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Theory of interface and anharmonic phonon interactions in nanocomposite materials

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Abstract.

We present a theory of phonon scattering rates resulting from mass smudging across interfaces and from anharmonicity in nanocomposite materials. We discuss the derivation of the anharmonic scattering term and present some recently published results indicating that if certain models of interface mass-mixing are adopted, the cross-planar thermal conductivity of an ultra-thin superlattice system will decrease dramatically with the number of bilayers n until $n \approx 4$, above which value it begins to increase with n .

1. Introduction

It is becoming clear that phonon properties of nanostructured materials can be ‘tuned’ to a large extent for future technological applications, such as thermoelectricity with an enhanced figure of merit. A key phonon property is the lattice thermal conductivity κ_{ph} , which can be significantly controlled through nanostructuring. There are several factors that can be monitored, either individually or jointly, to control κ_{ph} for nanocomposite materials. These include: inter-atomic bond length relaxation; new features in phonon dispersion curves, changes in phonon velocity; phonon-interface scattering effects, alteration in anharmonic phonon interactions due to the presence of more than one constituent material and larger unit cell size than in bulk materials, and the anisotropic nature of thermal conductivity. Two of these, *viz* phonon-interface scattering and anharmonic phonon interactions, are the most critical factors, but have been studied the least.

In this work we discuss a theory of phonon scattering rates resulting from mass smudging across interfaces and from anharmonicity in nanocomposite materials. We apply our formulations to calculate κ_{ph} of ultra-short period Si/Ge[001] superlattices within the single-mode relaxation time approximation for the solution of the phonon Boltzmann transport equation.

2. Theoretical Details

We consider the superlattice structure $A_{n_1}B_{n_2}[001]$, grown along [001], with each unit cell containing n_1 bilayers of A and n_2 bilayers of B. Within the single-mode relaxation time scheme,

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the phonon (lattice) thermal conductivity can be expressed as

$$\kappa_{\mu\nu} = \frac{\hbar^2}{N_0\Omega k_B T^2} \sum_{\mathbf{q}s} \omega^2(\mathbf{q}s) c_{s,\mu}(\mathbf{q}) c_{s,\nu}(\mathbf{q}) \tau(\mathbf{q}s) \bar{n}_{\mathbf{q}s} (\bar{n}_{\mathbf{q}s} + 1), \quad (1)$$

where N_0 is the number of unit cells, Ω the volume of each cell, \mathbf{q} and s label the wave-vector and polarisation of a phonon mode, and $\omega(\mathbf{q}s)$, $c_{s,\mu}(\mathbf{q})$ and $\bar{n}_{\mathbf{q}s}$ are the frequency of a given mode, its μ^{th} velocity component and the associated value of the Bose-Einstein distribution, respectively. The single mode relaxation time $\tau(\mathbf{q}s)$ is determined by $\tau(\mathbf{q}s)^{-1} = \tau_{\text{bs}}^{-1} + \tau_{\text{md}}^{-1} + \tau_{\text{ep}}^{-1} + \tau_{\text{ims}}^{-1} + \tau_{\text{anh}}^{-1}$. The first four terms are the boundary scattering contribution, the mass-defect scattering contribution, the electron-phonon contribution and the interface mixing contribution that arises due to imperfections in superlattice interfaces. These are routinely discussed in detail when dealing with κ_{ph} for bulk materials. In a recent publication [1] we have provided a formalism for phonon scattering due to anharmonicity and from mass smudging at superlattice interfaces. Here we shall discuss the anharmonic interaction, detailing the derivation of the so-called ‘dual mass term’ (also used in earlier formulations of the anharmonic scattering [2])

