THEORY OF PHONON TRANSPORT IN NANOCOMPOSITE MATERIALS

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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 \((\omega \tau > 1, \text{ or } \text{sample size} > \text{wavelength})\)
Three regimes for conductivity ($\kappa$) depending on the ratio phonon MFP ($\Lambda$) / 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) $d \sim \Lambda$: $1/\kappa = (d_1/\kappa_1 + d_2/\kappa_2 + 2/\sigma_K)/(d_1+d_2)$,

$$\sigma_K = \text{Kapitza resistance of interface}$$;

(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

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

\[ q=\text{phonon wavevector}; \ s=\text{phonon polarisation} \]

\[ N_0: \text{No. of unit cells}; \ \Omega: \text{Unit cell volume}, \]

\[ \bar{n}: \text{Bose-Einstein distribution function}, \]

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,

**Ab-initio pseudopotential DFPT**
I O Thomas and G P Srivastava, (Unpublished)
PHONONS IN BULK MATERIALS

![Graph showing phonon modes in bulk materials]

- LO,TO
- LA
- TA

Frequency (THz)

[001] [X]
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)
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

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

\(N_0\): No. of unit cells, \(\Omega\): Unit cell volume,

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

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

\(\tau_B^{-1}\): boundary scattering,

\(\tau_{MD}^{-1}\): isotope scattering,

\(\tau_{ID}^{-1}\): interface scattering,

\(\tau_{pp}^{-1}\): phonon-phonon scattering,

\(v_{qs,i}\): \(i^{th}\) velocity component for phonon \(\omega(qs)\)

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

\[
H'(IMS) = \frac{1}{2} \sum_{i=1}^{N} (M_i |v_i|^2 - M_A |v_A|^2) + \frac{1}{2} \sum_{i=N+1}^{N+M} (M_i |v_i|^2 - M_B |v_B|^2),
\]

M = mass; v = time derivative of atomic displacement
Interface mass-mixing scattering in A(n)/B(m) superlattice - 2

\[
\tau_{\text{IMS}}^{-1}(qs) = \frac{\alpha \pi}{2N_0(n+m)^2} \sum_{s'} d\omega(q's')g(\omega(q's'))\omega(qs)\omega(q's')
\]
\[
\times \frac{\bar{n}(q's') + 1}{\bar{n}(qs) + 1} \delta(\omega(qs) - \omega(q's')) \left[ (1 - \frac{e_A' e_A'}{e_B' e_B})^2 + (1 - \frac{e_B' e_B}{e_A' e_A})^2 \right],
\]

\(g(\omega)\): density of states,
\n\(\alpha\): interface atomic mixing parameter,
\n\(e_B/e_A\): interface atomic amplitude ratio.
Amplitude Ratio

For a diatomic linear chain with masses $M_A$ and $M_B$

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

$$M_0 = \frac{1}{2} \left( \frac{1}{M_A} + 1/M_B \right),$$
$$\Delta \left( 1/M \right) = \frac{1}{2} \left( 1/M_A - 1/M_B \right),$$

$l_z$ : period along the superlattice growth direction.

$$\frac{e_B}{e_A} = f(\omega)$$
Interface broken-bonds in A(N)/B(M) superlattice - 1

\[ H'(IDS) = \frac{1}{2} \sum_{i=1}^{N'} (K_0 |u_i|^2 - K_A |u_A|^2) + \frac{1}{2} \sum_{i=N'+1}^{N'+M'} (K_0 |u_i|^2 - K_B |u_B|^2), \]

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

\[ \tau_{IDS}(q_s) = \frac{\pi \omega_0^4}{4N_0(n+m)^2} \frac{\alpha'}{\Sigma_s'} \int d\omega(q's') \frac{g(\omega(q's'))}{\omega(qs)\omega(q's')} \times \frac{\bar{n}(q's') + 1}{\bar{n}(qs) + 1} \delta(\omega(qs) - \omega(q's')) \times \left[ 1 + \left( \frac{e_A e_A'}{e_B e_B'} \right)^2 + 1 + \left( \frac{e_B e_B'}{e_A e_A'} \right)^2 \right], \]

\[ \omega_0: \text{ highest phonon frequency,} \]

\[ \alpha': \text{ parameter for concentration of broken bonds.} \]
Anharmonic crystal potential

\[ V_3 = \frac{1}{3!} \sum_{q_5, q_5', q_5''} (a^\dagger_{q_5} - a_{-q_5})(a^\dagger_{q_5'} - a_{-q_5'}) (a^\dagger_{q_5''} - a_{-q_5''}) \Psi(q_5, q_5', q_5'') \delta_{q_5 + q_5' + q_5''}, \]

where

\[ \Psi(q_5, q_5', q_5'') = \frac{i}{\sqrt{N_0\Omega}} \sum_{b|q_5} \left( \frac{\kappa^3}{8M_bM_{b'}M_{b''}\omega(q_5')\omega(q_5'')\omega(q_5''')} \right)^{1/2} \psi_{\alpha\beta\gamma}(q_5, q_5', q_5'') e_{\alpha}(b|q_5') e_{\beta}(b'|q_5'') e_{\gamma}(b''|q_5'''), \]

with \( \Omega \) representing the unit-cell volume and \( e(b|q_5') \), etc., representing the polarization vectors. The Fourier components of the third-order interatomic force constant tensor \( \Psi(q_5, q_5', q_5'') \) can be expressed as

\[ \Psi(q_5, q_5', q_5'') = \sum_{h', h''} \Psi(0b, h' b', h'' b'') \phi^{h'} \phi^{h''}, \]

