THEORY OF PHONON TRANSPORT IN NANOCOMPOSITE MATERIALS

G P Srivastava

School of Physics,University of Exeter, Exeter, UK

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OUTLINE OF TALK

- Phonons in nanocomposites
- Theories of phonon transport
- Phonon scatterings due to nanocomposite formation
- Results for phonon conductivity in Si/Ge and GaAs/AlAs superlattices
- Summary

NANOCOMPOSITES: EXAMPLES

Nanometre-sized materials, e.g.

- Superlattices (…/A/B/A/B/…)
- Nanowires embedded in another bulk
- Nanodots embedded in another bulk
- etc

THEORIES OF PHONON TRANSPORT

- Using linear-response

Classical Green-Kubo formalism using Newtonian molecular dynamics of particles

Quantum Green-Kubo formalism using canonical average of phonon number operator

- Using Boltzmann eqn

Concept of semi-classical statistics of phonon distribution function in space and time. Solutions using:

Relaxation-time methods;

Iterative methods; or

Variational principles.

Validity limited by

Landau-Peierls-Ziman condition ($\omega\tau>1$, or

sample size>wavelength)

PHONON TRANSPORT IN NANOCOMPOSITES

Three regimes for conductivity (κ) depending on the ratio phonon MFP (Λ) / composite period ($d=d_1+d_2$):

(i) $d >> \Lambda$: $1/\kappa = (d_1/\kappa_1 + d_2/\kappa_2)/(d_1+d_2)$;

(ii) $d \sim \Lambda$: $1/\kappa = (d_1/\kappa_1 + d_2/\kappa_2 + 2/\sigma_K)/(d_1+d_2)$,

σ_K = Kapitza resistance of interface;

(iii) $d << \Lambda$: Formulate and use phonon dispersion relations and phonon scattering rates for nanocomposite.

Present treatment for regime (iii).

THERMAL CONDUCTIVITY: single-mode relaxation time approach

$$\kappa_{ij} = \frac{\hbar^2}{N_0 \Omega k_B T^2} \sum_{\boldsymbol{q},s} \omega^2(\boldsymbol{q}s) v_i(\boldsymbol{q}s) v_j(\boldsymbol{q}s) \tau(\boldsymbol{q}s) \bar{n}(\boldsymbol{q}s)(\bar{n}(\boldsymbol{q}s)+1),$$

q=phonon wavevector; s=phonon polarisation

N_0: No. of unit cells, Ω: Unit cell volume,

$\bar{n}$: Bose-Einstein distribution function,

Require to know:

(i) Phonon dispersion relations: $\omega = \omega(qs)$

(ii) Phonon group velocity: $v = d\omega/dq$

(iii) Relaxation time for all phonon modes: $\tau(qs)$

PHONON DISPERSION CURVES (Lattice dynamics)

Theories and references:

Adiabatic bond charge model;

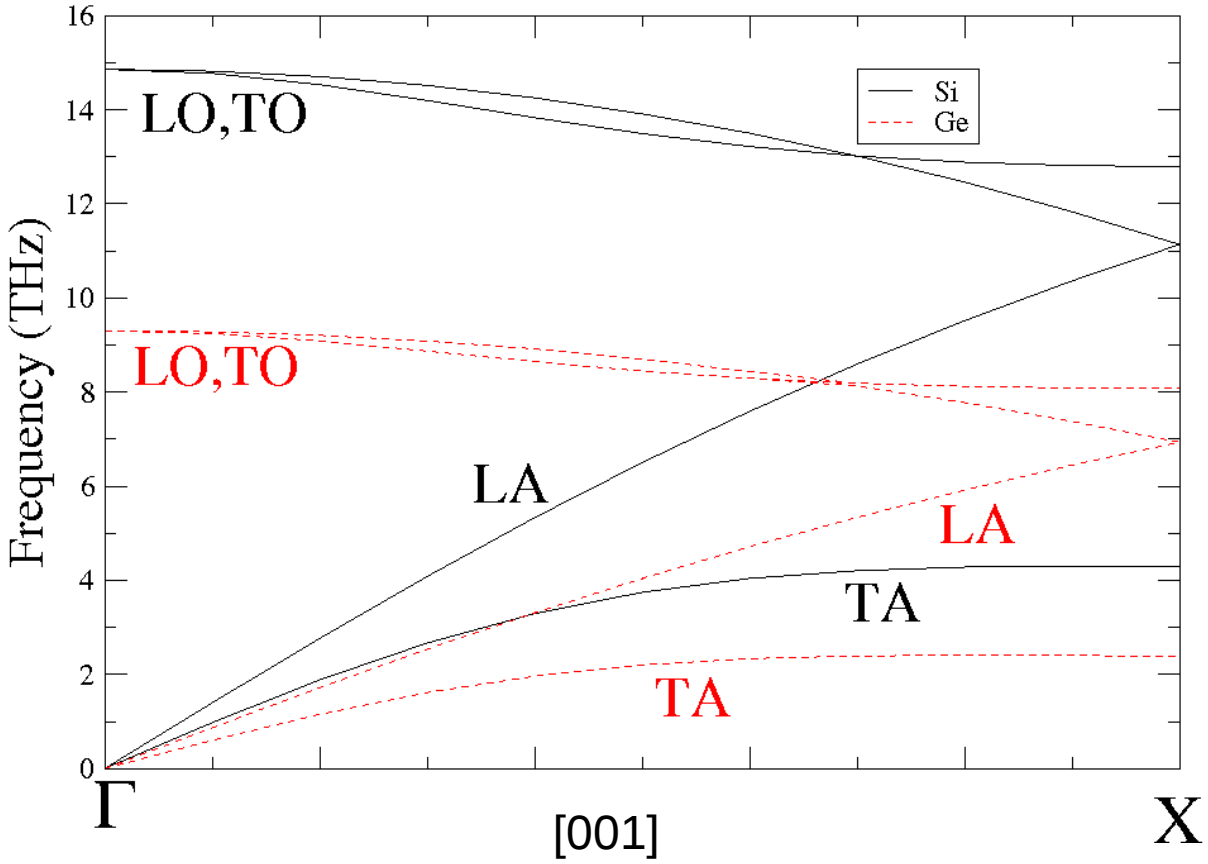
H M Tutuncu and G P Srivastava,PRB 53, 15675 (1996)