$$\begin{aligned} \tau_{\text{anh}}^{-1}(\mathbf{q}s) = & \frac{\pi\hbar\bar{\gamma}^2}{\rho_0 N_0 \Omega \bar{c}^2} \sum_{\mathbf{q}'s', \mathbf{q}''s'', \mathbf{G}} \frac{(\mathcal{R}_{\mathbf{q}s, \mathbf{q}'s', \mathbf{q}''s''})^2}{\omega(\mathbf{q}s)\omega(\mathbf{q}'s')\omega(\mathbf{q}''s'')} \mathcal{D}(\mathbf{q}, \mathbf{q}', \mathbf{q}'') \\ & \times \left[\frac{\bar{n}_{\mathbf{q}'s'}(\bar{n}_{\mathbf{q}''s''} + 1)}{(\bar{n}_{\mathbf{q}s} + 1)} \delta(\omega(\mathbf{q}s) + \omega(\mathbf{q}'s') - \omega(\mathbf{q}''s'')) \delta_{\mathbf{q}+\mathbf{q}', \mathbf{q}''+\mathbf{G}} \right. \\ & \left. + \frac{1}{2} \frac{\bar{n}_{\mathbf{q}'s'}\bar{n}_{\mathbf{q}''s''}}{\bar{n}_{\mathbf{q}s}} \delta(\omega(\mathbf{q}s) - \omega(\mathbf{q}'s') - \omega(\mathbf{q}''s'')) \delta_{\mathbf{q}+\mathbf{G}, \mathbf{q}'+\mathbf{q}''} \right], \quad (2) \end{aligned}$$

where $\bar{\gamma}$ is a mode-averaged Grüneisen constant, \mathbf{G} is a reciprocal lattice vector, ρ_0 is the average density, \bar{c} is the average acoustic velocity and

$$\mathcal{R}_{i,j,k} = \left[\sqrt{\omega(i)\omega(j)(\omega(i) + \omega(j))} |\omega_{\Gamma}(k) - \omega(k)| + \text{similar terms with } i, j \text{ and } k \text{ interchanged} \right] / 3!, \quad (3)$$

where i, j and k label modes and $\omega_{\Gamma}(i)$ is the frequency of mode i at the Brillouin zone centre. The ‘dual mass term’ $\mathcal{D}(\mathbf{q}, \mathbf{q}', \mathbf{q}'')$ accounts for the phase correlation of the anharmonic force constants within a unit cell of the superlattice structure.

In order to derive a simple and usable form for \mathcal{D} , we need to examine the structure of the scattering matrix element for bulk materials, as given in [3]. Typically, for an alloy we use the ansatz [4]

$$\frac{|\overline{A_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{ss's''}}|^2}{\rho_0} = \frac{4\rho_0^2\gamma^2 c_s^2(\mathbf{q})c_{s'}^2(\mathbf{q}')c_{s''}^2(\mathbf{q}'')}{\bar{c}^2\rho_0^3}, \quad (4)$$

where $\overline{A_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{ss's''}}$ is the matrix element for the appropriate polarisations and momenta; ρ_0 is the average density. Essentially, we are making the assumption that:

$$\frac{|\overline{A_{\mathbf{q}\mathbf{q}'\mathbf{q}''}^{ss's''}}|}{(\rho\rho'\rho'')} \propto (ee'e'')_{\text{CNT}}\rho_0, \quad (5)$$

where $(ee'e'')_{\text{CNT}}$ is some number which parameterises the overall behaviour of the eigenvector of each mode in the continuum limit. This simple assumption is justified in alloy systems, where effects arising from the random locations of different species of atoms may be assumed to average out, but it is not so clear that it is justified in ordered systems such as superlattices.

