**IMPROVEMENT IN THERMAL CONDUCTIVITY OF GRAPHENE BASED COMPOSITES FOR BETTER THERMAL INTERFACE MATERIALS.**

By

**Abir Chowdhury** (Student No. 0706021)

**Niloy Talukder** (Student No. 0706147)

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Supervised By

**Dr. Samia Subrina**

Assistant Professor

Department of Electrical and Electronic Engineering

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Department of Electrical and Electronic Engineering

Bangladesh University of Engineering and Technology

Dhaka-1000

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**Abstract**

Graphene, a planar single sheet of *sp*2-bonded carbon atoms arranged in honeycomb lattice, has a number of its unique properties including extremely high thermal conductivity. Graphene, as filler in nanocomposite, shows promising improvement in thermal conductivity of thermal interface material (TIM) because of its high thermal conductivity and planer geometry. Thermal coupling with base matrix is also strong as compared to the material with high thermal conductivity, CNT. Overall thermal resistance between two interfaces is reduced when highly conductive TIM is used. Experiments have shown significant improvement in heat conduction efficiency using graphene filler for TIM. Here heat conduction behavior of suspended and few layer graphene is reviewed. Different parameters influencing nano-composite thermal conductivity is also discussed. In this work, we have used silicone oil, a commercially available TIM, as base matrix of the composite. Effects of particle size, aspect ratio, thermal interface resistance and temperature on thermal conductivity of the composite have been observed using Effective Medium Approximation proposed by Nan. The thermal conductivity of graphene filler of different lateral sizes and layers have been approximated using landauer approach from ballistic to diffusive limit. Composite thermal conductivity varies significantly with the variation of the graphene flake dimension, from nanometer to micrometer range. For SLG-MLG mixture of nanometer to micrometer sized graphene flakes as filler we get thermal conductivity enhancement of around 5000%. Finally using simulation result it is shown that graphene nanocomposite as TIM in desktop or laptop significantly improves heat transfer efficiency.

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**List of Abbreviations & Acronyms**

|  |  |
| --- | --- |
| ∆T | thermal gradient |
| µm | micrometer |
| 1/τB | phonon scattering rate |
| 1D | one dimensional |
| 2D | Two dimensional |
| 3D | three dimensional |
| A | cross-sectional area |
| Anc | noncontact area |
| ASIC | Application-Specific Integrated Circuit |
| BLT | Bond Line Thickness |
| BLG | Bilayer graphene |
| C | specific heat |
| CNT | Carbon Nanotube |
| CTE | coefficient of thermal expansion |
| CVD | Carbon Vapor Deposition |
| d | material thickness |
| D | nanostructure or grain size |
| DWCNT | double-walled carbon nanotubes |
| E | phonon energy |
| EMA | Effective medium approximations |
| EMT | effective medium theory |
| et al. | And others |
| FLG | Few layer Graphene |
| fm | upper limit of the phonon frequencies defined by the phonon dispersion |
| Gball | Ballistic thermal conductance |
| GNPs | graphite nanoparticles |
| GNR | Graphene Nanoribbon |
| GONs | graphene oxide nanoparticles |
| H | micro-hardness of the softer material |
| ħ | reduced Planck’s constant |
| kAir | air thermal conductivity |
| kb | thermal conductivity of base matrix |
| kball | Ballistic thermal conductivity |
| kc | thermal conductivity of the composite |
| ke | electron thermal conductivity |
| kh | harmonic mean thermal conductivity of the interface |
| km | matrix thermal conductivity |
| kp | Phonon thermal conductivity |
| kp | Particle thermal conductivity |
| kTIM | thermal conductivity of the TIM |
| k-vector | Momentum vector |
| LA | longitudinal acoustic |
| m | mean asperity slope |
| M | mass of an atom |
| MD | Molecular Dynamics |
| MG-EMA | Maxwell-Garnett Effective medium approximation |
| MLG | Multilayer Graphene |
| MPa | Mega Pascal Pressure |
| MWCNT | multi-walled carbon nanotubes |
| N | number of atoms |
| nm | nanometer |
| P | applied pressure |
| p | specularity parameter |
| Psi | Per square inch |
| q | heat dissipative power |
| RB | Boundary resistance |
| Rc | thermal contact resistance |
| Rcs | surface contact resistance |
| SLG | Single Layer Graphene |
| TA | transverse acoustic |
| TBR | thermal boundary resistance |
| TEM | Transmission Electron Microscopy |
| TIM | Thermal Interface Material |
| TPa | Tera Pascal |
| U-process | Umklapp process |
| ZA | flexural out-of-plane acoustic |
| γ | Gruneisen parameter |
| γLA | Gruneisen parameter averaged separately for LA modes |
| γTA | Gruneisen parameter averaged separately for TA modes |
| Η | Thermal Conductivity enhancement |
| Λ,λ | Phonon mean free path |
| λeff | Effective mean free path |
| σ | root mean square roughness |
| σ/ws | Ballistic thermal conductance per unit cross section |
| τ | phonon relaxation time |
| τB | phonon lifetime |
| υ | phonon group velocity |
| υ⊥ | transverse component of group velocity |
| ω | phonon frequency |

**Chapter 1**

**Introduction**

The search for materials that conduct heat well has become essential for design of the next generation of integrated circuits and three-dimensional (3D) electronics. The excess heating generated by energy dissipation in electronic components such as microprocessors, which can degrade their performance, is hindered in the process of removal to the ambient environment. To maintain a better removal of heat from the device, the interfacial gap between the contacts which normally contains air having very poor thermal conductivity has to be replaced by some highly conducting material. These materials are typically referred as thermal interface materials (TIMs). We have discussed different significant characteristics of ideal thermal interface material. Several types of thermally conductive materials can be used including greases, reactive compounds, elastomer and pressure sensitive adhesive films, all are designed to conform to surface irregularities, thereby eliminating air voids and improving heat flow through the thermal interface. Inclusion of fillers like metals or different carbon based materials tends to increase thermal conductivity of TIMs. A mixture of commercial thermal paste or polymer with graphene flakes is another candidate TIM option. We have discussed heat conduction processes in material, specifically for carbon material. Many key factors that influence the thermal conductivity property of nanocomposite, mechanisms to explain the enhancement of thermal conductivity for filler inclusion are also mentioned briefly. Problems of CNT as filler are also featured. We have explored different prospects of graphene based nanocomposite. Graphene with its large thermal conductivity and size effect can become an important element in TIM. It showed the highest owing to its geometry and better coupling to base materials [1,9]. Many theoretical models are available to predict the composite thermal conductivity. But they have some limitations when graphene or carbon based composites are considered. We will use effective medium theory proposed by Nan to see the variation of a composite thermal conductivity with the inclusion of fillers. We have considered both nm and µm sized particles. First we have checked the validity of our approach by keeping similarity with the mentioned composition of different size and layer variation in graphene-MLG-epoxy composite, in the experiment done by Shahil et al. [2]. We have seen that our theoretically calculated values suit with the experimental result. In our analysis, we have considered silicone oil as a base matrix which has vast uses in commercial TIM products. We have observed how different parameters of filler and composite like volume fraction, filler size, aspect ratio, mean free path, interfacial resistance etc. affect the composite thermal conductivity. We have also discussed the change in thermal conductivity of the composite for the variation of graphene-MLG (filler) thermal conductivity with temperature. Matrix thermal conductivity is varied next. For each case first we have considered nm sized graphene flakes then µm sized graphene flakes and finally combination of nm and µm sized particles. For a commercial TIM of silicone oil, thermal conductivity variation with the inclusion of graphene is also observed. At the end of the report a typical configuration for a high power microprocessor or ASIC (Application-Specific Integrated Circuit) package attached to a heat sink is shown. Finite element analysis was conducted on a simplified solid model of the package and board using a software tool COMSOL Multiphysics 3.5. This model resembles to a thermal path from chip to heat sink where TIMs of different thermal conductivity are applied to see the effect in heat propagation. Better performance is achieved with the application of graphene based TIMs. In conclusion part we have summarized the result of our analysis.

**Chapter 2**

**Thermal Interface Material: Necessity and Application**

Heat removal has become a crucial issue for continuing progress in the electronic industry owing to increased levels of dissipated power. The search for materials that conduct heat well has become essential for design of the next generation of integrated circuits and three dimensional (3D) electronics.

When two typical electronic component surfaces are brought together, less than one percent of the surfaces make physical contact. As much as 99% of the surfaces are separated by a layer of interstitial air. Some heat is conducted through the physical contact points, but much more has to transfer through the air gaps. Since air is a poor conductor of heat, it should be replaced by a more conductive material to increase the joint conductivity and thus improve heat flow across the thermal interface.

**2.1 Thermal Contact Resistance**

Thermal contact resistance makes the vital role in conducting heat through two connected materials. When two solid surfaces are joined, as shown in Fig. 1, asperities on each of the surfaces limit the actual contact between the two solids to a very small fraction, perhaps just 1%–2% of the apparent area of lightly loaded interface [3, 4].

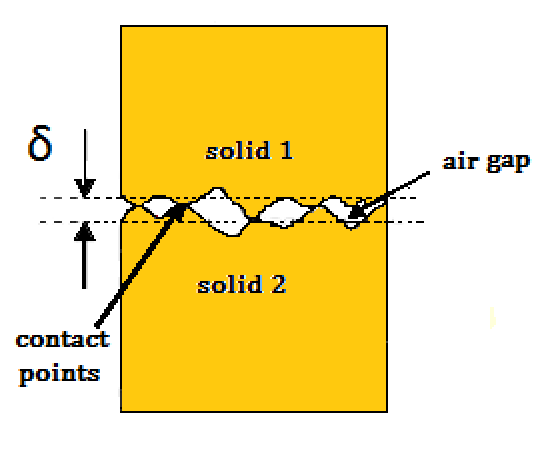


Figure 2.1: A schematic that shows real area of contact between two solid is less than apparent area of contact. ( courtesy- Ravi Prasher, Vol. 94, No. 8, August 2006 | Proceedings of the IEEE 1571)

The flow of heat across such an interface involves solid-to-solid conduction in the area of actual contact Ac and conduction through the fluid occupying the noncontact area Anc of the interface. The restriction in heat flow is manifested by the thermal contact resistance (Rc) at the interface. If we consider the solid–solid contact resistance between two nominally flat surfaces 1 and 2 as Rcs, then assuming plastic deformation of the asperities it is found that [3],

(2.1)

where, σ =(σ12 +σ22)1/2 , σ is the root mean square roughness ;

m = (m12+m22)1/2 , m is the mean asperity slope which is a measure of the slope of the rough surface,

H is the micro-hardness of the softer material,

P the applied pressure, and

is the harmonic mean thermal conductivity of the interface. .

Thus, due to the contact resistance, the excess heating generated by energy dissipation in electronic components such as microprocessors, which can degrade their performance, is hindered in the process of removal to the ambient environment. To reduce Rc i.e. to maintain a better removal of heat from the device, the interfacial gap between the asperities in Fig. 1 has to be replaced by some highly conducting material. These materials are typically referred as thermal interface materials (TIMs).

In the following figure we illustrate an example of thermal conduction pathway in a common packaging configuration for a microprocessor. These conduction pathways can contain several interfaces between materials (e.g. interfaces between die and heat spreader, and heat spreader and heat sink) that consume a significant portion of the thermal resistance budget[5].

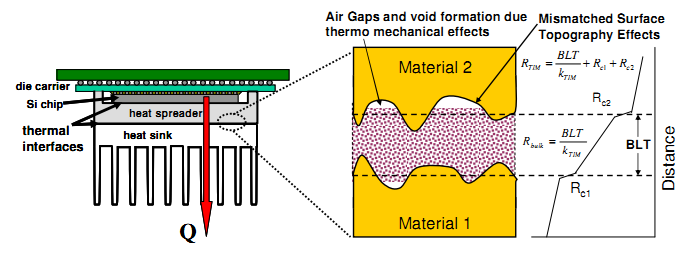


Figure 2.2: Illustration of thermal conduction pathways in a common configuration for a microprocessor and its packaging. (courtesy - Matthew A. Panzer, June 2010, Stanford University Dept. of Mechanical Engineering.)

The thermal interface resistances along the pathway from the generation region within the device to the ambient environment have to be minimized for better heat propagation. The TIM material increases the real contact area by conforming to the surface topography. The total resistance of the TIM is the sum of its interface resistances with the two materials and the volumetric contribution, which depends on the TIM thermal conductivity and the bond line thickness (BLT)[5].

Rc due to an ideal TIM RcTIM for nominally flat surfaces can be calculated as [1]

(2.2)

where, kTIM is the thermal conductivity of the TIM.

Eq. (2) is appropriate for an ideal TIM where it is assumed that the gap between two solids is completely filled with TIM. In Fig. 2, we can see the effect of a real TIM. This figure shows that real TIMs have finite BLT, and at the interface they do not completely fill the voids because of their inability to completely wet the surface. Therefore, the thermal performance of real TIMs falls short of that predicted by (2). From Fig. 2, we can be infer that the total thermal resistance for the presence of real TIM. RTIM can be written as [3],

(2.3)

where, Rc represents the contact resistances of the TIM with the two bounding surfaces.