S P Hepplestone and G P Srivastava,
PRL 101, 105502 (2008); J. Appl. Phys. 107, 043504 (2010)

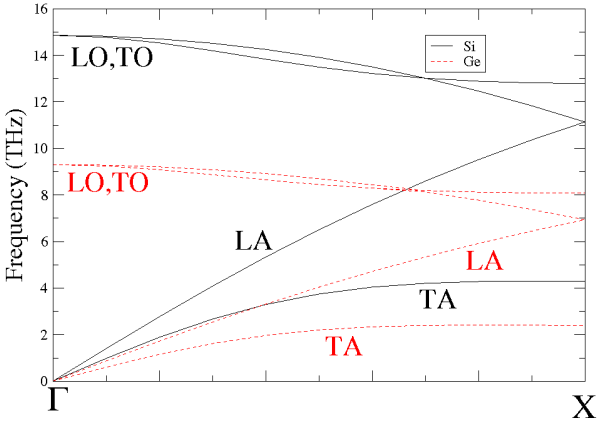
Ab-initio pseudopotential DFPT

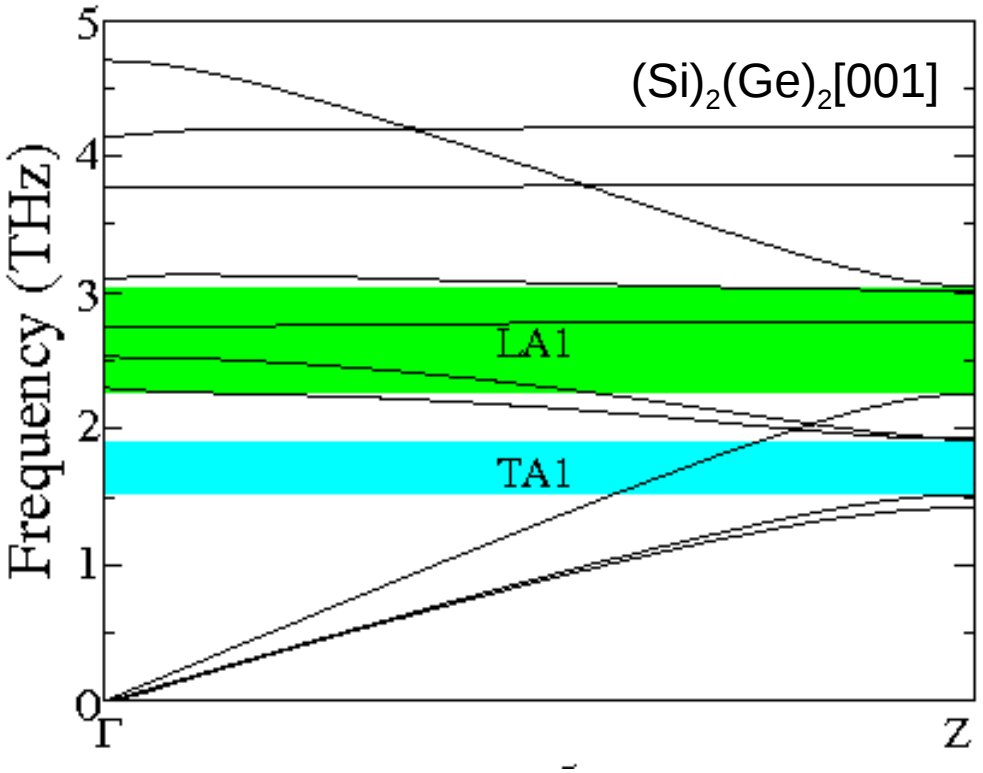
I O Thomas and G P Srivastava, (Unpublished)

PHONONS IN BULK MATERIALS



PHONONS IN THIN SUPERLATTICES





Characteristic features: Zone-folding; Gap openings; Confinement

Blue: band gap in TA branch; Green: band gap in LA branch

RELAXATION-TIME THEORY OF PHONON TRANSPORT IN NANOCOMPOSITES

Ingredients: Phonon Boltzmann equation +
single-mode relaxation time approach +
elastic continuum model for anharmonicity +
first-order time-dependent perturbation theory

References:

S. Y. Ren and J. D. Dow, PRB 25, 3750 (1982)

G. P. Srivastava, The Physics of Phonons (Taylor & Francis, 1990)

S. P. Hepplestone and G. P. Srivastava

PRB 82, 144303 (2010); *PRB 84, 115326 (2011)*

I. O. Thomas and G. P. Srivastava (unpublished)

THERMAL CONDUCTIVITY TENSOR

$$\kappa_{ij} = \frac{\hbar^2}{N_0 \Omega k_B T^2} \sum_{\boldsymbol{q},s} \omega^2(\boldsymbol{q}s) v_i(\boldsymbol{q}s) v_j(\boldsymbol{q}s) \tau(\boldsymbol{q}s) \bar{n}(\boldsymbol{q}s)(\bar{n}(\boldsymbol{q}s)+1),$$