For a superlattice structure $A_{n_1}B_{n_2}$, the atomic layers in sections A and B are treated as patches of densities ρ_1 and ρ_2 , respectively. Using Eqs. (4.83) to (4.85) in Ref. [3] as the basis of what follows, we define for each patch a within a period tensor $(A_{ijk}^{lmn})_a$ related to the third order elastic constants; the average of this over a superlattice period is $\overline{A_{ijk}^{lmn}}$. The atomic eigenvectors are approximated as their amplitudes and summation over different directions is neglected (since for superlattices the relevant physics occurs only in one direction). We define $\mathcal{E}(\mathbf{q}, q', q'')$ to be a quantity with dimensions of $\rho^{3/2}$ and take $A_{\mathbf{q}q'q''}^{ss's''}$ to be the following product of averages:

$$\begin{aligned} A_{\mathbf{q}q'q''}^{ss's''} \mathcal{E}(\mathbf{q}, q', q'') &= \frac{\overline{A_{ijk}^{lmn}}}{(n_1 + n_2)^3} \sum_{a, b, c=1}^{n_1+n_2} \frac{e_a e'_b e''_c}{\sqrt{\rho_a \rho_b \rho_c}} \\ &= \frac{\overline{A_{ijk}^{lmn}}}{(n_1 + n_2)^3} \left(\frac{n_1 e_1}{\rho_1^{1/2}} + \frac{n_2 e_2}{\rho_2^{1/2}} \right) \left(\frac{n_1 e'_1}{\rho_1^{1/2}} + \frac{n_2 e'_2}{\rho_2^{1/2}} \right) \left(\frac{n_1 e''_1}{\rho_1^{1/2}} + \frac{n_2 e''_2}{\rho_2^{1/2}} \right), \end{aligned} \quad (6)$$

where e_a is the amplitude of the eigenvector associated with patch a for momentum \mathbf{q} and band s , e'_b is the amplitude of the eigenvector associated with patch b for momentum q' and band s' and so on. The above consideration has similarities to the work in [5].

We want to express $A_{\mathbf{q}q'q''}^{ss's''} \mathcal{E}(\mathbf{q}, q', q'')$ in terms of ratios of e_1 and e_2 and some average of $e_1 e'_1 e''_1$ and $e_2 e'_2 e''_2$. Defining

$$\mathcal{A}_{ij} = \frac{\Gamma_i \rho_i^{3/2}}{e_i e'_i e''_i} \left(\frac{n_1 e_1}{\rho_1^{1/2}} + \frac{n_2 e_2}{\rho_2^{1/2}} \right) \left(\frac{n_1 e'_1}{\rho_1^{1/2}} + \frac{n_2 e'_2}{\rho_2^{1/2}} \right) \left(\frac{n_1 e''_1}{\rho_1^{1/2}} + \frac{n_2 e''_2}{\rho_2^{1/2}} \right), \quad (7)$$

where Γ_1 is the relative proportion of species 1 and $\Gamma_2 = 1 - \Gamma_1$ is the relative proportion of species 2, and replacing $e_1 e'_1 e''_1$ and $e_2 e'_2 e''_2$ in the denominator with a single mode-averaged parameter e_{over} (we assume that the deviations from this average arising from the effects of superlattice structuring are contained within the parameters \mathcal{A}_{ij}/ρ_i) we have:

$$A_{\mathbf{q}q'q''}^{ss's''} \mathcal{E}(\mathbf{q}, q', q'') = \frac{\overline{A_{ijk}^{lmn}} e_{\text{over}}}{(n_1 + n_2)^3} \left(\frac{\mathcal{A}_{12}}{\rho_1^{3/2}} + \frac{\mathcal{A}_{21}}{\rho_2^{3/2}} \right). \quad (8)$$

Comparing this with the standard expression for anharmonic continuum [3], we can write:

$$|A_{\mathbf{q}q'q''}^{ss's''}|^2 \mathcal{D}(\mathbf{q}, q', q'') = \frac{4\rho_0 \gamma^2 c_s^2 c_{s'}^2 c_{s''}^2}{c^2} \mathcal{D}(\mathbf{q}, q', q''), \quad (9)$$

where the prefactor is assumed to approximate the behaviour of the square of $\overline{A_{ijk}^{lmn}} e_{\text{over}}$ and $\mathcal{D}(\mathbf{q}, q', q'') = (\mathcal{E}(\mathbf{q}, q', q''))^2$ is the dual mass term, given by

$$\mathcal{D}(\mathbf{q}, q', q'') = \frac{1}{(n_1 + n_2)^6} \left(\frac{\mathcal{A}_{12}}{\rho_1^{3/2}} + \frac{\mathcal{A}_{21}}{\rho_2^{3/2}} \right)^2. \quad (10)$$

Following previous work [5, 2, 1], we calculate \mathcal{A}_{ij} using an expression that describes the ratio of amplitudes in the diatomic linear chain model.