Figure 3 shows the variation of contact resistance between copper and silicon (from Eq. 1) and change in contact resistance with the application of ideal TIMs of two thermal conductivity values (Eq. 2) for pressure range applicable to electronics cooling [6]. H of copper, which is the softer material, is taken as 1280 MPa. In Fig. 3, σ of the Cu is assumed 1 μm and σ of the Si is assumed 0.1 μm (assuming polished Si). m is calculated by the relation m = 0.076(σ x 106)1/2[4].

0

2

4

6

8

10

12

0

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

0.9

1

Pressure P x 105 ( Pa)

Contact resistance Rc (Kcm2W-1)

Bare Si and Cu

…… RTIM (TIM k =0.2 Wm-1K-1)

RTIM (TIM k =1.0 Wm-1K-1)

Figure 2.3: Thermal contact resistance between two solids without TIM and with TIMs of two values for different applied pressure (theoretical analysis from Eq. (1) and Eq.(2)) [courtesy- Ravi Prasher].

We see from figure 3 that Rcs is very high at low pressures. It shows that even for kTIM = 0.2 W mK-1 (typical value for pure polymers) ,RcTIM is very small compared to Rcs. The total Rc is given by

(2.4)

because these resistances are in parallel. We can also see that with higher thermal conductivity value for TIM (say 1W mK-1) contact resistance degrades which signifies that TIMs with higher thermal conductivity is better for heat propagation.

**2.2 Thermal Conductivity**

Thermal interface materials (TIMs) minimize the thermal gradient ∆T, which is a physical quantity that describes in which direction and at what rate the temperature changes, thus reducing the thermal resistance between two contact surfaces. The thermal conductivity k is the intrinsic property of materials to conduct heat.

The thermal conductivity is defined by the induced heat dissipative power Q through the contact surface A along the length of the thermal path - corresponding to the material thickness (d) - and the temperature gradient ∆T by,

(2.5)

with d/ ∆T is const. for homogeneous materials.

The thermal resistance through the material itself, is an internal resistance and is defined after Fourier series development:

(2.6)

It depends on the following factors:

* material thickness
* the thermal conductivity
* surface area

In addition to the internal material resistance, we have to consider the contact resistances (at both sides of the material) to measure total thermal resistance which hinders the heat flow through the thermal path. Thermal contact resistances are mainly caused by incomplete fitting and air interstitials affecting the border areas with kAir = 0.027 W/mK acting as thermal insulators.

Thermal contact resistances depend on:

* Surface structures, surface roughness and surface unevenness
* Pressure
* Volumetric expansion

The overall thermal resistance is defined as:

(2.7)

Eq.2.7 is analogous to Eq. 2.3 with,

(2.8)

To improve the heat dissipation across an interface it is important to minimize the value of total contact resistance . From Eq.7 we see this can be achieved by reducing the bond line thickness and employing a TIM with the highest possible thermal conductivity. On the other hand reducing surface roughness and applying pressure can reduce contact resistance. A smoother surface reduces the heights and depths of the peaks and valleys that a TIM has to fill and pressure acts to mate the interface material to its surfaces, minimizing the amount of air remaining at the interface. Pressure can also reduce thermal resistance of soft materials by reducing the material thickness [6].

Although the use of TIMs helps to improve heat transfer across an interface, it is widely recognized that TIMs increasingly account for most of the system total thermal resistance [7]. So it is needed that TIM material thickness should be as small as possible.

The ideal thermal interface material should have the following characteristics:

1. High thermal conductivity
2. Easily deformed by small contact pressure to contact all uneven areas of both mating surfaces, including surface pores, eliminating Rcontact.
3. Minimal thickness
4. Would not leak out of the interface.
5. Would maintain performance indefinitely.
6. Non-toxic,
7. Manufacturing friendly (easy to apply and remove )

**2.3 TIM Classification**

Several types of thermally conductive materials can be used to eliminate air gaps from a thermal interface, including greases, reactive compounds, elastomers and pressure sensitive adhesive films. All are designed to conform to surface irregularities, thereby eliminating air voids and improving heat flow through the thermal interface. Following table summarizes different types of TIMs.

Table 2.1: Different TIM materials with their advantages and disadvantages.

|  |  |  |  |
| --- | --- | --- | --- |
| TIM type | General  Characteristics | Advantages | Disadvantages |
| Greases | Typically silicone based matrix loaded with  particles to enhance thermal conductivity | i)High bulk thermal conductivity.  ii)Thin BLT with minimal attach pressure  iii)Low viscosity enables matrix materials to easily fill surface crevices  iv)TIM curing not required  v)TIM delamination is not a concern  vi)very low thermal resistance | i)susceptible to grease pump-out and phase separation  ii)considered messy in a manufacturing environment due to the tendency of migrate  iii)no electrical insulation |
| Phase  Change  Materials | Polyolefin, epoxy, low molecular weight, polyesters, acrylics typically with BN or Al2O3 fillers | i)higher viscosity leads to increased stability and hence less susceptible to pump-out  ii)Application and handling is easier compared to greases  iii) no cure required  v) Delamination is not a concern | i)lower thermal conductivity than greases  ii)surface resistance can be greater than greases. Can be reduced by thermal pre-treatment  iii)requires attach pressure to increase thermal effectiveness and hence and can lead to increased mechanical stresses |
| Gels | Al, Al2O3, Ag particles in silicone, olefin matrices that require curing | i)conforms to surface irregularity before cure  ii)no pump-out or migration concerns | i)cure process needed  ii)lower thermal conductivity than grease  iii)lower adhesion than adhesives, delamination can be a concern |
| Elastomers | silicone elastomer pads filled with thermally conductive ceramic particles | i) As pressure is increased, more of the microscopic voids are filled by the elastomer  ii) As pressure is increased, thermal resistance decreases.  iii) Pads can conduct very large heat loads from discrete power semiconductors to heat sinks  iv)can provide long term electrical insulation | i)not flow freely like the greases or compounds  ii) At low pressures the elastomer cannot fill the voids between the surfaces  iii) At low pressures the thermal interface resistance is high. |
| Adhesives | Typically Ag particles in cured epoxy matrix | i)conform to surface irregularity before cure  ii)no pump out  iii)no migration | i)cure process needed  ii)delamination post-reliability testing is a concern  iii)since cured epoxies have high post-cure modulus, CTE mismatch induced stress is a concern |

**2.4 TIM Application:**

Thermal interface materials (TIMs) are necessary for heat dissipation because microscale gaps/voids between thermal transfer surfaces (e.g., between a CPU and heat sink) which is unavoidable.

Following figure shows TIM application in desktop and laptop. Here it is shown that the Si die or the chip is flat. In reality, the Si die or the chip surface is not flat. The chip is typically warped due to the coefficient of thermal expansion (CTE) mismatch between the die and the package substrate.

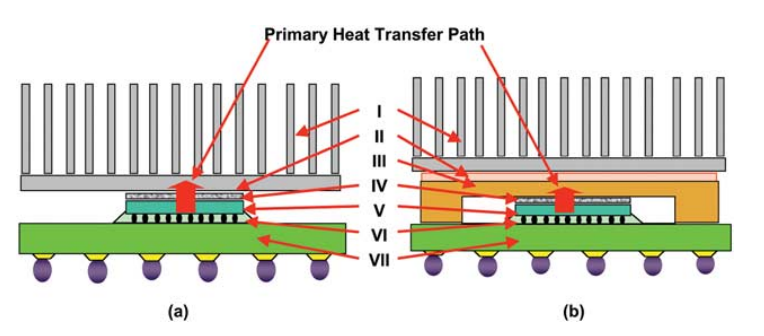


Figure 2.4: Schematic illustration of the two thermal architectures. (a) Architecture I, typically used in laptop applications. (b) Architecture II, typically used in desktop and server applications.

In the figure: I-heat sink; II-TIM; III-HeatSink; IV-TIM; V-die; VI-underfill; and VII-package substrate.

TIMs are also used in other electronic devices, mechanical tools where quick heat removal is needed.

**Chapter 3**

**Graphene: Heat Transport**

**3.1 Introduction of Graphene**

Graphene is a wonder material that has initiated a new horizon to materials science with its many unique properties. It is a substance made of pure carbon, with atoms arranged in a regular hexagonal pattern similar to graphite, but in a one-atom thick sheet. It is an allotrope of carbon whose structure is a single planar sheet of sp2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice [8]. This strictly two-dimensional material exhibits exceptionally high crystal and electronic quality and has already revealed many prospects of new physics and potential applications. The term graphene was coined as a combination of graphite and the suffix-ene by Hanns-Peter Boehm, who described single-layer carbon foils in 1962 [10].

Graphene is the basic structural element of some carbon allotropes including graphite, charcoal, carbon nanotubes and fullerenes (shown in figure 3.1). Graphene’s monolayer in structure makes more advantageous due to its flexibility in chemical and electronic structures such as it can be rolled-up into metallic or semiconducting carbon nanotubes, wrapped to form buckyballs, or even graphite when they are piled-up [8]. The carbon-carbon bond length in graphene is about 0.142 nanometers [11] and graphene sheets stack to form graphite with an inter-planar spacing of 0.35 nm.

The atomic structure of isolated, single-layer graphene was studied by transmission electron microscopy (TEM) on sheets of graphene suspended between bars of a metallic grid [12]. Electron diffraction patterns showed the expected honeycomb lattice of graphene. Graphene differs from most conventional three-dimensional materials. Intrinsic graphene is a semi-metal or zero-gap semiconductor.

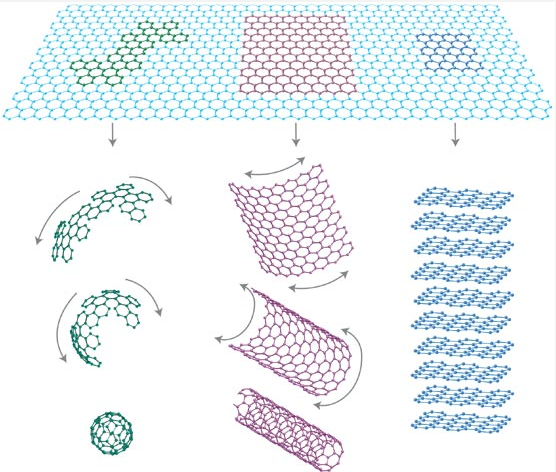


Figure 3.1: Graphene: Mother of all graphitic forms. It is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotubes or stacked into 3D graphite [8].

Experimental results from transport measurements show that graphene has a remarkably high electron mobility at room temperature, with reported values in the excess of 15,000 cm2V−1s−1 [8] which is nearly independent of temperature between 10 K and 100 K [13, 14]. This implies that the dominant scattering mechanism is defect scattering. Scattering by the acoustic phonons of graphene places intrinsic limits on the room temperature mobility to 200,000 cm2V−1s−1 at a carrier density of 1012 cm−2 [15,16] The corresponding resistivity of the graphene sheet would be 10−6 Ω·cm. This is less than the resistivity of silver, the lowest resistivity substance known at room temperature [17]. However, for graphene on SiO2 substrates, scattering of electrons by optical phonons of the substrate is a larger effect at room temperature than scattering by graphene’s own phonons. This limits the mobility to 40,000 cm2·V−1·s−1[15].

The near-room temperature thermal conductivity of graphene was measured to be around 5000 Wm−1K−1 but it varies with length and other aspects. A brief description of heat propagation in graphene is given later. Graphene appears to be one of the strongest materials ever tested. Measurements have shown that graphene has a breaking strength over 100 times greater than a hypothetical steel film of the same (incredibly thin) thickness, with a tensile modulus (stiffness) of 1 TPa (150,000,000 psi) [18].

Bilayer graphene having two layers also shows interesting electrical properties, such as the quantum hall effect, a tunable band gap [19], and potential for excitonic condensation [20]-making them promising candidates for optoelectronic and nano-electronic applications. In the form of Graphene nanoribbons (GNRs), which are essentially single layers of graphene that are cut in a particular pattern to give them certain electrical properties, many excellent physical properties like high electrical and thermal conductivity, low noise etc. are achieved which can lead to vast applications in integrated circuit designs and semiconductor devices.

Several potential applications for graphene are under development, and many more have been proposed. These include lightweight, thin, flexible, yet durable display screens, electric circuits, and solar cells, as well as various medical, chemical, and industrial processes enhanced or enabled by the use of new graphene materials.

**3.2** **Basics of Heat Conduction**

As device scales down to nanometer range heat generation is on the rise. New material is required for efficient heat removal from device. Graphene is the latest member in the family of carbon materials. Recent experiments [21, 22] suggest graphene as a good candidate, with measured thermal conductivities of 3000- 5000 W/mK for layer lengths of ∼10 µm. It shows significant improvement in thermal conductivity over bulk graphite (~2000 W mK-1). After that researchers have started seeing heat conduction properties of graphene from a new angle.

Thermal conductivity is introduced through Fourier’s law, q = −K ΔT, where q is the heat flux, K is the thermal conductivity and ΔT is the temperature gradient. In this expression, K is treated as a constant, which is valid for small temperature (T) variations. In a wide temperature range, K is a function of T. In anisotropic materials, K varies with crystal orientation and is represented by a tensor. [23-25]

In solid materials heat is carried by acoustic phonons — that is, ion-core vibrations in a crystal lattice — and electrons so that , where and are the phonon and electron contributions, respectively. In metals, is dominant owing to large concentrations of free carriers. Heat conduction in carbon materials is usually dominated by phonons, even for graphite, which has metal-like properties. This is explained by the strong covalent sp2 bonding resulting in efficient heat transfer by lattice vibrations.