N_0: No. of unit cells, Ω: Unit cell volume,

$\bar{n}$: Bose-Einstein distribution function,

$$\tau^{-1} = \tau_B^{-1} + \tau_{MD}^{-1} + \tau_{ID}^{-1} + \tau_{pp}^{-1}$$

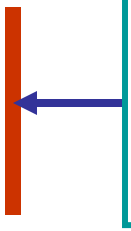
τ_B^{-1}: boundary scattering,

τ_{MD}^{-1}: isotope scattering,

τ_{ID}^{-1}: interface scattering,

τ_{pp}^{-1}: phonon-phonon scattering,

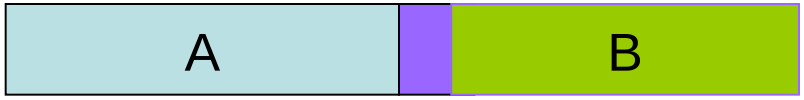
$v_{\mathbf{q}s,i}$: i^{th} velocity component for phonon $\omega(\mathbf{q}s)$



Important for nanocomposites and different from single crystals

Interface mass-mixing in A(N)/B(M) superlattice - 1

Ideal interface



Smudged interface

Perturbation in Hamiltonian due to interface mass mixing

$$H'(\mathrm{IMS}) = \frac{1}{2}\sum_{i=1}^{N}(M_i|\mathbf{v}_i|^2 - M_A|\mathbf{v}_\mathbf{A}|^2) + \frac{1}{2}\sum_{i=N+1}^{N+M}(M_i|\mathbf{v}_i|^2 - M_B|\mathbf{v}_\mathbf{B}|^2)],$$

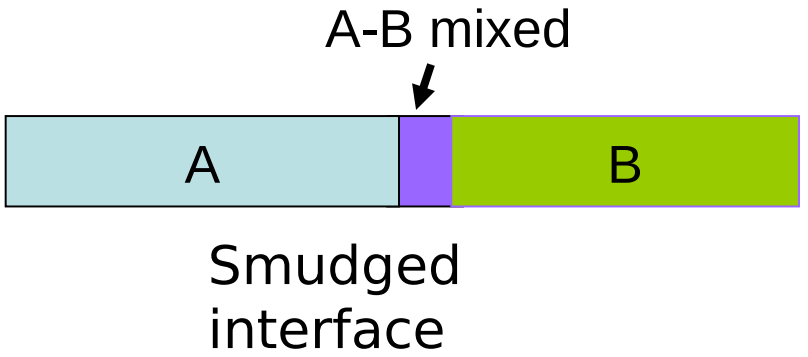
M = mass; v = time derivative of atomic displacement

Interface mass-mixing scattering in A(n)/B(m) superlattice - 2

$$\tau_{\mathrm{IMS}}^{-1}(\boldsymbol{q}s) = \frac{\alpha\pi}{2N_0(n+m)^2} \Sigma_{s'} \int d\omega(\boldsymbol{q}'s')g(\omega(\boldsymbol{q}'s'))\omega(\boldsymbol{q}s)\omega(\boldsymbol{q}'s') \times \frac{\bar{n}(\boldsymbol{q}'s')+1}{\bar{n}(\boldsymbol{q}s)+1}\delta(\omega(\boldsymbol{q}s)-\omega(\boldsymbol{q}'s')\left[(1-\frac{e_Ae'_A}{e_Be'_B})^2+(1-\frac{e_Be'_B}{e_Ae'_A})^2\right],$$

$g(\omega)$: density of states,

α : interface atomic mixing parameter,
e_B/e_A : interface atomic amplitude ratio.



Amplitude Ratio

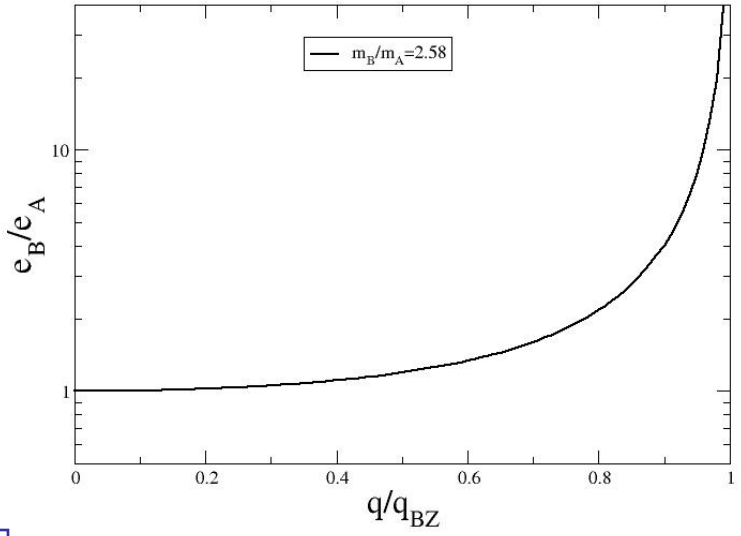
For a diatomic linear chain with masses M_A and M_B

$$\frac{e_B}{e_A} = \frac{\left[\frac{1}{M_0} - \Delta\left(\frac{1}{M}\right)\right]\cos(l_z q_z)}{\left[\left(\frac{1}{M_0}\right)^2 \cos^2(l_z q_z) + \left(\Delta\left(\frac{1}{M}\right)\right)^2 \sin^2(l_z q_z)\right]^{\frac{1}{2}} - \Delta\left(\frac{1}{M}\right)},$$

$$M_0 = \tfrac{1}{2}(1/M_A + 1/M_B),$$

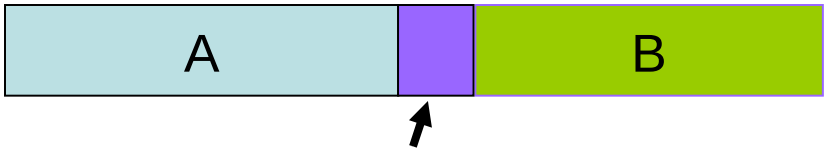
$$\Delta(1/M) = \tfrac{1}{2}(1/M_A - 1/M_B),$$

l_z : period along the superlattice growth direction.



