\alpha_{ij} = \sum_{n, \mathbf{k}} S_{ijkl} \gamma_{kl n \mathbf{k}} c_{n\mathbf{k}},$$

where the

$$\gamma_{kl n \mathbf{k}} = -\frac{1}{\omega_{n\mathbf{k}}} \left( \frac{\partial \omega_{n\mathbf{k}}}{\partial \epsilon_{kl}} \right)$$

are referred to as Grüneisen parameters.

## Grüneisen formalism

- ▶ Graphene has one free lattice parameter  $a$  whose temperature dependence is characterised by the linear thermal expansion coefficient

$$\alpha = \frac{1}{a} \left( \frac{\partial a}{\partial T} \right)_{\sigma}.$$

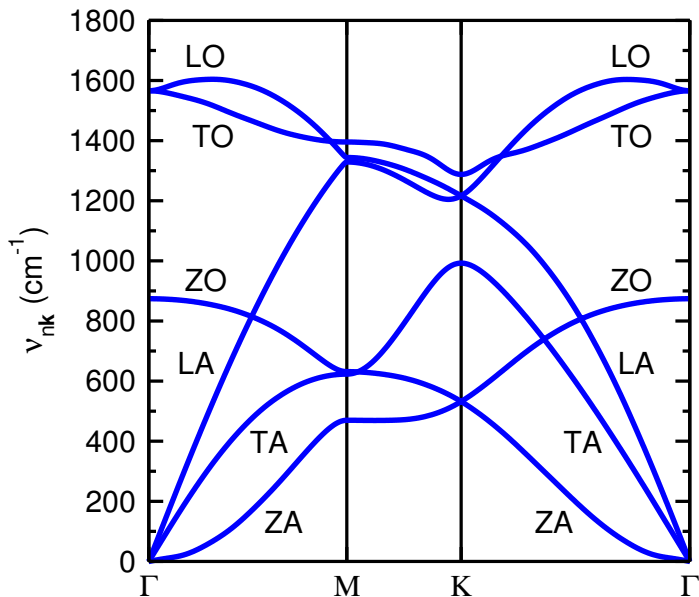
- ▶ The phonon frequencies are assumed to be linear functions of the lattice parameter and the Grüneisen parameters are given by

$$\gamma_{n\mathbf{k}} = - \left. \frac{a}{\omega_{n\mathbf{k}}} \right|_0 \left( \frac{\partial \omega_{n\mathbf{k}}}{\partial a} \right)_0,$$

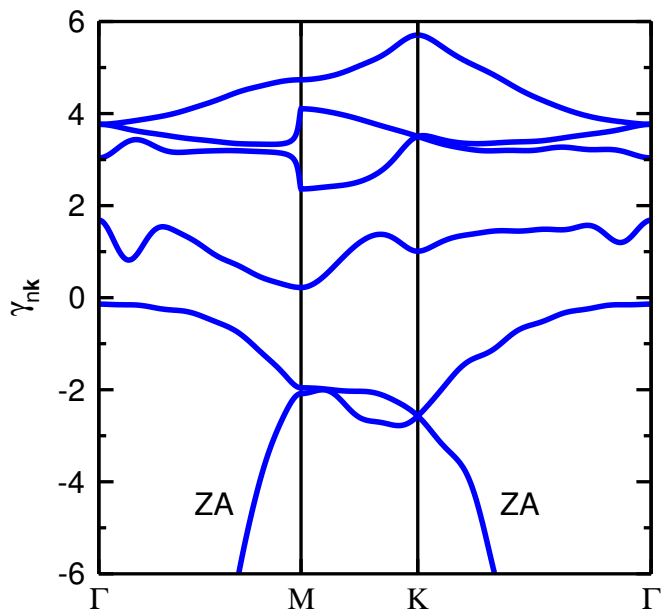
where the subscript 0 indicates a quantity evaluated at the static lattice parameter  $a_0$ .