The phonon thermal conductivity is expressed as

(3.1)

Here j is the phonon polarization branch, that is, two transverse acoustic branches and one longitudinal acoustic branch; υ is the phonon group velocity, which, in many solids, can be approximated by the sound velocity; τ is the phonon relaxation time, ω is the phonon frequency and C is the specific heat [26].

Acoustic phonons are scattered by other phonons, lattice defects, impurities, conduction electrons and interface. In relaxation-time approximation various scattering mechanisms are additive i.e. τ-1= Στi-1, where i indicates different scattering processes.

Phonon mean free path (Λ) is the distance that a phonon travels before scattering. However, in nano-structured materials the reduction in system sizes to dimensions comparable to the mean free path or phonon wavelength strongly modifies the conduction physics. Phonon mean-free path (λ) is related to the relaxation time as Λ = τυ. [26]

The thermal transport is called diffusive if the size of the sample, L > Λ and when L < Λ the thermal transport is termed ballistic. Fourier law assumes diffusive transport. A simple equation for thermal conductivity derived from the kinetic theory of gases, is kp = (1/3) CpυΛ, where kp is thermal conductivity and Cp is specific heat capacity.

High thermal conductivity of graphene surpasses graphite and is in part attributed to the long phonon mean free path Λ in carbon nanostructures, exceeding 500 nm in nanotubes [27,28] and graphene sheets.[21].The phonon mean-free path for suspended graphene layers was estimated to be ~775 nm near room temperature [26]. Therefore, it is expected that thermal transport at the nanoscale will be dominated by a ballistic rather than a diffusive mechanism.

**3.2.1 Nano-scale Physical Considerations**

In nanostructure energy is transported from high temperature to low temperature reservoir in the form of electron and phonon conduction. There may be no clear distinction between nanostructure and the reservoirs. To enter and conduct across the nanostructure, the phonons must traverse an interface between the reservoir and the nanostructure, which are in general two different materials. The abrupt change in material properties and geometry at the interface creates additional phonon scattering events, resulting in a thermal boundary resistance (TBR) highly localized near the interface. We can compare scattering of phonons due to impedance mismatches between the two domains to sound waves reflecting off of a wall. In nanostructure, the phonons can scatter with other phonons, electrons, boundaries, or defects,

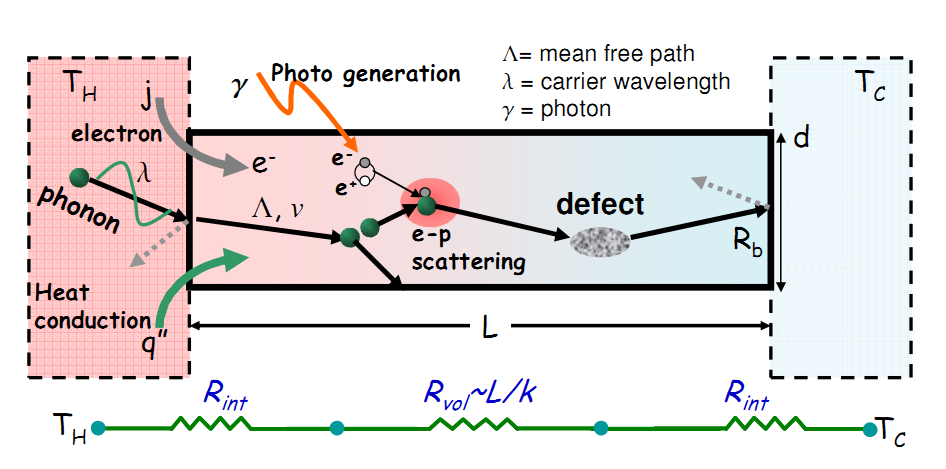
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Figure 3.2: Illustration of a common general geometry encountered in nanoscale energy transport. . (courtesy: Matthew A. Panzer, June 2010, Stanford University Dept. of Mechanical Engineering.)

creating volumetric contributions to the thermal resistance. Electrical current or optical interactions can also generate phonons (i.e. heating) and local scattering within the volume.

Figure explanation: In general, the nanostructure can sustain an electric current (j) and a heat flux (q”); in dielectrics, the heat flux is dominated by phonon (illustrated by green circle) conduction. The total thermal resistance is due to a combination of interface scattering (illustrated by dotted gray arrows) and volumetric effects such as scattering with defects, boundaries, and carriers, the physics of which are strongly modified in the ballistic and mesoscopic regimes due to reduced dimensions. In the continuum transport regime, the volumetric contribution to the thermal resistance scales strongly with length, Rvol ~ L/ k(L). Intrinsic conductivity, k(L), is a weak function of length [29]. However, thermal boundary resistance, tends to fall within a small range of values 10-7-10-9m2K/W [30,31].

**3.2.2 Classification of thermal conductivity**

Thermal conductivity can be intrinsic or extrinsic. The data for suspended or partially suspended graphene is closer to the intrinsic K because suspension reduces thermal coupling to the substrate and scattering on the substrate defects and impurities.

Thermal conductivity is called intrinsic when it is limited by the crystal-lattice anharmonicity. The lattice anharmonicity refers to the vibrational effects that do not follow simple harmonic motion. This effect is generally small and can be usually neglected. If the lattice vibration is purely simple harmonic, two localized wave-packets (phonons) will have zero interaction, they will pass through each other and we can use the principle of superposition when they coincide. Physical system is not harmonic which means that when two phonons pass each other they will have nontrivial interaction [43]. Potential energy has terms higher than the second order with respect to the ion displacements from equilibrium. The intrinsic K limit is reached when the crystal is perfect, i.e. without defects or impurities, and phonons can only be scattered by other phonons.

Thermal conductivity is extrinsic when it is mostly limited by the extrinsic effects, such as phonon-rough-boundary or phonon-defect scattering.

**3.2.3 Phonon Scattering**

Normally thermal transport in graphene is dominated by intrinsic properties of strong sp2 bonding which gives rise to high k value. But in nanostructure**,** k is reduced by scattering from boundaries. It is evaluated as

(3.2)

Here τB is the phonon lifetime and 1/τB is the phonon scattering rate, D is the nanostructure or grain size and p is the specularity parameter defined as a probability of specular scattering at the boundary. The momentum-conserving specular scattering (p = 1) does not add to thermal resistance. One can find p from the surface roughness or use it as a fitting parameter to experimental data. The commonly used expression for the phonon specularity is given by

(3.3)

where η is the root mean square deviation of the height of the surface from the reference plane and λ is the wavelength of the incident phonon.[39]

When the phonon-boundary scattering is dominant, K scales with D as kp ~  CpυΛ  ~  CpυτB ~ CpυD [26].

Anharmonic potential scatter phonons make them unstable which leads to finite thermal conductivity. But not all phonon-phonon scatterings contribute to the finite thermal conductivity. The anharmonic phonon interactions, which lead to the finite thermal conductivity in three dimensions, can be described by the umklapp processes [40]. The umklapp scattering rates depend on the Gruneisen parameter γ, which determines the degree of the lattice anharmonicity [40,41]. Umklapp scattering is due to impurities, defects, and the finite size of the crystal.

**3.2.4 Umklapp Scattering**

Umklapp scattering (also U-process or Umklapp process) is the transformation, of a wave vector to another Brillouin zone as a result of a scattering process, for example an electron-lattice potential scattering or an anharmonic phonon-phonon (or electron-phonon) scattering process, reflecting an electronic state or creating a phonon with a momentum k-vector outside the first Brillouin zone.    
Umklapp scattering is one process limiting the thermal conductivity in crystalline materials, the others being phonon scattering on crystal defects and at the surface of the sample [42].

**3.2.5 Phonon dispersion of graphene:**

Knowledge of phonon dispersion in graphene is important to understand its thermal properties. Related terms of phonon dispersion for graphene are introduced here.

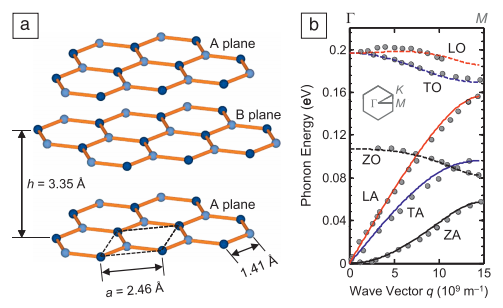
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Figure 3.3: (a) Schematic of the atomic arrangement in graphene sheets. Dashed lines in the bottom sheet represent the outline of the unit cell. (b) Graphene phonon dispersion obtained by the force constant method along the Γ-to-M crystallographic direction. Here linear in-plane acoustic modes (longitudinal acoustic, LA; transverse acoustic, TA), as well as flexural out-of-plane acoustic (ZA) modes with a quadratic dispersion are shown.(courtesy: Eric Pop et.al. MRS BULLETIN ,DECEMBER 2012)

The graphene unit cell, marked by dashed lines in Figure 3a, contains N =2 carbon atoms. This leads to the formation of three acoustic (A) and 3N – 3 = 3 optical (O) phonon modes, with the dispersions shown in figure 3.3(b).

The dispersion is the relationship between the phonon energy E and frequency ω (E= ħω , where ħ is the reduced Planck’s constant) and the phonon wave vector q. Longitudinal (L) modes correspond to atomic displacements along the wave propagation direction, whereas transverse (T) modes correspond to in-plane displacements perpendicular to the propagation direction. In typical three-dimensional (3D) solids, transverse modes can have two equivalent polarizations, but the unique 2D nature of graphene allows out-of-plane atomic displacements, also known as ﬂexural (Z) phonons [32].

In nanostructures, the phonon energy spectra are quantized due to the spatial confinement of the acoustic phonons. The quantization of the phonon energy spectra usually leads to decreasing phonon group velocity. Thermal conductivity is affected by the modification of the phonon energies, group velocities and density of states, together with phonon scattering from boundaries. In most cases, the spatial confinement of acoustic phonons results in a reduction of the phonon thermal conductivity.[33,34] However, it was predicted that the thermal conductivity of nanostructures embedded within the acoustically hard barrier layers can be increased via spatial confinement of acoustic phonons.[35-38]

**3.2.6 Few-layer graphene**

As more layers stack on graphene sheet thermal transport becomes limited by

(1) intrinsic properties of the FLG lattice, that is, crystal anharmonicity; and

(2) extrinsic effects, for example, by phonon-boundary or defect scattering.

The optothermal Raman study found that k of suspended uncapped FLG decreases with increasing n, approaching the bulk graphite limit. The bulk value of k along the basal planes is recovered at n≈8. The ambiguity of the data point for n≈8 is explained by the fact that n in FLG can be determined accurately from Raman spectrum only if n≤6. [44,45]

This evolution of K was explained by considering the intrinsic quasi-2D crystal properties described by the phonon Umklapp scattering. As n in FLG increases, the phonon dispersion changes and more phase-space states become available for phonon scattering leading to a decrease in k. The phonon scattering from the top and bottom boundaries in suspended FLG is limited if constant n is maintained over the layer length [46].

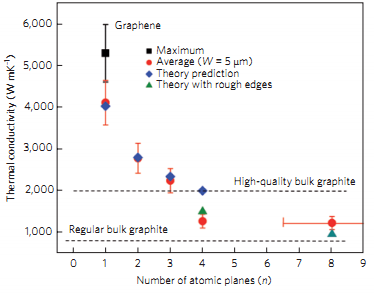


Figure 3.4: Measured and calculated thermal conductivity of suspended FLG as a function of n (at the fixed flake width, W). For n > 4, K can drop below the bulk graphite limit owing to the onset of the phonon-boundary scattering from the top and bottom interfaces; K recovers for sufficiently thick films.(courtesy: Balandin A A. 2011. 10 569 )

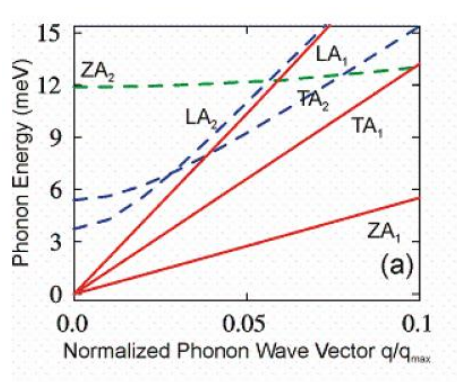


Figure 3.5: Phonon dispersion in graphene (solid curves) and bilayer graphene (added dashed curves). Note that the longitudinal acoustic (LA2) and transverse acoustic (TA2) phonon branches in bilayer graphene have very small slope, which translates to low phonon group velocity.(courtesy: Ref [46])

The small thickness of FLG (n < 4) also means that phonons do not have a transverse component in their group velocity (υ⊥ = 0) leading to even weaker 1/τB term for phonon scattering from the top and bottom boundaries. In FLG films with n > 4 the boundary scattering can increase, because υ⊥ ≠ 0, and it is harder to maintain constant n through the whole area of a FLG flake, resulting in k below the graphite limit [46].

Conventional thin films or nanowires still retains “bulk” features as the cross-sections of these structures are measured in many atomic layers.