$e_B/e_A = f(\omega)$

Interface broken-bonds in A(N)/B(M) superlattice - 1



$$H'(\mathrm{IDS}) = \frac{1}{2}\sum_{i=1}^{N'}(K_0|\mathbf{u}_i|^2 - K_A|\mathbf{u}_A|^2) + \frac{1}{2}\sum_{i=N'+1}^{N'+M'}(K_0|\mathbf{u}_i|^2 - K_B|\mathbf{u}_B|^2),$$

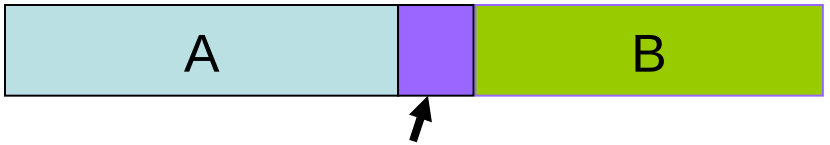
where $K_A(K_B)$ represents the inter-atomic spring constant in the layer A(B), $N' + M'$ is the total number of atomic bonds and K_0 represents a spring constant in the dislocation region (i.e. has a value equal to zero, or close to zero, for missing or broken bonds).

Interface broken-bonds scattering in A(n)/B(m) superlattice - 2

$$\tau_{\mathrm{IDS}}^{-1}(\boldsymbol{q}s) = \frac{\pi\omega_0^4}{4N_0(n+m)^2}\frac{\alpha'}{}\Sigma_{s'}\int d\omega(\boldsymbol{q}'s')\frac{g(\omega(\boldsymbol{q}'s'))}{\omega(\boldsymbol{q}s)\omega(\boldsymbol{q}'s')}$$
$$\times\frac{\bar{n}(\boldsymbol{q}'s')+1}{\bar{n}(\boldsymbol{q}s)+1}\delta(\omega(\boldsymbol{q}s)-\omega(\boldsymbol{q}'s'))$$
$$\times\left[1+\left(\frac{e_Ae'_A}{e_Be'_B}\right)^2+1+\left(\frac{e_Be'_B}{e_Ae'_A}\right)^2\right],$$

ω_0: highest phonon frequency,

α': parameter for concentration of broken bonds.



Anharmonic crystal potential in A(n)/B(m) superlattice -- 1

Anharmonic crystal potential

$$V_3 = \frac{1}{3!} \sum_{qs,q's',q''s''} (a^{\dagger}_{qs} - a_{-qs})(a^{\dagger}_{q's'} - a_{-q's'})(a^{\dagger}_{q''s''} - a_{-q''s''})\Psi(qs,q's',q''s'')\delta_{G,q+q'+q''},$$

where

$$\Psi(qs,q's',q''s'') = \frac{i}{\sqrt{N_0\Omega}} \sum_{\substack{bb'b'' \\ \alpha\beta\gamma}} \left(\frac{\hbar^3}{8M_bM_{b'}M_{b''}\omega(qs)\omega(q's')\omega(q''s'')} \right)^{1/2} \Psi_{\alpha\beta\gamma}(qb,q'b',q''b'')e_\alpha(b|qs)e_\beta(b'|q's')e_\gamma(b''|q''s''),$$

with Ω representing the unit-cell volume and $e(b|qs)$, etc., representing the polarization vectors. The Fourier components of the third-order interatomic force constant tensor $\Psi(qb,q'b',q''b'')$ can be expressed as

$$\Psi(qb,q'b',q'',b'') = \sum_{h',h''} \Psi(0b,h'b',h''b'')e^{iq'\cdot h'}e^{iq''\cdot h''},$$

where $\Psi(0b,h'b',h''b'')$ is the third-order interatomic force constant tensor, and h' and h'' are lattice translation vectors for the superlattice structure.

Anharmonic crystal potential in A(n)/B(m) superlattice -- 2

Our model anharmonic crystal potential

$$\mathcal{V}_3 = \bar{\gamma}\sqrt{\frac{\hbar^3}{2\rho V}} \sum_{\substack{qs,q's',\\ q''s''}} \frac{\mathcal{B}_{qs,q's',q''s''}}{\sqrt{\omega(qs)\omega(q's')\omega(q''s'')}} \delta_{q+q'+q'',G}$$
$$\times (a^\dagger_{qs} - a_{-qs})(a^\dagger_{-q's'} - a_{q's'})(a^\dagger_{q''s''} - a_{-q's'}),$$

with

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

$\omega_\Gamma(j)$ = zone centre frequency for j^{th} branch;

$C(j)$ = phase velocity for j^{th} branch;

γ = Grüneisen's constant

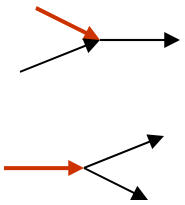
A continuum model that includes acoustic as well as optical modes

Anharmonic scattering in A(n)/B(m) superlattice -- 1

When both acoustic and optical phonons are considered

$$\tau_{\mathrm{AH}}^{-1}(\boldsymbol{q}s) = \frac{\pi\hbar\bar{\gamma}^2}{\rho V}\sum_{\boldsymbol{q}'s',\,\boldsymbol{q}''s'',\,\boldsymbol{G}}\frac{\left(\mathcal{B}_{\boldsymbol{q}s,\,\boldsymbol{q}'s',\,\boldsymbol{q}''s''}\right)^2}{\omega(\boldsymbol{q}s)\omega(\boldsymbol{q}'s')\omega(\boldsymbol{q}''s'')}$$