# Phonon dispersion



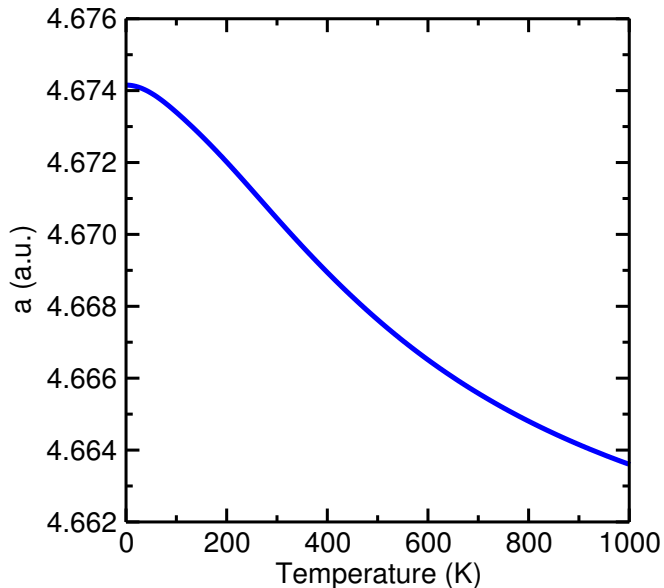
# Grüneisen parameters



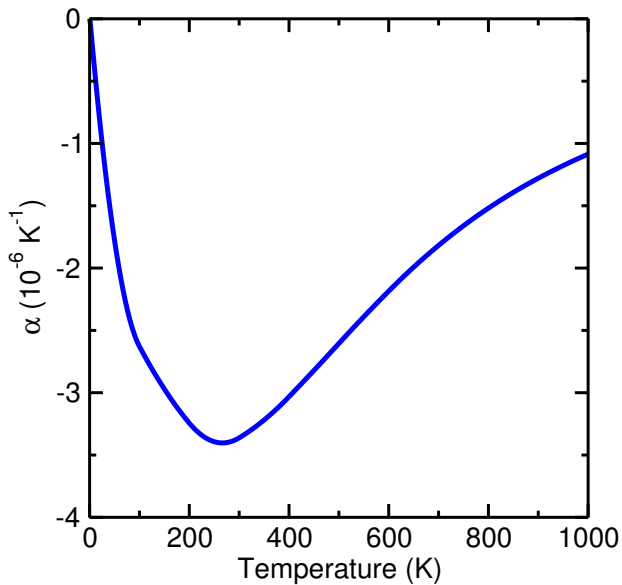
## Direct minimisation of the free energy

- ▶ An obvious limitation of the Grüneisen formalism is the assumption that the phonon frequencies are linear functions of the lattice parameter.
- ▶ Instead, we can calculate the Helmholtz free energy at several different values of the lattice parameter and use it to determine the Gibbs free energy.
- ▶ Direct minimisation of the Gibbs free energy with respect to the lattice parameter provides the equilibrium structure at any temperature.
- ▶ We could calculate the vibrational Helmholtz free energy using a more accurate method than the quasiharmonic approximation.
- ▶ In general, this approach is restricted to highly symmetric systems with only one or two free lattice parameters.

## Quasiharmonic lattice parameter



## Quasiharmonic thermal expansion coefficient



## The vibrational stress tensor from first principles (i)

- ▶ The stress tensor of a system described by a Hamiltonian  $\hat{H}$  is

$$\sigma_{ij} = \frac{1}{\mathcal{Z}} \sum_s \frac{1}{\Omega} \frac{\partial \langle \Phi_s | \hat{H} | \Phi_s \rangle}{\partial \epsilon_{ij}} e^{-\beta E_s},$$

where  $\mathcal{Z}$  is the partition function and  $|\Phi_s\rangle$  is an eigenstate of  $\hat{H}$  with energy  $E_s$ .

- ▶ The vibrational Hamiltonian is given by

$$\hat{H}^{\text{vib}} = \sum_{\kappa, \lambda} \frac{1}{2m_{\kappa}} \hat{\mathbf{p}}_{\kappa\lambda}^2 + V_{\text{BO}},$$

where  $\hat{\mathbf{p}}_{\kappa\lambda}$  is the momentum of the  $\kappa$ th atom in the  $\lambda$ th primitive cell and  $V_{\text{BO}}$  is the Born-Oppenheimer potential energy surface.