The presence of the evaporated oxide on top of the graphene is known to cause defects in the graphene layer. In conventional crystalline thin films, where H < Λ, but still much larger than the lattice constant, K grows with H as K ≈ CυH until it reaches the bulk limit K ≈ CυΛ. [26]

The observed differences in K of graphene can be attributed to: [39]

1. variations in the graphene sample lateral sizes (length and width),
2. thickness non-uniformity due to the mixing between single-layer and few-layer graphene,
3. material quality (e.g. defect concentration and surface contaminations),
4. grain size
5. orientation and
6. strain distributions.

Unique features of heat conduction in two-dimensional crystals:

Intrinsic k reveals a logarithmic divergence in 2D crystals, k ~ ln(N), and with the system size N (where N is number of atoms). The extraordinary high value of k for SLG is related to the logarithmic divergence of the 2D intrinsic thermal conductivity. The logarithmic divergence can be removed by the introduction of extrinsic scattering mechanisms, such as scattering on defects, or by pinning (for example, coupling to substrates) [26].

**3.2.7 Klemens Theory**

The uniqueness of heat conduction in graphene can be illustrated with an expression, derived by Klemens, for the intrinsic Umklapp-limited thermal conductivity of graphene:[42,43]

(3.4)

Here fm is the upper limit of the phonon frequencies defined by the phonon dispersion, and, where M is the mass of an atom, is the size-dependent low-bound cut-off frequency for acoustic phonons, introduced by limiting the phonon mean-free path with the graphene layer size L. Klemens neglected the contributions of out-of-plane acoustic phonons because of their low group velocity and large γ [26].

Qiu and Ruan addressed the problem of relative contributions of ZA phonons to thermal transport in the framework of the equilibrium MD simulations. They found out that in suspended SLG out-of-plane ZA phonons are coupled with in-plane phonons due to the third-order and higher-order anharmonic interactions. Contribution of ZA phonons to the thermal conductivity of graphene is 25%-30%. The contributions of ZA phonons are suppressed more strongly than the contributions of TA and LA phonons. Qiu and Ruan [64, 65] stated that the in-plane TA and LA phonons are the dominant heat carriers in supported SLG and make a major contribution in suspended SLG.

**3.3 Graphene Thermal Conductivity**

Thermal conductivity of graphene has been calculated both theoretically and experimentally. Following table shows some of the major findings.

Table 3.1: Graphene thermal conductivity from different studies.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample | k (W mK-1) | Method | Comments | Ref |
| Graphene | ∼2000-5000 | Raman Optothermal | suspended, exfoliated | 47,48 |
| FLG | ∼1300-2800 | Raman Optothermal | suspended, exfoliated, n=4-2 | 49 |
| Graphene | ∼2500 | Raman Optothermal | suspended, CVD | 50 |
| Graphene | 1500-5000 | Raman Optothermal | suspended, CVD | 51 |
| Graphene | 600 | Raman Optothermal | suspended, exfoliated, T∼660K | 52 |
| FLG ribbon | 1100 | Electrical self-heating | Supported; exfoliated; n < 5 | 53 |
| Graphene | 600 | Electrical | Supported; exfoliated | 54 |
| Graphene | 2000–5000 | Theory: valence force field, Boltzmann  transport equation, γ(q) | Strong width dependence | 55 |
| Graphene | 1000–5000 | Theory: relaxation-time approximation, γTA, γLA | Strong size dependence | 56 |
| Graphene | 8000–10000 | Theory: molecular dynamics, Tersoff | Square graphene sheet | 57 |
| Graphene | 1400–2400 | Theory: Boltzmann transport equation | Length dependence | 58 |
| Graphene | ~4000 | Theory: ballistic | Strong width dependence | 59 |
| γ(q), Gruneisen parameter dependent on the phonon wave vector; γLA and γTA, Gruneisen parameter averaged separately for LA and TA phonon modes. The data is for near room temperature unless otherwise specified. | | | | |

**3.3.1 Diffusive thermal conductivity of graphene**

A theoretical approach for predicting thermal conductivity of graphene has been mentioned by Nika et al. [40] which shows the variation for lateral sizes of μm range. It also predicts the thermal conductivity of graphene for temperature variation. The variation of thermal conductivity with lateral size is shown below –

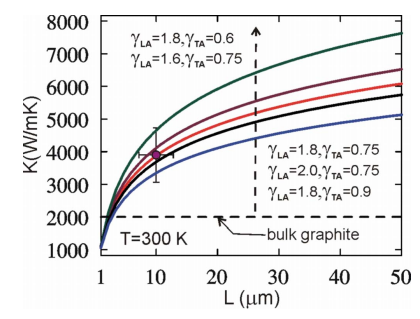


Figure 3.6: Thermal conductivity of graphene as a function of the graphene flake size (L) [40]. Note that the thermal conductivity of graphene exceeds that of basal planes of graphite when the ﬂake size is larger than few micrometers.

According to their theory SLG thermal conductivity variation with temperature is shown below.

280

300

320

340

360

380

400

420

440

460

500

1000

1500

2000

2500

3000

3500

4000

4500

5000

Temperature (K)

Thermal conductivity (W/mK)

L=20 μm

L=10 μm

L=5 μm

L=3 μm

L=1 μm

Figure 3.7: Estimated thermal conductivity of single layer graphene as a function of temperature for different flake size from theory of Nika et al.[40].

Using the relation Kp =1/3 Cvλeff, where 1/λeff=1/λ+1/L, we can estimate the value of graphene thermal conductivity for different sizes (L) and mean free paths(λ) . We consider specific heat per unit volume of graphene C=700\*2300 Jm-3K-1and phonon velocity 2\*104ms-1.We can get an estimation of thermal conductivity of graphene for different mean free paths in the next plot.

0

2

4

6

8

10

12

14

16

18

20

0

2000

4000

6000

8000

10000

12000

length L(um)

thermal conductivity kp (W/mK)

λ =775 nm

1000 nm

600 nm

Figure 3.8: A theoretical estimation of graphene thermal conductivity variation with lateral size for mean free path of 775 nm from the relation Kp =1/3 Cvλeff. Thermal conductivity variation is also shown for λ=1000nm and 600 nm.

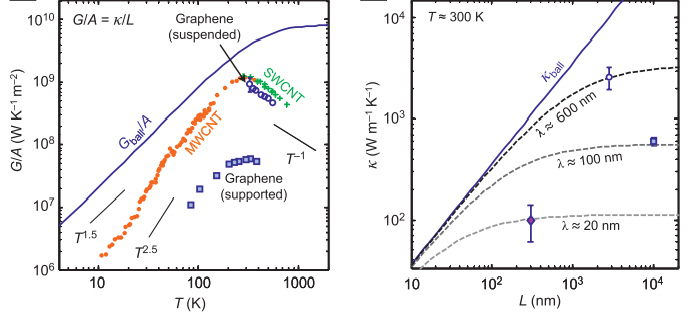
This estimation resembles to the theoretical thermal conductivity achieved by molecular dynamic theory where graphene thermal conductivity is estimated to be varied from 8000-10000 Wm-1K-1 [57]. But experimental values are below from the value shown in previous figure.

The experimental mean free path of 775nm is for suspended SLG [26] and assuming no defects or scattering. For smaller graphene flakes mean free path is restricted by physical size (L) [61]. The size effect in cross plane direction also has effects on thermal conductivity. With the increase of layers scattering, mean free path reduces. So, for MLG, with the presence of defects and scattering, mean free path varies.

**3.3.2 Ballistic limit of graphene thermal conductivity**

Whereas the classical regime of large sample size (L>> λ0 ) suggests a constant thermal conductivity, k , and a thermal conductance that scales inversely with length, G = (KA)/ L , quantum treatment of small graphene devices ( L<< λ0) reveals that the thermal conductance approaches a constant ( Gball), independent of length, in ballistic, scattering-free transport. Thus, the relationship between conductivity and conductance imposes that the effective thermal conductivity of a ballistic sample must be proportional to its length as where, A is the cross-sectional area, A = Wh.[46-48]

**(b)**

****

(b)

(a)

Figure 3.9: (a) Thermal conductance G per unit cross-sectional area A for graphene and related materials (symbols), compared to the theoretical ballistic limit, G ball/ A (solid line) (b) Expected scaling of thermal conductivity κ with sample length L in the quasi-ballistic regime at T ≈ 300 K. The solid line is the ballistic limit, κball= (Gball/A)L, and dashed lines represent κ estimated with phonon mean free paths as labeled. .(courtesy: Eric Pop et.al. MRS BULLETIN ,DECEMBER 2012)

Eric Pop et. al. approximated the transition of thermal conductivity from the ballistic ( L << λ0 ) to the diffusive ( L >> λ0 ) heat-ﬂow regime through a Landauer-like approach [69,70] as

(3.5)

where the factor of π /2 accounts for angle averaging [71] in 2D to obtain the backscattering length responsible for the thermal resistance. Fitting this simple expression to the experimental data in Figure 3.8b using Gball/A=3.7\*109 reveals phonon mean free paths at room temperature of λ0 ≈ 600 nm in suspended graphene (also known as the intrinsic mean free path), λ ≈ 100 nm in graphene supported on SiO2 , and λ ≈ 20 nm in GNRs (of width ∼ 20 nm) supported on SiO2.

At low temperature the thermal conductance per unit cross section approximately follows a power law of σ/A∼Tβ where the exponent β varies with the ribbon width. For small ribbons, β=1 corresponds to the quantum wire behavior. Each of the conduction channels of the wire corresponds to one acoustic mode, including torsion. For wider ribbons, the spectrum becomes denser, with this effect being more dramatic for the bending mode. Because the speed of sound in the torsion mode is inversely proportional to the ribbon width, in the limit of a very wide graphene sheet the torsion contribution vanishes while the exponent increases toward β =1.5 in the infinite graphene sheet. Following figure summarizes ballistic thermal conductance behavior of graphene nano-ribbon with temperature [67].

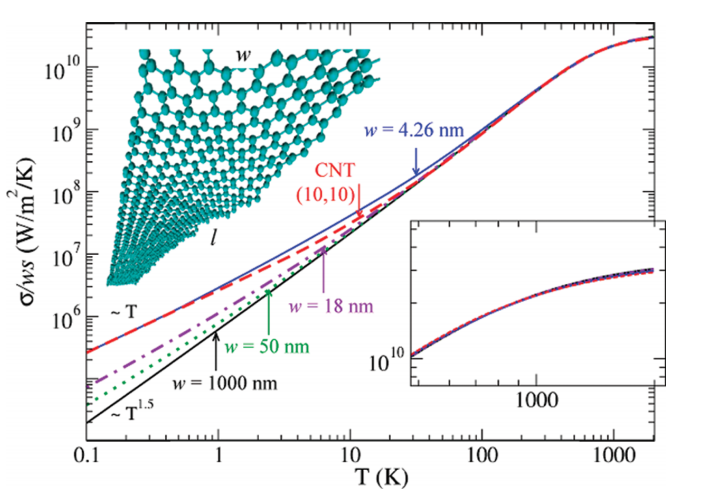
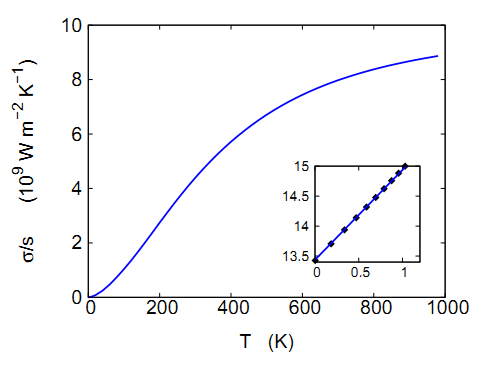


Figure 3.10: Ballistic thermal conductance per unit cross section (σ/ws) as a function of temperature. that does not depend on length l but varies with the width w of the ribbon. The curve becomes independent of width for w > 500 nm, reaching the limit of an inﬁnite graphene sheet. The inset shows the high-T behavior. (courtesy- Ref [67])



σ/A X 109 (Wm−2K−1)

Figure 3.11: The thermal conductance of the graphene sheet v.s temperature. Inset is log σ/A vs. log T in extremely low temperature region. The calculated results (ﬁlled squares) can be ﬁtted by function f(x)=13.44+1.5x (blue line). It indicates that the thermal conductance has a T1.5dependence in this region. (courtesy: Jin-Wu Jiang et.al November 3, 2012 [72])

Another theoretical prediction of graphene thermal conductance indicates the value as around 4.4 × 109Wm−2K−1 at room temperature T = 300K. Jin-Wu Jiang et al. [72] calculated the phonon thermal conductance for the graphene in the ballistic region, by considering the graphene as the large width limit of graphene strips. The calculated value for the thermal conductance at room temperature is in good agreement with the recent experimental result, while at high temperature region our results are consistent with the previous theoretical calculations.

In , using Gball/A= 4.4\*109 we determine the value of mean free path λ for different layers of 5 µm FLG (Fig. 3.4).

Layer n=1, for k=4000 W/mK we get λ=700nm.

Layer n=2, for k=2700 W/mK we get λ=450nm.

Layer n=3, for k=2200 W/mK we get λ=360nm.

Layer n=4, for k=1300 W/mK we get λ=200nm.