DM(q,q',q'')



$$\times\left[\frac{\bar{n}_{\boldsymbol{q}'s'}(\bar{n}_{\boldsymbol{q}''s''}+1)}{(\bar{n}_{\boldsymbol{q}s}+1)}\delta(\omega(\boldsymbol{q}s)+\omega(\boldsymbol{q}'s')-\omega(\boldsymbol{q}''s''))\delta_{\boldsymbol{q}+\boldsymbol{q}',\,\boldsymbol{q}''+\boldsymbol{G}}\right.$$

$$\left.+\frac{1}{2}\frac{\bar{n}_{\boldsymbol{q}'s'}\bar{n}_{\boldsymbol{q}''s''}}{\bar{n}_{\boldsymbol{q}s}}\delta(\omega(\boldsymbol{q}s)-\omega(\boldsymbol{q}'s')-\omega(\boldsymbol{q}''s''))\delta_{\boldsymbol{q}+\boldsymbol{G},\,\boldsymbol{q}'+\boldsymbol{q}''}\right],$$

where

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

DM = dual mass term ($M_A \neq M_B$)

Anharmonic scattering in A(n)/B(m) superlattice -- 2

When only acoustic phonons are considered

$$\tau^{-1}(\boldsymbol{q}s) = \frac{\pi\hbar\rho_{av}^2\gamma^2}{N_0\Omega\bar{c}^2} \sum_{\boldsymbol{q}'s',\boldsymbol{q}''s'',\boldsymbol{G}} \omega(\boldsymbol{q}s)\omega(\boldsymbol{q}'s')\omega(\boldsymbol{q}''s'')DM(\boldsymbol{q}s,\boldsymbol{q}'s',\boldsymbol{q}''s'')$$
$$\times \{ \left[\frac{\bar{n}(\boldsymbol{q}'s')(\bar{n}(\boldsymbol{q}''s'')+1)}{\bar{n}(\boldsymbol{q}s)+1} \delta(\omega(\boldsymbol{q}s)+\omega(\boldsymbol{q}'s')-\omega(\boldsymbol{q}''s''))\delta_{\boldsymbol{q}+\boldsymbol{q}',\boldsymbol{q}''+\boldsymbol{G}} \right]$$
$$+ \left[\frac{1}{2} \frac{\bar{n}(\boldsymbol{q}'s')\bar{n}(\boldsymbol{q}''s'')}{\bar{n}(\boldsymbol{q}s)} \delta(\omega(\boldsymbol{q}s)-\omega(\boldsymbol{q}'s')-\omega(\boldsymbol{q}''s''))\delta_{\boldsymbol{q}+\boldsymbol{G},\boldsymbol{q}'+\boldsymbol{q}''} \right] \},$$

ρ_{av} : average density of SL, $\bar{c}$: average acoustic velocity,

$\boldsymbol{G}$: reciprocal lattice vector $= 0$ $(\neq 0)$ for Normal (Umklapp) processes,

γ : Grüneisen's constant.

DM = dual mass term ($M_A \neq M_B$)

Anharmonic scattering in A(n)/B(m) superlattice – 3

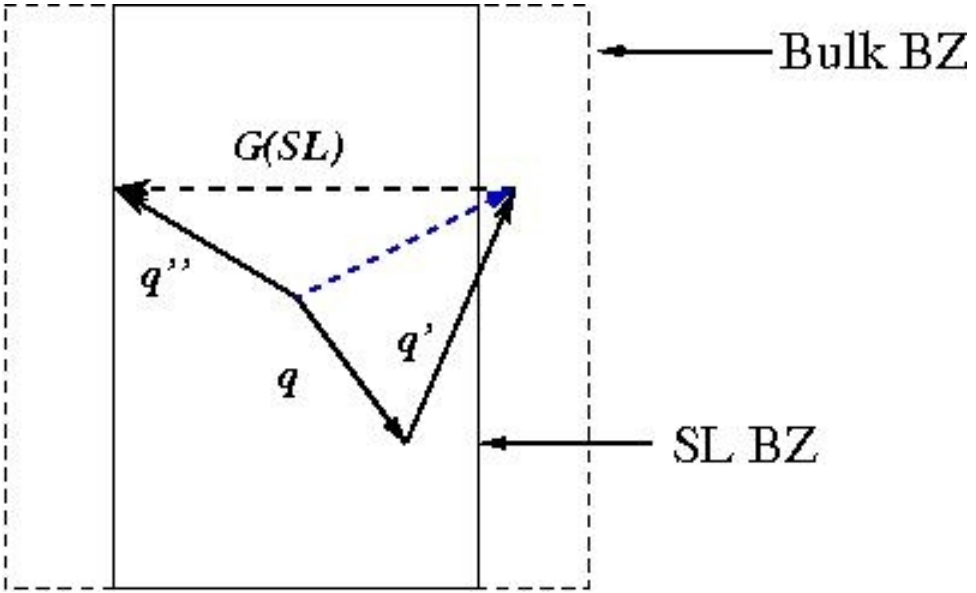
Dual Mass Term

$$DM(\boldsymbol{q}s,\boldsymbol{q}'s',\boldsymbol{q}''s'') = \frac{1}{64}\{\frac{1}{2\rho_A^{\frac{3}{2}}}\times$$
$$\left[1+\frac{\rho_A^{\frac{1}{2}}}{\rho_B^{\frac{1}{2}}}\left(\frac{e_B}{e_A}+\frac{e'_B}{e'_A}+\frac{e''_B}{e''_A}\right)+\frac{\rho_A}{\rho_B}\left(\frac{e_Be'_B}{e_Ae'_A}+\frac{e'_Be''_B}{e'_Ae''_A}+\frac{e_Be''_B}{e_Ae''_A}\right)+\frac{\rho_A^{\frac{3}{2}}}{\rho_B^{\frac{3}{2}}}\left(\frac{e_Be'_Be''_B}{e_Ae'_Ae''_A}\right)\right]+$$
$$\frac{1}{2\rho_B^{\frac{3}{2}}}\left[1+\frac{\rho_B^{\frac{1}{2}}}{\rho_A^{\frac{1}{2}}}\left(\frac{e_A}{e_B}+\frac{e'_A}{e'_B}+\frac{e''_A}{e''_B}\right)+\frac{\rho_B}{\rho_A}\left(\frac{e_Ae'_A}{e_Be'_B}+\frac{e'_Ae''_A}{e'_Be''_B}+\frac{e_Ae''_A}{e_Be''_B}\right)+\frac{\rho_B^{\frac{3}{2}}}{\rho_A^{\frac{3}{2}}}\left(\frac{e_Ae'_Ae''_A}{e_Be'_Be''_B}\right)\right]\}^2$$