## The vibrational stress tensor from first principles (ii)

- ▶ The contribution to the vibrational stress tensor from the kinetic energy part of the vibrational Hamiltonian is

$$\sigma_{ij}^{\text{vib,kinetic}} = -\frac{1}{\mathcal{Z}} \sum_s \frac{1}{\Omega} \left\langle \Phi_s \left| \sum_{\kappa,\lambda} \frac{1}{m_\kappa} \hat{p}_{i\kappa\lambda} \hat{p}_{j\kappa\lambda} \right| \Phi_s \right\rangle e^{-\beta E_s} .$$

- ▶ The contribution to the vibrational stress tensor from the potential energy part of the vibrational Hamiltonian is

$$\sigma_{ij}^{\text{vib,potential}} = \frac{1}{\mathcal{Z}} \sum_s \left\langle \Phi_s \left| \sigma_{ij}^{\text{elec}} \right| \Phi_s \right\rangle e^{-\beta E_s} ,$$

where  $\sigma_{ij}^{\text{elec}}$  can be determined from the electronic Hamiltonian  $\hat{H}^{\text{elec}}$ .

## Effective external stress

- ▶ The vibrational Helmholtz free energy is an approximately linear function of strain for the system configurations relevant to thermal expansion.
- ▶ Define an effective external stress tensor

$$\boldsymbol{\sigma}^{\text{eff}} = \boldsymbol{\sigma}^{\text{ext}} - \boldsymbol{\sigma}^{\text{vib}},$$

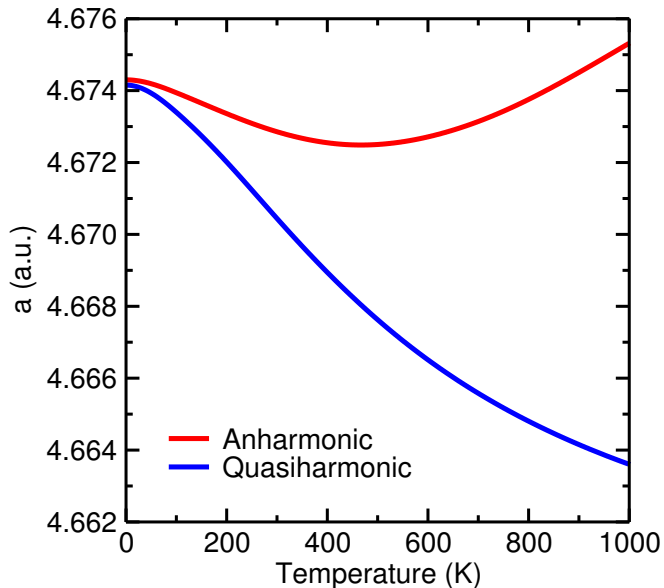
such that

$$d\mathcal{G} = d\mathcal{F}^{\text{elec}} - \Omega \sigma_{ij}^{\text{eff}} d\epsilon_{ij}.$$

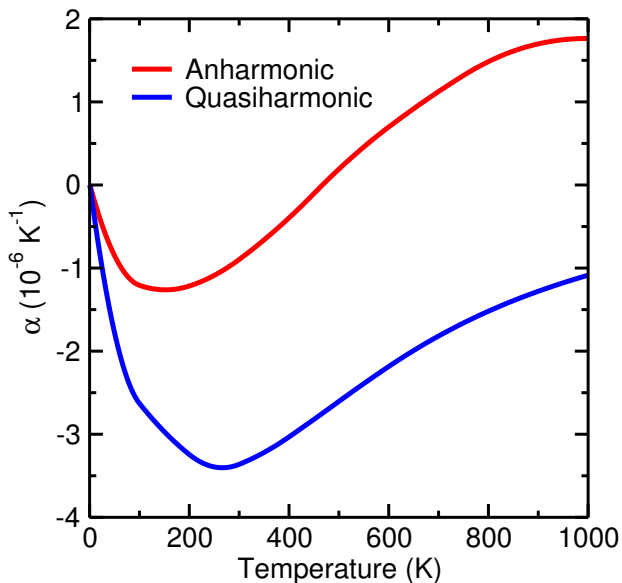
- ▶ This reformulation allows us to use electronic structure methods to minimise the Gibbs free energy with respect to strain, but still include vibrational effects.
- ▶ May need to solve self-consistently, depending on how much the vibrational stress tensor varies over the configurations involved.



## Anharmonic lattice parameter



## Anharmonic thermal expansion coefficient



# Conclusions

- ▶ Discrepancy between quasiharmonic and anharmonic calculations of thermal expansion coefficient of graphene.
- ▶ Quasiharmonic calculations predict that the lattice parameter monotonically decreases with temperature between 0 K and 1000 K.
- ▶ Anharmonic calculations predict that the lattice parameter has a minimum at about 500 K.

# Acknowledgements



Bartomeu  
Monserrat



Richard  
Needs