So, the relation can be a useful tool for predicting graphene thermal conductivity for various lateral size and mean free path.

**Chapter 4**

**Nano-Composite: Thermal Conductivity Analysis**

Graphene flakes cannot be directly used as TIM materials. It can be used as filler in a matrix material with base material having low thermal conductivity. A nano-composite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 [nanometers](http://en.wikipedia.org/wiki/Nanometers) (nm), or structures having nano-scale repeat distances between the different phases that make up the material.

The base fluid thermal conductivity is usually well-known, or can be measured directly. However, the thermal conductivity of dispersed particles is not always known exactly, especially in the case of nanoparticles, when it can be quite different from the thermal conductivity of bulk material. Nevertheless, a rough estimate is sometimes enough to use [73].

Experimental studies show that thermal conductivity of composite with nano and micro fillers depends on many factors such as heat conduction process, particle volume fraction, particle material, particle size, particle shape, base fluid material, clustering, stability, dispersion behavior and temperature.

**4.1 Parameters Affecting Composite**

Many parameters have influence on composite materials. They determine composite’s many physical characteristics. These parameters are discussed here briefly.

**4.1.1 Particle Volume Fraction**

Normally with the increase of particle volume fraction (having larger thermal conductivity than base material) the composite thermal conductivity tends to increase. But there is always a limitation for it as after a limit higher particle volume fraction leads to change the necessary properties of a thermal interface material. Most of the researchers report increasing thermal conductivity with increasing particle volume fraction and the relation found is usually linear [74]. However, there are also some studies which indicate nonlinear behavior [75].

A nonlinear relationship was observed between thermal conductivity ratio and particle volume fraction, especially at low volume fractions. Choi et al. [77] investigated the thermal conductivity of nanofluids prepared by dispersing multi-walled carbon nanotubes (MWCNT) in oil. They also found a nonlinear relation between thermal conductivity ratio and particle volume fraction. According to the authors, such a nonlinear relation is an indication of interactions between particles.

**4.1.2 Particle Material**

Not only has the difference between thermal conductivity of the particle and base matrix but also particle type has effects on composite thermal conductivity. For example, Lee et al. [78] found that composites with CuO particles showed better enhancement when compared to the composites prepared using Al2O3 nanoparticles although Al2O3 has higher thermal conductivity than CuO. According to the authors, the factor is that Al2O3 nanoparticles formed relatively larger clusters when compared to CuO nanoparticles. Some conventional fillers and carbon based materials with their thermal conductivity are shown in the table below:

Table 4.1: Thermal conductivity of some conventional filler materials and other carbon based materials.

|  |  |
| --- | --- |
| Material | Thermal conductivity (at room temperature, 300K) |
| Copper | 483 |
| Silver | 450 |
| Boron Nitride | 250 ~ 300 |
| Aluminum Oxide | 20 ~ 29 |
| Graphite | 100 ~ 400 (on plane) |
| Carbon Black | 6 ~174 |
| PAN based Carbon Fiber | 8-70 (along the axis) |
| Pitch based Carbon Fiber | 530 ~ 1100 (along the axis) |
| Carbon Nanotubes | 2000~6000 |
| Diamond | 2000 |
| Graphene | 800-5000 |

Effect of particle material is much more pronounced when carbon nanotubes are used for the preparation of nanofluids. Assael et al. [79] compared the nanofluids containing double-walled CNT (DWCNT) and MWCNT. A thermal conductivity enhancement as high as 34% was achieved for the 0.6 vol.% MWCNT/water nanofluid, whereas the 0.75 vol.% DWCNT/water nanofluid showed only 3% enhancement. The authors noted that the reason of such low enhancement was that the size of the DWCNT reached the order of micrometers due to clustering effects. Clustering effect will be discussed shortly. Higher thermal conductivity of CNT or graphene makes them superior as fillers in composite materials.

**4.1.3 Particle Size**

Particle size is another important parameter of thermal conductivity of nanofluids. It is possible to produce nanoparticles of various sizes.

Eastman et al. [80] studied Cu nanoparticles, with ethylene glycol as the base fluid. A 40% increase in thermal conductivity was observed at a particle volume fraction of 0.3% (with thioglycolic acid). In the study of Lee et al. [78], the researchers obtained 20% enhancement with 4 vol.% CuO(23.6 nm)/ethylene glycol nanofluid. Eastman et al. [80] concluded that the size of the nanoparticles is an important factor that affects the thermal conductivity enhancement. But many theoretical models like Hamilton and Crosser model [81] do not consider the effect of particle size.

The general trend in the experimental data is that the thermal conductivity of nanofluids increases with decreasing particle size. This trend is theoretically supported by two mechanisms of thermal conductivity enhancement; Brownian motion of nanoparticles and liquid layering around nanoparticles [74]. However, there is also a significant amount of contradictory data in the literature that indicate decreasing thermal conductivity with decreasing particle size. Feng et al. [82] showed that clustering effects are more pronounced in nano-composite samples with smaller particles. This may explain the results in which nanofluids with smaller particles show lower enhancement.

**4.1.4 Particle Shape**

Before the use of graphene there were mainly two particle shapes used in nanofluid research- spherical particles and cylindrical particles. Composites with carbon nanotubes (which are cylindrical in shape) generally show greater thermal conductivity enhancement than nanofluids with spherical particles.

Cylindrical nanoparticles provide higher thermal conductivity enhancement than spherical particles. One of the possible reasons of this is the rapid heat transport along relatively larger distances in cylindrical particles since cylindrical particles usually have lengths on the order of micrometers [74]. However, it should be noted that nanofluids with cylindrical particles usually have much larger viscosities than those with spherical nanoparticles [83]. As a result, the associated increase in pumping power is large and this reduces the feasibility of usage of nanofluids with cylindrical particles.

**4.1.5 Base Matrix**

The effect of base fluid in the composite thermal conductivity is not simple. With conventional thermal conductivity models such as the Maxwell model [84], as the base fluid thermal conductivity of a mixture decreases, the thermal conductivity ratio (thermal conductivity of composite divided by the thermal conductivity of base matrix) increases. But when it comes to nanometer sized fillers, the situation is more complicated due to the fact that the viscosity of the base fluid affects the Brownian motion of nanoparticles and that in turn affects the thermal conductivity of the composite [85]. Brownian motion will be discussed in enhancement techniques.

Most of the matrices are polymer materials. They have certain qualities that make them useful in many applications. Some of them like silicone oil, epoxy , ethylene glycol etc. have been used to make TIMS. Different fillers are used to make composite of them to enhance their thermal conductivity. Some of the base polymer materials with their thermal conductivity is shown in the next table [76]:

Table 4.2: Thermal conductivity of some polymer materials.

|  |  |
| --- | --- |
| Material | Thermal conductivity  at 25 oC (W/m-1K-1) |
| Low density polyethylene (LDPE) | 0.30 |
| High density polyethylene (HDPE) | 0.44 |
| Polypropylene (PP) | 0.11 |
| Polystyrene (PS) | 0.14 |
| Polymethylmethacrylate (PMMA) | 0.21 |
| Nylon-6 (PA6) | 0.25 |
| Poly(acrylonitrile-butadiene-styrene)  copolymer (ABS) | 0.33 |
| Polyvinyl chloride (PVC) | 0.19 |
| Poly(ethylene vinyl acetate) (EVA) | 0.34 |
| Polytetrafluoroethylene (PTFE) | 0.27 |
| Epoxy resin | 0.19 |
| Silicone Oil | 0.1 |
| Silicone elastomer | 0.2 |

From the table we see that most of the base polymers have thermal conductivity in the range of 0.1-0.3 W/m-1K-1. Higher thermal conductivity of a polymer does not mean better TIM performance because it also depends on matrix physical characteristics and how it acts with fillers.

Base fluid effect was also investigated with MWCNT composites. Ethylene glycol and synthetic engine oil were used as base fluids in the experiments conducted by Liu et al [86]. 1 vol% MWCNT/ethylene glycol nanofluid showed 12.4% thermal conductivity enhancement, whereas for 2 vol% MWCNT/synthetic engine oil nanofluid, enhancement was 30%. It was observed that higher enhancements were achieved with synthetic engine oil as the base fluid, in general.

**4.1.6 Temperature**

In conventional suspensions of solid particles (with sizes on the order of millimeters or micrometers) in liquids, thermal conductivity of the mixture depends on temperature only due to the dependence of thermal conductivity of base liquid and solid particles on temperature [74]. In case of nanofluids, change of temperature affects the Brownian motion of nanoparticles and clustering of nanoparticles [87], which results in dramatic changes of thermal conductivity of nanofluids with temperature.

Temperature dependence of thermal conductivity of composites was also investigated for the case of composites with carbon nanotubes. Ding et al. [88] measured the thermal conductivity of MWCNT/water nanofluid. It was found that thermal conductivity ratio increases with both particle volume fraction and temperature. A maximum enhancement of 80% was achieved at 30°C for 1 wt% of MWCNT/water nanofluid.

In graphene as well as other crystalline materials, K decreases with increasing T. K is proportional to 1/T. It accounts to stronger phonon umklapp scattering in bulk crystals. [26,55] On the other side, in the disordered and nano-structured materials, K(T) can grow with T as a result of better phonon transmission through the interfaces and decreasing Kapitza resistance at higher T[89].

Optimized mixture of graphene and multilayer graphene – produced by the high-yield inexpensive liquid-phase-exfoliation technique – can lead to an extremely strong enhancement of the cross-plane thermal conductivity K of the composite [2].

**4.1.7 Clustering**

Clustering is the formation of larger particles through aggregation of nanoparticles. Clustering effect is always present in nanofluids and it is an effective parameter in thermal conductivity. It was seen that thermal conductivity ratio increased with increasing vibration time and the rate of this increase became smaller for longer vibration time. Furthermore, the variation of thermal conductivity of nanofluid with time after the application of vibration was investigated and it was found that thermal conductivity decreased as time progressed. These results show that clustering degrades composite thermal conductivity. Immediately after the application of vibration, clusters start to form again and size of the clusters increases as time progresses [90]. The time between the application of vibration and measurement of thermal conductivity, duration of vibration, and intensity of vibration also affect the thermal conductivity of nanofluids, which creates discrepancy in experimental data in the literature [74].

Particles in the micro and nano size range have attracted most of the interest because of their stability against sedimentation which reduces the possibility of clogging a flow system.

Thermal conductivity in suspensions increases significantly containing long fibers with respect to dispersed spherical inclusions. It is only true when particles are isolated from each other. At low concentration particle clustering significantly reduce the effective aspect ratio of suspended medium, thus reducing the effective conductivity.

This phenomenon is illustrated schematically in the following figure.

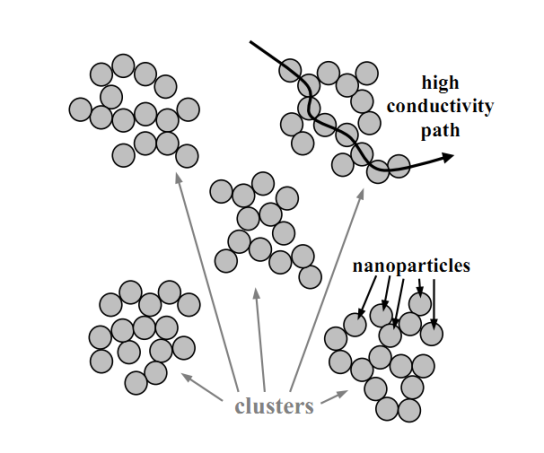
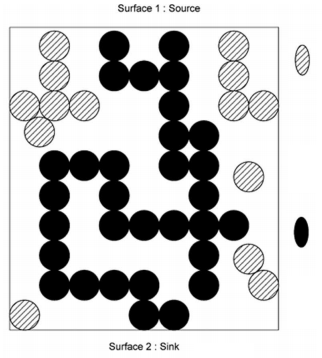


Figure 4.1: Schematic illustration representing the clustering phenomenon [91]. High conductivity path or percolation path results in fast transport of heat along large distances.

However, at higher concentration particle interaction may create a percolation path for thermal energy which would increase the effective thermal conductivity. Percolation can effectively increase the length of the dispersed phase, which may result in heat-transfer augmentation in suspensions despite the increased interfacial resistance for nanoscale particles.

Obtaining a stable suspension of the non-clustering nanoparticle is the primary issue in nano-fluid research. If particles are well dispersed and separated from one another, their stability against gravitational is very high [73].

****

Higher conductivity particles forming a continuous chain between the two surfaces participate in percolation

Higher conductivity particles which do not form a continuous chain between the two surfaces

Figure 4.2: The phenomenon of site percolation occurring with the formation of a continuous chain between the two surfaces by the highly conducting particles.

**4.1.8 Dispersion behavior of suspension**

The dispersion behavior of suspension is defined by the balance between the attractive and the repulsive forces that particles experience as they approach each other. If the attractive component is dominant over the repulsive one, particles aggregate easily. It makes the resulting nanofluid unstable. The attractive component of the intermolecular potential, or Van der Waals force, is responsible for the coagulation of nanoparticles in the nanofluids. The main part of this attractive force is the London dispersion force, which exists between any two molecules or particles and is liable for existence of the liquid itself. The nature of the repulsion between particles lays in the electrostatic force that exists between any two charged objects. The repulsive force is the only mechanism to prevent particles from agglomeration in fluid. The balance between these two types of interaction influences the overall stability of the nanofluids.[92,93]

**4.1.9 Thermal Interface Resistance:**

Thermal resistance at the particle/liquid interface must be accounted for in the case of nanoﬂuids. It can significantly lower the expected thermal conductivity enhancement. The interfacial thermal resistance becomes more and more important as the size of dispersed particles decreases since the total surface area of particle/liquid interfaces is increasing [73].