ρ_j =mass density of j^{th} material

Anharmonic scattering in A(n)/B(m) superlattice – 4 ‘mini-Umklapp’ processes

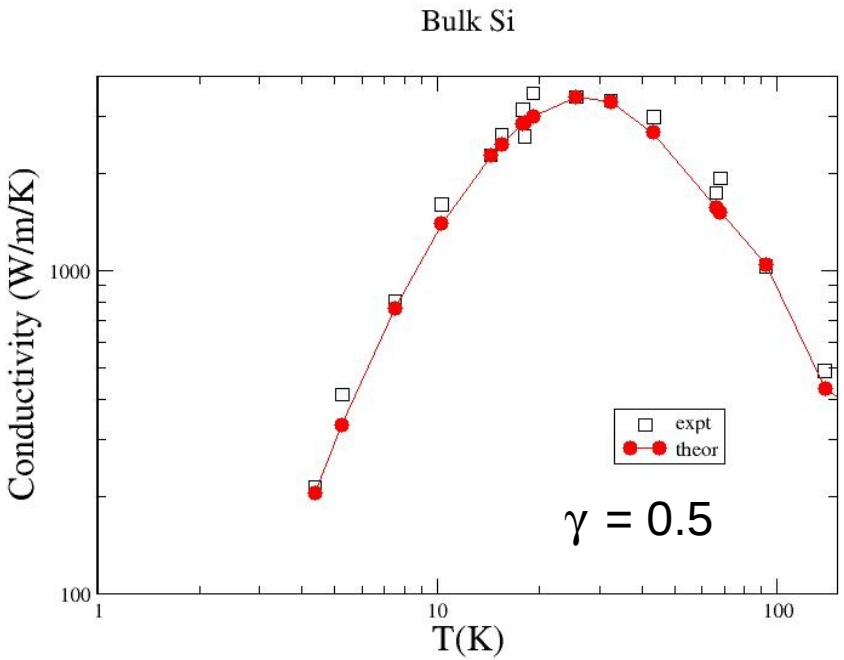
A Normal three-phonon process in bulk turns into a ‘mini-Umklapp’ process upon superlattice formation

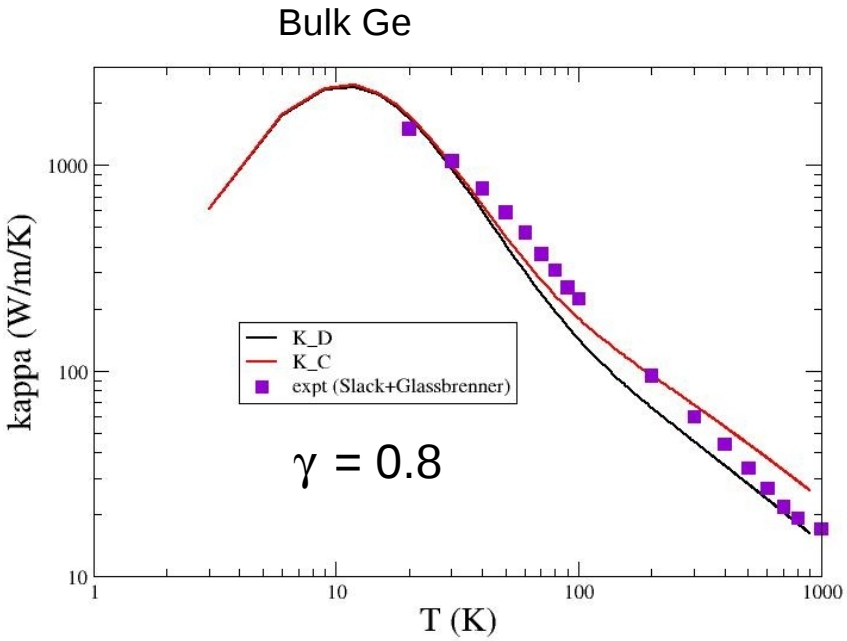


Numerical calculations

- Phonon frequencies and group velocity using adiabatic bond charge model
- Realistic Brillouin zone summation using ‘special q-points’ scheme
  - Monkhorst & Pack (1976)
- Grüneisen’s parameter γ adjusted to fit Si bulk thermal conductivity