3. Review of Some Recent Results

Calculations of κ_{ph} of ultra-thin $\text{Si}_n\text{Ge}_n[001]$ superlattices, with each unit cell containing n atomic bi-layers, were carried out in [1]. We consider \mathcal{P} as the probability of the interchange of

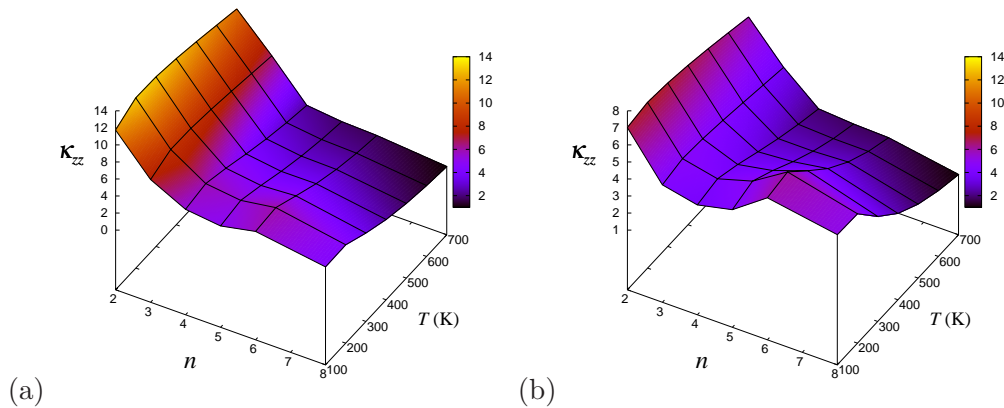


Figure 1. Variation of κ_{ph} (in units of $\text{W m}^{-1} \text{K}^{-1}$) along the growth direction in the $\text{Si}_n\text{Ge}_n[001]$ superlattices for: (a) with a fixed interface mass mixing ($\mathcal{P} = 0.05$), and (b) with \mathcal{P} varying with n . The figures are taken from [1].

a number of pairs of bilayers, one from one half of Si and one from the neighboring half of Ge. Figure 1(a) displays the behaviour of κ_{ph} along the growth direction for a number of superlattice periods and temperatures with a fixed amount of interface mass-smudging, which is expressed in terms of the constant probability factor $\mathcal{P} = 0.05$. Figure 1(b) displays κ_{ph} when the interface mass-smudging parameter \mathcal{P} is allowed to vary according to a simple model $\mathcal{P} = 0.24/(n-1)$ of how the degree of mixing should vary with the number of bilayers n in the superlattice. One notable feature of these results is that for fixed \mathcal{P} , there is a decrease in κ_{ph} as n is increased. For varying \mathcal{P} , we see that κ_{ph} has a minimum at $n = 4$ for temperatures in the vicinity of 100 K, increasing rapidly as n is reduced and more slowly as n is increased, possibly with some degree of oscillation.

4. Summary

We have summarised the derivation of the dual mass term that appears in the anharmonic phonon interaction for superlattice systems. Using this, we have discussed the phonon conductivity results for ultra-thin $\text{Si}_n\text{Ge}_n[001]$ superlattices with two different scenarios for mass-smudging across interfaces. For decreasing probability of mass-smudging away from interfaces, we find that κ_{ph} attains a minimum value for a number of bilayers of around $n = 4$.

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