In Table1 thermal resistance values of some composites are shown [126].

Table 4.3: Thermal resistance values of different composites [126]

|  |  |  |
| --- | --- | --- |
| Interface | Thermal resistance (Km2W-1) | Method |
| Alumina-Polymer | 2.5 X 10-8− 5 X 10-8 | 3ω method |
| CNT–D2O | 8.3 X 10-8 | Transient absorption |
| Carbon nanoﬁber–Cu | 0.25 X 10-8 | ASTM |
| Aligned MWCNT | 8 − 18 X 10-8 | Photo-acoustic technique |
| CNT–CNT interface | 3.8 X 10-8 | Infrared technique |
| Graphene–SiO2 | ~4 X 10-8 | Raman and electrical |
| Graphene–SiO2 | ~(0.6 − 12) X 10-8 | Electrical |
| Graphene–SiO2 | ~2 X 10-8 | Pump and probe |
| Metal-graphene-SiO2 | ~4 X 10-8 | Raman and electrical |
| Graphite–metal | ~(1−3) X 10-8 | Reﬂectance |
| Graphene/a-SiO2 | ~4 X 10-8 | Theory |
| Graphene–oil | ~(0.4 − 4) X 10-8 | Theory |
| Graphene–epoxy | ~3.5 X 10-9 | Laser ﬂash |

Knowledge of thermal boundary resistance can help in understanding graphene thermal coupling to matrix materials. Controlling RB is important for graphene’s electronic- and thermal-management applications. It is defined as RB = (q/ΔT)-1, where ΔT is the temperature difference between two sides of the interface. It has a non-zero value even at the perfect interfaces owing to differences in the phonon density of states — an effect known as Kapitza thermal resistance [94]. The actual RB is usually higher than the Kapitza resistance owing to interface imperfections. Kapitza resistance can lower nanoﬂuid thermal conductivity signiﬁcantly as interface density increases.

**4.2 Mechanisms of Enhancement in Thermal Conductivity for Filler Inclusion**

In the following sections, we will discuss some mechanisms to explain the enhancement of thermal conductivity for filler inclusion.

**4.2.1 Brownian Motion of Nanoparticles**

Brownian motion is the random motion of particles suspended in a fluid. When nanocomposites are considered, this random motion transports energy directly by nanoparticles.

The prediction of the Hamilton and Crosser [95] model under-predicted the effective thermal conductivity of the nanofluid, since it does not take into accounts the Brownian motion of the particles within the base fluid.

**4.2.2 Clustering of Particles:**

Nanoparticles tend to form clusters [91, 96]. Evans et al. [97] proposed that clustering can result in fast transport of heat along relatively large distances since heat can be conducted much faster by solid particles when compared to liquid matrix. It happens when percolation path is formed.

It was shown that the effective thermal conductivity increased with increasing cluster size. However, as particle volume fraction increased, the nanofluid with clusters showed relatively smaller thermal conductivity enhancement. When it comes to interfacial resistance, it was found that interfacial resistance decreases the enhancement in thermal conductivity, but this decrease diminishes for nanofluids with large clusters.

It was noted that effective medium theories can predict the experimental data well when the effect of clustering is taken into account. It was found that forming percolation path improves thermal conductivity enhancement and it is more pronounced in nanofluids with smaller nanoparticles since distances between nanoparticles are smaller in those nanofluids, which increases the importance of van der Waals forces attracting particles to each other.

**4.2.3 Liquid Layering around Nanoparticles:**

In a recent study it is showed that liquid molecules form layered structures around solid surfaces [98] and it is expected that those nanolayers have a larger effective thermal conductivity than the liquid matrix [99]. As a result of this observation, the layered structures that form around nanoparticles are proposed to be responsible for the thermal conductivity enhancement of nanofluids [99]. But there is no experimental data available regarding the thickness and thermal conductivity of these nanolayers.

**4.3 Problem of Using CNT as Filler:**

Conventional TIMs filled with thermally conductive particles require high volume fractions f of filler (f~50%) to achieve thermal conductivity K of the composite in the range of ~1-5 W/mK at room temperature (RT).

Earlier attempts of utilizing highly thermally conductive nano materials, e.g. carbon nanotubes (CNTs), as fillers in TIMs, have not led to practical applications. Failure was due to weak thermal coupling at CNTs/base interface and prohibitive cost.

The measured TCE factors were moderate which is in the range ~50-250% at f~7% of the CNT loading.[100,101]. In some cases k was not improved substantially [102] or even decreased with addition of single-wall CNTs [103]. It was explained as although CNTs have excellent k they do not couple well to matrix material or contact surface. The reported thermal boundary resistance (TBR) between CNTs and polymer matrix was as high as ~10-7m2 KW-1[104]. The large TBR at CNT/matrix interface can be attributed to the fundamental property – high Kapitza resistance [105] between one-dimensional (1D) CNTs and 3D bulk owing to the large difference in the phonon density of states (DOS). It was also suggested that the lack of thermal percolation in CNT composites can negatively affect their heat conduction properties [106].

**4.4 Graphene Nano-composites**

Along with other carbon based materials, graphene based polymer composite is an exciting topic of research. Graphene is found to improve electrical, thermal, mechanical, optical, and gas barrier properties of polymer matrices. Graphene as a nanoﬁller in polymer matrixes maybe preferred over other conventional nanoﬁllers (CNT, CNF, EG, etc.) owing to its high surface area, aspect ratio, tensile strength, thermal conductivity and electrical conductivity.

In one study it was seen that some of the graphene based polymer composites like polystyrene-graphene, polyaniline-graphene, epoxy-graphene nanocomposites, PVA-graphene nanocomposites, PVDA (ploy vinylidene fluoride)- graphene nanocomposites, poly(3,4-ethyldioxythiophene)-graphene nanocomposites, polycarbonate-graphene nanocomposites improved their base matrix characteristics significantly [107]. The improvements of graphene based nanocomposites are in mechanical properties (Young’s modulus), thermal properties (thermal strength, thermal conductivity), electrical properties (electrical conductivity, conductance) etc.

Graphene and other carbon based materials have also been used to improve thermal conductivity of thermal interface materials. Due to higher thermal conductivity and particle size effects, carbon based nanocomposites with fillers like CNTs, graphite nanoparticles (GNPs), graphene oxide nanoparticles (GONs) and graphene flakes have shown high thermal conductivity enhancement where is the thermal conductivity of the composite, is the thermal conductivity of base matrix. In Table-2 we can see the enhancement of thermal conductivity of some carbon based materials.

Table 4.4: Enhancement in thermal conductivity of some carbon based materials

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *Filler* | *Enhancement* | *Volume Fraction* | *Base Material* | *Ref.* |
| MW-CNT 160% 1.0 vol% oil 77  SW-CNT 125% 1.0 wt% epoxy 108  SW-CNT 200% 5.0 wt% epoxy 100 | | | | |
| GNP 3000% 25.0 vol% epoxy 109  GON 30-80% 5.0 vol% glycol; paraffin 110 | | | | |
| Graphene Oxide 400% 5.0 wt% epoxy resin 111  Graphene 500% 5.0 vol% silver epoxy 9  Graphene 2300% 10.0 vol% epoxy 9 | | | | |

From the table, we see that above 100% improvement in thermal conductivity is achieved for different carbon materials with low amount of inclusion. Graphene showed the highest owing to its geometry and better coupling to base materials [1, 9].

Graphene as filler has some advantages over CNTs. For epoxy - graphene composites, coefficient of thermal expansion (CTE) was found to vary in the range ~(5-30)×10-5 (1/oC) and decreased with increasing graphene fraction [8]. Graphene has high temperature stability (verified up to 2600 K [112]) which is an important characteristic for TIM application. The use of liquid-phase exfoliated graphene [113] in advanced TIMs can become the first industry application.

**Chapter 5**

**Theoretical Modeling for measuring thermal conductivity of Composite**

**5.1 Conventional Models for Composite Thermal Conductivity:**

Many theoretical models are proposed to predict the composite thermal conductivity. Here we will discuss some of them. These models are shown in the table.

The two basic models representing the upper bound and the lower bound for thermal conductivity of composites are the rule of mixture and the series model [114], respectively. Most of the experimental results were found to fall in between these two models.

Many models were derived from the basic series model, generally introducing some more complex weighted averages on thermal conductivities and volume fractions of particles and matrix. These are called second order models which include models of Hashin and Shtrikman, Hamilton and Crosser, Hatta and Taya, Agari, Cheng and Vachon as well as by Nielsen. The basic assumption of separated particles in the effective medium approach is not valid in principle for highly filled composites, where contacts are likely to occur, possibly leading to thermally conductive paths.

More sophisticated heat transfer models may be classified as either flux law models, where the temperature field is solved for an assumed geometry, or ohm’s law models based on an electrical series analogy [115].

Halpin-Tsai model [116] is widely used thermal transport formula for transverse conductivity. Modifying it, Lewis and Nielsen gave another model which included the effect of the shape of the particles and the orientation or type of packing for a two-phase system. It is also shown in the table.

Table 5.1: Different theoretical models proposed for composite thermal conductivity.

|  |  |  |  |
| --- | --- | --- | --- |
| Name of the model | Formula | Remark | Ref. |
| Rule of mixture model | Where,kc, kp, km are the thermal conductivity of the composite, particle, matrix, respectively, and  Φp, Φm volume fractions of particles and matrix, respectively. | considering the thermal interaction between particlesassumes perfect contact between particles | [117] |
| basic series model |  | assumes no contact between particles | [114] |
| Geometric mean model |  |  | [114] |
| Halpin-Tsai model | Where and is dependent on shape of the particles ( for spherical fillers) | thermal transport formula for transverse conductivity | [116] |
| Lewis and Nielsen model | where, ; and  Here, KE is Einsteinconstant and A depends upon the shape and orientation of the dispersed particles. Фmax is the maximum packing fraction of the dispersed particles | includes the effect of the shape of the particles and the orientation or type of packing for a two-phase system | [118] |
| Hamilton and Crosser model | where, n is the empirical shape factor and it is defined as: where, ψ is the sphericity. | effect of the shape of the solid particles into account | [95] |
| Name of the model | Formula | Remark | Ref. |
| Maxwell  model/  Maxwell Garnett EMA | where, kc, kp, and kf are the thermal conductivity of the composite, particles and base fluid respectively. φ is the volume fraction of particles in the mixture. | For randomly distributed and non-interacting homogeneous spheres in a homogeneous medium.  The effect of the size and shape of the particles was not included in the analysis.  The interaction between the particles was also neglected in the derivation. | [84,  119] |
| Lord Rayleigh model | For a cubic array  Where kc, km and kp are the thermal conductivity of composite, matrix and particle filler; is the particle volume fraction. | considering the thermal interaction between particles | [115] |
| Bruggeman  Symmetric model |  | For spherical particles;  Interface resistance is not included; typically good at higher | [120] |
| Bruggeman  asymmetric model with interface resistance |  | Spherical particle | [121, 122] |
| Percolation model with interface resistance |  | Cubical particles | [123,  124] |

Lord Rayleigh extended Maxwell’s solution by considering the thermal interaction between particles and proposed a model. Hamilton and Crosser [95] extended the Maxwell model in order to take the effect of the shape of the solid particles into account, in addition to the thermal conductivities of solid and liquid phases and particle volume fraction.

**5.2 Limitations of Theoretical Models**

The models that have been discussed have their own criteria for applications. Some are suitable for spherical particle inclusion whether some are for cylindrical particles. So, there are limitations of these models considering particle size and other factors. In case of nano particles, these models show very different results comparing experimental results. The anomalous thermal conductivity improvement in polymer matrixes for the inclusion of CNT or graphene cannot be predicted by these models. The main demerits of the models are-

* Most of these models were developed many years ago. These models were mainly used for fillers like Al2O3 or CuO. At that time mainly spherical particles were used as fillers. So when more recent particles like CNT and graphene with different shape (CNT has cylindrical tube like shape and graphene has plane/flat shape) are considered in these models, the result starts to deviate from the experimental ones.
* These models give nearly accurate prediction for fillers of μm size of their mentioned criteria; but for nm sized material fillers (CNT, graphene or other nanoparticles) variation of the model result and experiment results is very explicit.
* Some of these models do not consider particle properties like particle size, aspect ratio etc. These parameters are very crucial for composite thermal conductivity enhancement. For example, in case of CNT or graphene, the ratio of their longitudinal and transverse dimension is very noticeable. Aspect ratios of these materials make a vital effect on their thermal conductivity as well as composite thermal conductivity.
* When particle size is reduced to nm range (for nano particles), thermal resistance at the particle/matrix interface ( Kapitza resistance) becomes more important because as the size of dispersed particles decreases total surface area of particle/liquid interfaces is increasing [73]. But most classical models do not consider interface resistance and their prediction becomes inaccurate.