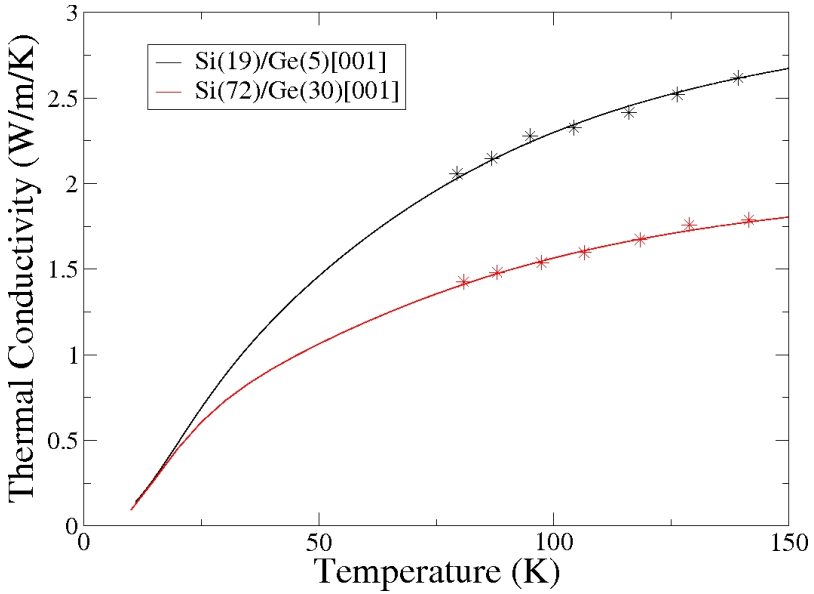
THERMAL CONDUCTIVITY RESULTS - Bulk

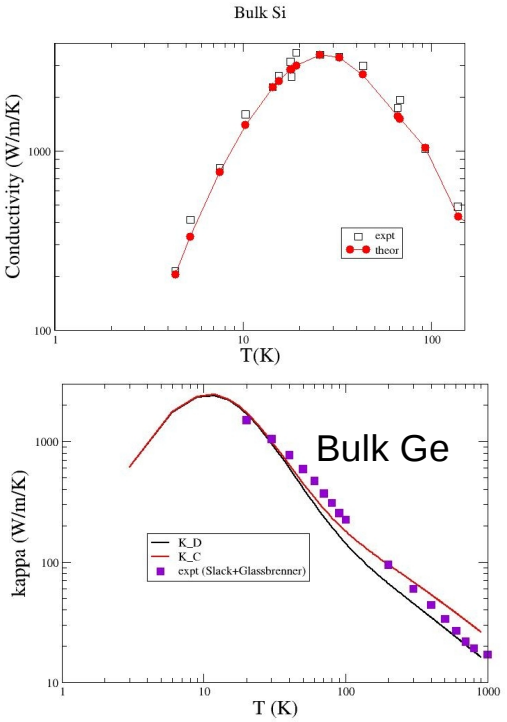




Expt. Data: Glassbrenner and Slack, PR, A1058 (1964)

THERMAL CONDUCTIVITY RESULTS – Si(n)/Ge(m)[001] superlattices





Symbols: Expt: Lee et al, APL 70, 2957 (1997)

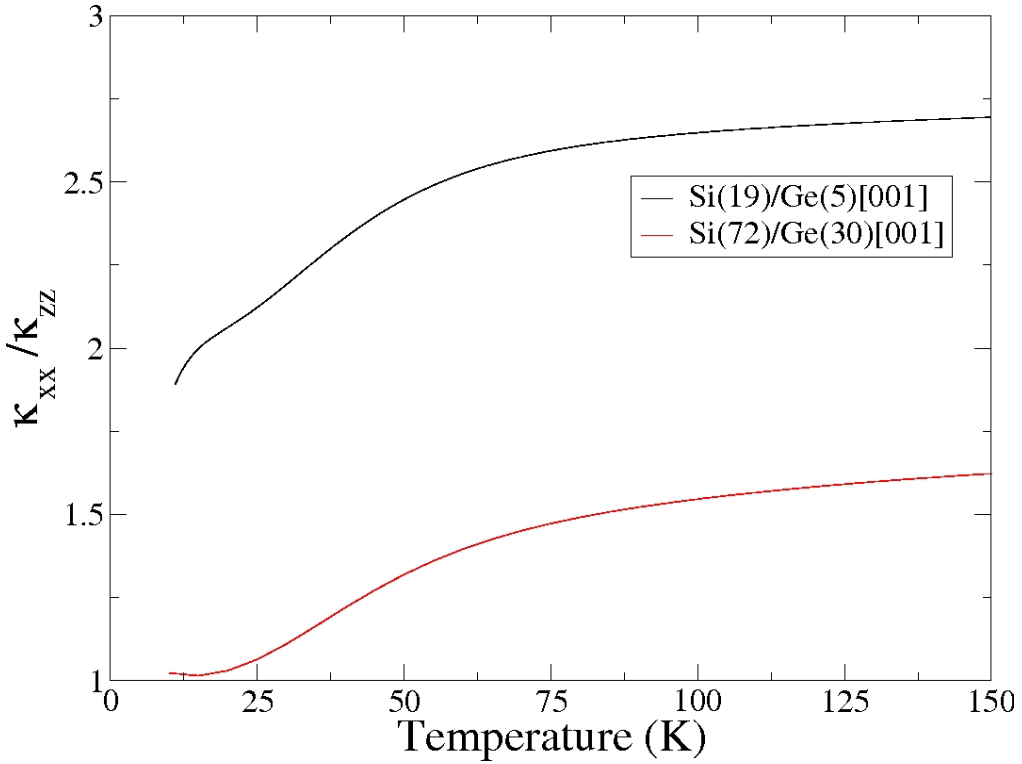
Dominant factors:
α(IMS) &
α'(IDS)

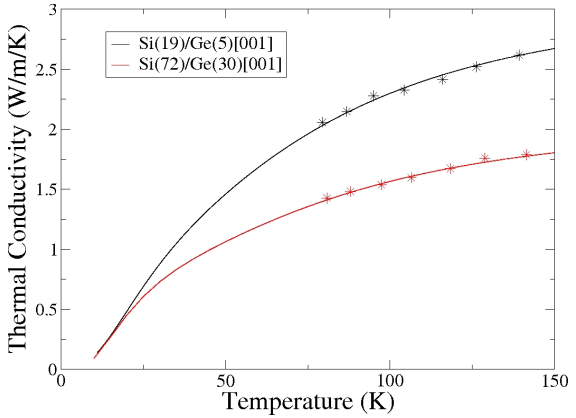
	α (s^3)	α' (s^3)
Si(19)/Ge(5)	550	0
Si(72)/Ge(30)	10^7	10^{-4}