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

\[ v_3 = \bar{\gamma} \sqrt{\frac{\hbar^3}{2\rho V}} \sum_{q_3, q_3', q_3''} \frac{E_{q_3, q_3', q_3''}}{\sqrt{\omega(q_3)\omega(q_3')\omega(q_3'')}} \delta_{q_3 + q_3' + q_3'', G} \times (a_{q_3}^\dagger - a_{-q_3})(a_{-q_3'}^\dagger - a_{q_3'})(a_{q_3''}^\dagger - a_{-q_3''}), \]

with

\[ E_{i,j,k} = \left[ \sqrt{\omega(i)\omega(j)(\omega(i) + \omega(j))}\omega(k) - \omega(k) \right]/c_m(k) + \text{similar terms with } i, j \text{ and } k \text{ interchanged} \]/3!,

\[ \omega_R(j) = \text{zone centre frequency for } j^{\text{th}} \text{ branch}; \]

\[ C(j) = \text{phase velocity for } j^{\text{th}} \text{ branch}; \]

\[ \gamma = \text{Grüneisen's constant} \]

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

\[
\tau_{AH}^{-1}(qs) = \frac{\pi\hbar^2}{\rho V} \sum_{q's', q''s''} \frac{(B_{qs}, q's', q''s'')^2}{\omega(qs)\omega(q's')\omega(q''s'')} \text{DM}(q, q', q'')
\]

\[
\times \left[ \frac{\bar{n}_{q's'}(\bar{n}_{q''s''} + 1)}{\bar{n}_{qs} + 1} \delta(\omega(qs) + \omega(q's') - \omega(q''s''))\delta_{q+q', q''+q} 
+ \frac{1}{2} \frac{\bar{n}_{q's'}\bar{n}_{q''s''}}{\bar{n}_{qs}} \delta(\omega(qs) - \omega(q's') - \omega(q''s''))\delta_{q+\Gamma, q'+q''} \right],
\]

where

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

\[
\text{DM} = \text{dual mass term} \quad (M_A \neq M_B)
\]
When only acoustic phonons are considered

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

$\rho_{av}$: average density of SL, $\bar{c}$: average acoustic velocity, $G$: reciprocal lattice vector = 0 ($\neq 0$) for Normal (Umklapp) processes, $\gamma$: Grüneisen’s constant.

$DM = \text{dual mass term } (M_A \neq M_B)$
Anharmonic scattering in A(n)/B(m) superlattice – 3

Dual Mass Term

\[
DM(q_s, q_s', q_s'') = \frac{1}{64} \times \frac{1}{2\rho_A^3}
\left[ 1 + \frac{\rho_A^2}{\rho_B^3} \left( \frac{e_B}{e_A} + \frac{e_B'}{e_A'} + \frac{e_B''}{e_A''} \right) + \frac{\rho_B}{\rho_A^3} \left( \frac{e_B e_B'}{e_A e_A'} + \frac{e_B e_B''}{e_A e_A''} + \frac{e_B e_B'}{e_A e_A'} \right) + \frac{\rho_A^3}{\rho_B^2} \left( \frac{e_B e_B'}{e_A e_A'} \right) \right]
\]

\[
\frac{1}{2\rho_B^3} \left[ 1 + \frac{\rho_B^2}{\rho_A^3} \left( \frac{e_A}{e_B} + \frac{e_A'}{e_B'} + \frac{e_A''}{e_B''} \right) + \frac{\rho_A}{\rho_B^3} \left( \frac{e_A e_A'}{e_B e_B'} + \frac{e_A e_A''}{e_B e_B''} + \frac{e_A e_A'}{e_B e_B'} \right) + \frac{\rho_B^3}{\rho_A^2} \left( \frac{e_A e_A'}{e_B e_B'} \right) \right]^2
\]

\( \rho_j = \text{mass density of } j^{\text{th}} \text{ material} \)
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 $\gamma$ 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)

<table>
<thead>
<tr>
<th>Structure</th>
<th>α (s^3)</th>
<th>α' (s^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(19)/Ge(5)</td>
<td>550</td>
<td>0</td>
</tr>
<tr>
<td>Si(72)/Ge(30)</td>
<td>10^7</td>
<td>10^-4</td>
</tr>
</tbody>
</table>

No dislocations
Large concentration of defects and dislocations
THERMAL CONDUCTIVITY RESULTS – Si(n)/Ge(m)[001] superlattices
Thermal conductivity of \((\text{GaAs})_2(\text{AlAs})_2[001]\) SL


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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