Although these models have many limitations, they are utilized frequently due to their simplicity in the study of composites to have a comparison between theoretical and experimental findings. Now we will discuss effective medium theory (EMT) for composite thermal conductivity proposed by Nan. This model includes many parameters which play a dominant role in composite thermal conductivity and becomes a better model over others.

**5.3 Effective medium theory: Nan’s proposed model**

Effective medium approximations (EMA) or effective medium theory (EMT) are physical models that describe the macroscopic properties of a medium based on the properties and the relative fractions of its components. Many thermal conductivity models are bases on EMA. Nan et al. [125] introduced a model for predicting the effective thermal conductivity of arbitrary particulate composites including interfacial thermal resistance by an approach where effective medium approximation is combined with the concept of Kapitza thermal contact resistance. They considered the multiple scattering theory in Maxwell-Garnett Effective medium approximation (MG-EMA) and formulated a general EMA for arbitrary ellipsoidal particulate composites with interfacial thermal resistance. This model accounts for properties of the matrix and reinforcement, particle size and size distribution, volume fraction, and interfacial thermal resistance. Though this theory is based on ellipsoidal particle in a matrix, the shape of the particles can be changed for different filler dimensions.

The ellipsoidal particles can be grouped in two ways – prolate and oblate. If a1 and a3 are, respectively, radii of the ellipsoid along the X/1 and X/3 axes, p = a3/a1 is the aspect ratio of the ellipsoid; then we get p > 1 for prolate ellipsoid (a1=a2 < a3) and p<1 for oblate ellipsoid (a1 =a2 > a3). For spherical particles p is equal to 1.

For a two-phase composite containing ellipsoidal inclusions with the interfacial thermal resistance existing between the matrix and inclusions, in which the materials axes are denoted by Xi, and the local, oriented axes by Xi ‘, with X3 ‘coinciding with the symmetric axis of the inclusion particles considered. We get the effective thermal conductivity of composite with ellipsoidal particles from EMA of Nan as,

Here, is the thermal conductivity along the axis of the composite

where, is the thermal conductivity of the filler particle;

is the thermal conductivity of the matrix;

is the volume fraction of particles;

is the angle between the materials axis X3 and the local particle symmetric axis X3/ ;

is the distribution function describing ellipsoidal particle orientation ;

is the interfacial resistance;

From eqn. 1(a) and 1(b) we can simplify the thermal conductivity equations for different cases. For randomly oriented ellipsoidal inclusions, simplified effective thermal conductivity becomes,

For flat particle inclusions oriented perpendicular to X3 axis, the simplified equation becomes,

And for spherical particle inclusion, the simplified equation is,

We will mainly use EMA equation for completely disoriented particles as we will get samples of composite with disoriented filler composition. But particles oriented into a particular direction will also be analized and these 2 cases will be compared. Since we are using graphene as a filler which has a plane geometry and very low thickness considering lateral dimensions[2] ; aspect ratio, p will be less than 1. An ideal graphene flake can be treated as an oblate spheroid with α=a3/a1→0. Our calculations are shown in the next sections.

**Chapter 6**

**Calculation and Result Analysis**

**6.1 Calculation Parameters and Process**

Now, we will use effective medium theory proposed by Nan to see the variation of a composite thermal conductivity with the inclusion of fillers. In our analysis we have considered filer particles of different sizes separately and also combinations of different sizes. When combinations are used, filler thermal conductivity is not fixed. So, we have to codify EMA of Nan to analyze the effect of combination of different fillers. Here we have calculated total thermal conductivity of composite as , where kci is the composite thermal conductivity for filler thermal conductivity Kpi and Fi is the fraction of total volume of fillers with thermal conductivity Kpi. We have seen a linear relationship between composite thermal conductivity and filler volume fraction and between composite thermal conductivity and particle thermal conductivity. So considering a superposition theorem is justifiable. To start our analysis, at first we have to mention basic parameters.

**6.1.1 Filler and Its Thermal Conductivity**

Graphene-MLG composition is the filler material of our concern. Graphene’s thermal properties were mentioned in previous section and thermal conductivity was also shown. Thermal conductivity data which we will use later is shown in figure-6.1

For nm sized SLG and MLG, theoretical prediction by the relation is used for predicting thermal conductivity [1] and it is plotted in figure-1(a) for different mean free paths. This relation has been discussed in previous section. We are considering graphene flakes of square dimension as data for variation of width are not available. Mean free path is comparable to length for lateral sizes of less than 1 μm and it does not affect much on graphene thermal conductivity in this situation. Thermal conductance per unit area is considered as 3.7 X 109 Wm-2K-1 [32]. For μm sized SLG we will use the theoretical model proposed by Nika et al.[60] which gives thermal conductivity variation like figure-1(b). It is plotted for different Gruneisen parameters (γLA and γTA). For our analysis we will consider γLA =1.8 and γTA =0.75 and calculated values indicate thermal conductivity of SLG of μm size. In figure-6.1(c) graphene thermal conductivity by theoretical prediction and experimental result (considering average width=5μm) is shown for different no. of layers which will be used in our analysis for μm sized MLG [46].

(a)

0

500

1000

1500

2000

2500

0

500

1000

1500

2000

2500

3000

3500

Thermal conductivity kp (W/mK)

λ=775 nm

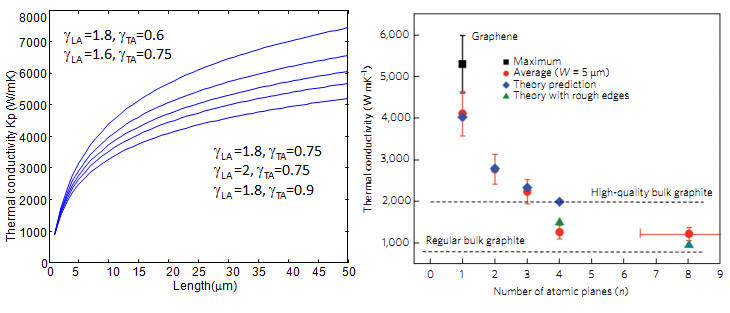
λ=600 nm

λ=500 nm

λ=300 nm

λ=100 nm

Length L (nm)



(c)

(b)

Figure 6.1: Graphene thermal conductivity variation with length and layers (a) graphene thermal conductivity estimation with the relation with = 3.7 X109 Wm-2K-1for various mean free paths. This figure shows ballistic to diffusive transition of thermal conductivity of graphene flakes. It is used for predicting thermal conductivity of SLG and MLG of nm sized flakes by taking different values of mean free path. (b) Theoretical thermal conductivity estimated for SLG of μm sized from a theory proposed by Nika et al. [3] . (c) Theoretical prediction and experimental value for graphene thermal conductivity for different no of layers. Experimental data is shown for average width 5μm [32,46,60].

**6.1.2 Thermal interface resistance**

Thermal resistance of some composites is shown in Table 1. Graphene-oil composites have interfacial resistance in the range 4X10-9-40 X 10-9m2KW-1. We will consider graphene – silicone oil thermal resistance of 10 X 10-9m2KW-1 in our analysis. Also variation of thermal resistance will be analyzed.

**6.1.3 Base Matrix**

In our analysis, we will consider silicone oil as a base matrix which has vast uses in commercial TIMs as grease. Though surfactant is used to decrease its surface tension in commercial TIMs, we will not consider it here. Later we will show effect of other base matrixes of different thermal conductivity on the value of composite thermal conductivity. Silicon oil has thermal conductivity of 0.1 Wm-1K-1 .

Now we will see how different parameters of filler and composite like volume fraction, filler size, aspect ratio, interfacial resistance etc. affect the composite thermal conductivity with base TIM material Silicone oil.

**6.2 Analogy with Experimental Result**

At first we want to see how our approach can lead to give similar result got from the experimental one. Keeping similarity with the mentioned composition of different size and layer variation in graphene-MLG-epoxy composite in the experiment done by Shahil et al. [2], we have taken a composition of graphene MLG.

We have found that for a composition of

1. 10% SLG with average length L=100nm,
2. 80% MLG with average length L=240 nm,
3. 10% MLG with average length L=5μm,

theoretical value can be very close to experimental one. This composition resembles to the mentioned sample composition of around 90% graphene and MLG flakes of lateral dimensions in the range L≈50 nm - 0.5μm and around 10% flakes (with n<5) of lateral size L≈ 2-5 μm.

For SLG with average lateral size 100nm thermal conductivity is used as 440 Wm-1K-1 from the relation (also shown in figure 6.1 (a)) with λ=500nm, For MLG with average lateral size 240nm we have used the same relation to find MLG graphene thermal conductivity(with λ=300nm and no. of layers =3 ) which is calculated as 700 Wm-1K-1. For MLG with average size in μm range we have used experimental data from figure-6.1(c) with L=5 μm and with k=1300 Wm-1K-1  for 4 layers.

As we are considering fillers with three different thermal conductivity values, we have to use the EMA model proposed by Nan with some modification. Here we have calculated total thermal conductivity of composite as , where kci is the composite thermal conductivity for filler thermal conductivity Kpi and Fi is the fraction of total volume of fillers with thermal conductivity Kpi. We have seen a linear relationship between composite thermal conductivity and filler volume fraction and between composite thermal conductivity and particle thermal conductivity. So considering a superposition theorem is justifiable. The result is shown below.

0

1

2

3

4

5

6

7

8

9

10

0

1

2

3

4

5

6

Volume fraction f (%)

Thermal conductivity kc (W/mK)

Figure 6.2: Thermal conductivity vs. volume fraction for graphene-MLG epoxy composite: theoretical result from EMA & experimental result from Shahil et al [2].

Here we can see the theoretical value suits with the experimental result.

**6.3 Result Analysis**

We have seen in previous section that graphene varies it thermal conductivity with its length and theory is different. So we will go with our analysis for graphene flakes of nm and μm size separately and later we will see the effect of their combination. In our thermal conductivity prediction we will calculate values normally up to 10% volume fraction.

**6.3.1 Effect of different parameters considering nm sized graphene flakes:**

**Effect of changing lateral size:**

Initially we have seen the effect of nm sized MLG flakes. We can use figure-6.1(a) where thermal conductivity is estimated from relation with mean free path 300nm for MLG. We have also considered three atomic planes; so H=3\*h (h=0.35 nm, thickness of graphene monolayer) and aspect ratio is p =H/L. We have taken a considerable value of interfacial resistance R=10\*10-9 m2KW-1. Then we have taken different average lateral dimensions of nm range and measured the composite thermal conductivity. The result is shown below.

0

1

2

3

4

5

6

7

8

9

10

0

0.5

1

1.5

2

2.5

3

3.5

Volume fraction f (% )

Thermal conductivity Kc (W/mK)

L=800 nm

L=700 nm

L=500 nm

L=300 nm

L=100 nm

Figure 6.3: Thermal conductivity of composite vs. volume fraction for different nm sized MLG flakes.

From the figure, we see that composite thermal conductivity increases proportionally with graphene flake size. For 100 nm lateral sized length, composite thermal conductivity is around 0.52 W m-1K-1 and for 800 nm lateral sized length, composite thermal conductivity is around 3.37 W m-1K-1 for 10% volume fraction. So enhancement is 420% and 3270% respectively.

Here we have used mean free path length λ =300 nm. As flakes are considered with lengths comparable to mean free paths, graphene thermal conductivity will not vary largely on mean free path and in composite thermal conductivity its effect is negligible.

**Effect of changing aspect ratio:**

Now we will see the variation of composite thermal conductivity with volume fraction for different aspect ratios considering nm range length. In this case we can take only few variations because of the limitations for graphene thickness.

For lateral size L=500nm we have taken aspect ratio (p =H/L) as 0.0007 (for thickness H ≈ 0.35 nm, SLG), 0.0014(for bilayer graphene), 0.0021 (for 3 layer), 0.005 (for thickness H≈2.5 nm) and 0.01(for thickness H≈5nm).

It should be mentioned that aspect ratio must have effects on the values of mean free path and particle thermal conductivity. But here, for showing the effect of aspect ratio, we have used a fixed value of mean free path of 300nm and filler thermal conductivity estimated from figure 6.1(a) and R=10\*10-9 m2KW-1.

The outcome is shown below.

0

1

2

3

4

5

6

7

8

9

10

0

0.5

1

1.5

2

2.5

3

3.5

Volume fraction f (%)

Thermal conductivity Kc (W/mK)

p=0.0007

p=0.0014

p=0.0021

p=0.005

p=0.01

Figure 6.4: Composite thermal conductivity vs. volume fraction for different aspect ratio of fillers.

We know that with the increase of aspect ratio (i.e. no. of layers) thermal conductivity of graphene flake drops. Thus composite thermal conductivity also falls down. We see that considering graphene flake thickness of 0.35 nm (SLG), composite thermal conductivity is found 3.024 Wm-1K-1 and for thickness of 5 nm (p=0.01), composite thermal conductivity drops to 0.86 Wm-1K-1 .So aspect ratio change in composite thermal conductivity is very significant.

**Effect of changing thermal interface resistance:**

Now we will show the effect of thermal interfacial resistance on composite thermal conductivity. We have taken four R values of 1\*10-9 m2KW-1 , 5\*10-9 m2KW-1,10\*10-9 m2KW-1 and 20\*10-9 m2KW-1,H=3\*h(h= 0.35 nm); λ is assumed 300nm ; L is considered as 500nm and got the result which is shown below.