← No dislocations

← Large concentration of defects and dislocations

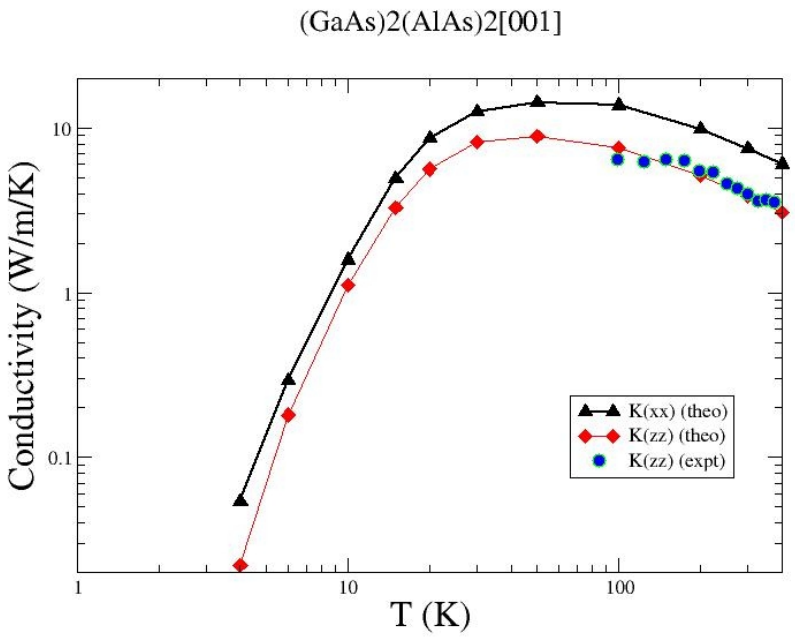
THERMAL CONDUCTIVITY RESULTS – Si(n)/Ge(m)[001] superlattices

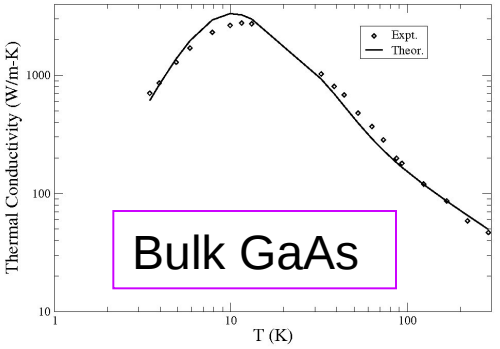


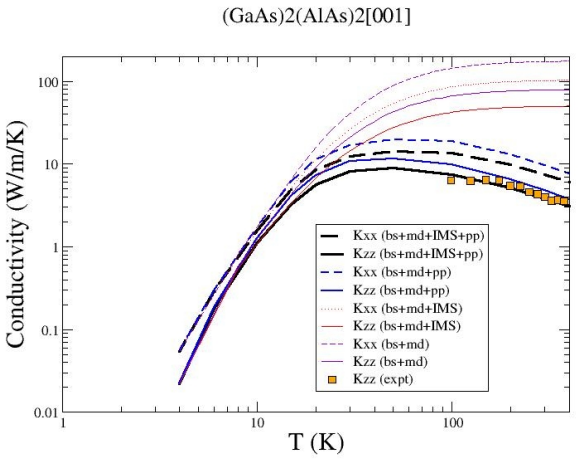


Thermal conductivity of $(GaAs)_2(AlAs)_2[001]$ SL

Expt: Capinski et al, PRB 59, 8105 (1999)

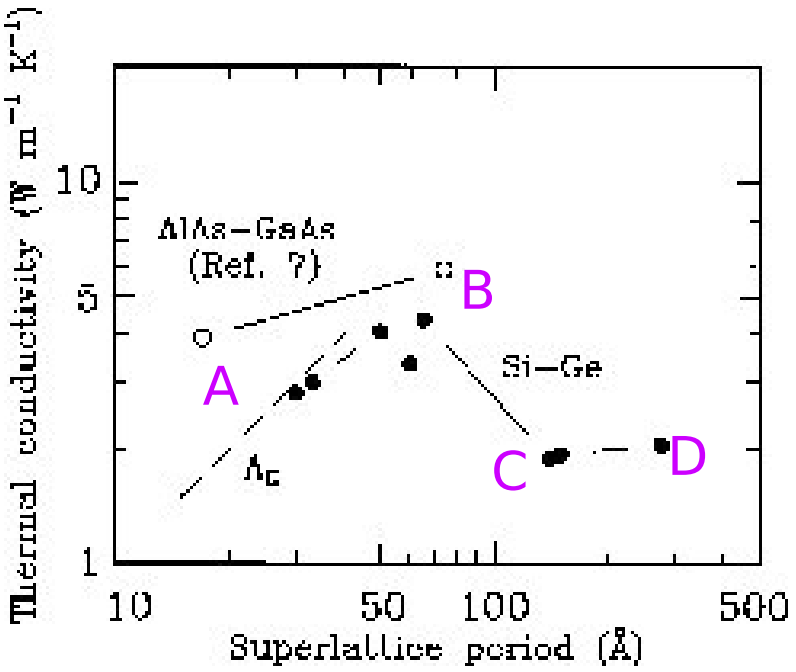






Important role of anharmonicity

Conductivity *vs* SL period: Explanation of experimental results



GaAs/AlAs:

Capinski et al, PRB 59, 8105 (1999)

Si/Ge:

Lee et al, APL 70, 2957 (1997)

'Increase' from A to B due to decrease of IMS scattering rates in short-period (n,m) superlattices as $1/(n+m)^2$.

'Flat' behaviour from C to D due to plastic deformation of structure (presence of large density of dislocations and stacking faults) in large-period strained-layer Si/Ge superlattices.

SUMMARY

- Derived expressions for model Hamiltonians and phonon relaxation rates arising from interface mass mixing, interface dislocations, and anharmonicity in nanoscale semiconductor superlattices;
- Presented numerical results for phonon conductivity tensor, within single-mode relaxation time scheme, using accurate phonon dispersion relations for acoustic as well as optical branches, and a realistic method for Brillouin zone summation;
- Explained experimental conductivity results for Si/Ge and GaAs/AlAs superlattices;
- Further progress desirable and in progress.

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