0

1

2

3

4

5

6

7

8

9

10

0

0.5

1

1.5

2

2.5

3

3.5

4

Volume fraction f (%)

Thermal conductivity Kc (W/mK)

R=1\*10-9 m2KW-1

R=5\*10-9 m2KW-1

R=10\*10-9 m2KW-1

R=20\*10-9 m2KW-1

Figure 6.5: Thermal conductivity of composite vs. volume fraction for different thermal interfacial resistance considering lateral size is 500 nm.

Change of thermal resistance causes very significant change in composite thermal conductivity. For 500nm lateral size, change of thermal resistance from 1x10-9 to 20X10-9 m2KW-1 leads to composite thermal conductivity change from 3.92 to 1.43 Wm-1K-1.

**6.3.2 Effect of different parameters considering µm sized graphene flakes**

In this case lateral dimension becomes greater than mean effective path. From theoretical model proposed by Nika et al.[60] the variation of thermal conductivity of graphene as a function of length for different Gruneisen parameters γs is shown in figure 6.1(b). That figure is used to predict single layer graphene thermal conductivity for lateral size in μm range. For thermal conductivity of MLG of μm sized particle, data from figure 6.1(c) is used.

**Effect of changing lateral size:**

At first we can see how composite thermal conductivity changes with filler volume fraction with average lateral sizes of few micrometers. From the theoretical model we have calculated graphene thermal conductivity for different μm sized flakes for Gruneisen parameters γLA =1.8 and γTA =0.75. Interfacial resistance is considered 10\*10-9m2KW-1 and temperature is considered 300K. We have got the plot for L=1, 2,3,4,5 μm which is shown next.

0

1

2

3

4

5

6

7

8

9

10

0

5

10

15

20

25

30

Volume fraction f (%)

Thermal conductivity Kc (W/mK)

L=5 μm

L=4 μm

L=3 μm

L=2 μm

L=1 μm

Figure 6.6: Thermal conductivity of composite vs. volume fraction for different µm sized SLG.

Composite thermal conductivity continues to increase with lateral size. For μm sized flakes composite thermal conductivity increases in a large amount. For 1μm lateral sized length, composite thermal conductivity is around 5.54 W m-1K-1 at 10% volume fraction while for 5μm lateral sized length, composite thermal conductivity becomes around 25.75 W m-1K-1. Here enhancement is 5440% and 25650% respectively. This huge enhancement is predicted by EMA because of the very small aspect ratio (for 5 μm p=H/L =0.00007) and large length. In practical application, other physical considerations will affect and composite thermal conductivity may not be so large.

It is interesting to see that though different approach is used to calculate graphene thermal conductivity for nm and μm sized flakes, composite thermal conductivity maintains a sequence. For graphene flake size variation from few hundred nm size to few μm size we can combine the separately measured plots and show the result.

0

1

2

3

4

5

6

7

8

9

10

0

5

10

15

20

25

30

Volume fraction f (%)

Thermal conductivity Kc (W/mK)

L=5 μm

L=3 μm

L=1 μm

L=700 nm

L=300 nm

Figure 6.7: Thermal conductivity of composite vs. volume fraction for graphene flake length of nm to µm size.

For example, for 10% inclusion of 700nm graphene flakes, composite thermal conductivity is achieved 3.054 Wm-1K-1 (figure-3) from the relation and for 1 μm sized flakes (SLG ) , it is found to be around 5.535 Wm-1K-1 (figure-6.7 ) form another theoretical calculation of graphene.

**Aspect ratio effect:**

Now we will see the effect of aspect ratio on composite thermal conductivity. From figure -6.1(c) we can have data for graphene thermal conductivity at different layers for average width 5μm. Assuming square graphene sheet, lateral size is considered as L=5μm. With the change of no. of layers, thickness and aspect ratio of fillers change and we get variation in composite thermal conductivity. We have varied thickness with no. of layers =1, 2, 3 and 4 and corresponding aspect ratios are p =0.00007(H=0.35 nm, SLG), 0.00014 (layer number n=2), 0.00021(layer number n=3) and 0.00028(layer number n=4).R is considered as 10\*10-9 m2KW-1. From figure-6.1(c), we have used graphene thermal conductivity values (for 1, 2, 3 and 4) as4000, 2700, 2200 and 1300 Wm-1K-1 respectively. The result is shown in the next figure.

0

1

2

3

4

5

6

7

8

9

10

0

5

10

15

20

25

30

Volume fraction f (%)

Thermal conductivity Kc (W/mK)

p=0.00007

p=0.00014

p=0.00021

p=0.00028

Figure 6.8: Thermal conductivity of composite vs. volume fraction for different aspect ratio of fillers with lateral size 5 μm. Thickness is varied for 1, 2, 3 and 4 layers (n).

From the figure, it is clear that, with the increase of layer number, composite thermal conductivity drops. Here, with the increase of layer number, graphene thermal conductivity drops; so both the effects – particle thermal conductivity and its size (aspect ratio) make impact on composite thermal conductivity. But graphene size effect is more dominant for change in composite thermal conductivity than its conductivity.

**Effect of changing thermal interface resistance:**

To see how composite thermal conductivity varies with interfacial resistance for μm range lateral size, we have considered length as L=2 μm with SLG and taken the resistance value as R= 5\*10-9 m2KW-1, 10\*10-9 m2KW-1, 20\*10-9 m2KW-1 and 30\*10-9 m2KW-1. Thermal conductivity of SLG is used from figure-6.1(b) as 1625 Wm-1K-1. The output is shown in the figure-6.9(a). For interface resistance variation from 5\*10-9 m2KW-1 to 30\*10-9 m2KW-1, composite thermal conductivity varies from 17.1 Wm-1K-1 to 3.96 Wm-1K-1. Thermal conductivity enhancement drops from 17000% to 3860%.

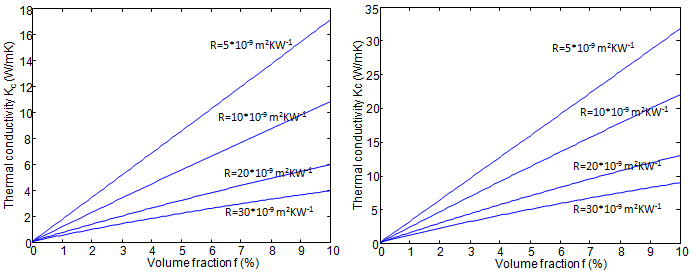


Figure 6.9: Thermal conductivity of composite vs. volume fraction for different interfacial resistance. In (a) SLG with lateral size of 2 μm is used. In (b) MLG of lateral size 5μm with 4 layers is used.

Now we can take MLG with 4 layers and lateral size of 5μm for which thermal conductivity is around 1300 Wm-1K-1 (from figure- 6.1(c)) and see the variation for composite thermal conductivity for different interfacial resistances. The output is shown in figure -6.9(b). For interface resistance variation from 5\*10-9 m2KW-1 to 30\*10-9 m2KW-1, composite thermal conductivity varies from 31.9 Wm-1K-1 to 8.95 Wm-1K-1 at 10% volume fraction. The variation is evident from the lateral size of graphene. So for a particular thermal resistance, lateral size of 5 μm leads to higher composite thermal conductivity than 2 μm SLG.

**6.3.3 Effect of different parameters considering combination of nm and μm sized graphene flakes**

Though we have analyzed composite thermal conductivity of graphene-MLG-silicone elastomer for particular average lateral size of nm or μm length, we will get graphene solutions where lateral dimensions from nm to μm range will be present. Now we will consider composites where graphene flakes of both nm and μm sized length is present. We can consider 3 samples having graphene-MLG with different lateral sizes.

Sample 1 consists of

1. 10% SLG with average length L=100 nm,
2. 75% MLG (n=3) with average lateral size L=400nm,
3. 15% MLG(n=3) with lateral size L=5 μm.

Sample 2 consists of

1. 10% SLG with average length L=100 nm,
2. 70% MLG (n=3) with average lateral size L=400nm,
3. 20% MLG(n=3) with average lateral size L=5 μm.

Sample 3 consists of

1. 10% SLG with average length L=100 nm,
2. 65% MLG (n=3) with average lateral size L=400nm,
3. 25% MLG(n=3) with lateral size L=5 μm.

All the samples consist of 3 combinations. The average lateral size is varied for different combinations but for all samples this variation is kept same. The difference between the samples is the volume percentage of the combinations.

For nm sized flakes thermal conductivity value estimated in figure 6.1(a) from the relation with λ=500 nm for SLG and 300 nm for MLG. So, for SLG with average length 100nm and for MLG with average lateral size L=400nm, we consider thermal conductivity as 328 Wm-1K-1 and 800 Wm-1K-1 respectively. For μm sized flakes, from figure 6.1(c), we get thermal conductivity as 2200 Wm-1K-1 for 5 μm lateral size of MLG(n= 3).

The variation of composite thermal conductivity is shown in the next plot.

0

1

2

3

4

5

6

7

8

9

10

0

1

2

3

4

5

6

Volume fraction f (%)

Thermal conductivity of composite kc (W/mK)

Sample 3

Sample 2

Sample 1

Figure 6.10: Thermal conductivity of composite vs. volume fraction for different combination of samples including nm and μm sized filler particles.

We see that for 10% volume fraction of particle, composite thermal conductivity becomes 4.215 Wm-1K-1, 5.017 Wm-1K-1 and 5.862 Wm-1K-1 respectively. Thermal conductivity enhancement is correspondingly 4115%, 4917% and 5762%.

Here we can see that with the increase of graphene flakes of μm range, composite thermal conductivity increases as an effect of higher thermal conductivity for large lateral sized graphene. But we also need to consider that large lateral sized fillers tend to change the properties of TIMs. So, without changing necessary properties of thermal interface materials larger lateral sized flake will lead to higher composite thermal conductivity. Again a maximum value of volume fraction of fillers has to be identified which will ensure highest composite thermal conductivity maintaining other TIM characteristics.

**Thermal interface resistance Effect:**

Now we will see the effects of thermal interface resistance in the composite thermal conductivity with the filer combination mentioned for sample 2 which is - (i)10% SLG with average length L=100 nm, (ii) 70% MLG (n=3) with average lateral size L=400nm, (iii) 20% MLG(n=3) with average lateral size L=5 μm. We have taken four values of R as 1\*10-9 m2KW-1, 5\*10-9 m2KW-1, 10\*10-9 m2KW-1 and 20\*10-9 m2KW-1. The result is shown next.

0

1

2

3

4

5

6

7

8

9

10

0

1

2

3

4

5

6

7

8

9

Volume fraction f (%)

Thermal conductivity kc (W/mK)

R=1\*10-9 m2KW-1

R=5\*10-9 m2KW-1

R=20\*10-9 m2KW-1

R=10\*10-9 m2KW-1

Figure 6.11: Thermal conductivity of composite vs. volume fraction for different interfacial resistance of a sample including nm and μm sized fillers.

For thermal resistance variation from 1x10-9 to 20X 10-9m2KW-1, composite thermal conductivity of the sample drops from 8.054 to 3.12 Wm-1K-1 for 10% inclusion of fillers. So once again we can see a very significant change of composite thermal conductivity with interfacial thermal resistance.

**6.3.4 Temperature Effect**

Variation of thermal conductivity with temperature is very crucial for TIM performance. We want low change in thermal conductivity with temperature for better TIM performance. Here we have discussed the change in thermal conductivity of the composite for the variation of graphene-MLG (filler) thermal conductivity with temperature by the EMA model proposed by Nan.

At first we will see how graphene thermal conductivity changes with temperature. In case of ballistic thermal transport (lateral size less than mean free path) thermal conductivity is related by where (σ/A) term is thermal conductance per unit cross-sectional area. This has been discussed before at graphene thermal conductivity part. In this part we will again consider the relation for graphene size of nm range where variation with temperature is got from Jin-Wu Jiang et al. which has been shown in figure 3.9(a). This theoretical value is used here to estimate graphene thermal conductivity and composite thermal conductivity for different temperature.

**Effect for nm sized particles:**

Now the composite thermal conductivity is measured as a function of temperature for nm sized MLG flakes. We have calculated graphene thermal conductivity variation for nm sized flakes (figure 3.9(a) and Eq. 3.5)and used it to measure composite thermal conductivity. For different nm range lateral size, we have got the plot which is shown next.

280

300

320

340

360

380

400

420

440

460

0

0.5

1

1.5

2

2.5

3

3.5

4

Temperature (K)

Thermal conductivity Kc (W/mK)

L=800nm

L=700nm

L=500nm

L=300nm

L=100nm

Figure 6.12: Thermal conductivity of composite vs. temperature for different nm sized filler

Here, thermal interface resistance is considered as 10x10-9 m2KW-1, MLG is considered with 3 layers and volume fraction is considered as 10%. Mean free path is considered as 300 nm. So we see that EMA of Nan predicts a very flat temperature effect of composite thermal conductivity. This is because particle thermal conductivity change with temperature is not large enough to make impact on composite thermal conductivity. But in practical situation, other physical effects can dominate and there may be considerable change in composite thermal conductivity.

**Effect for μm sized particles:**

For μm sized single layer graphene, we can use the theory given by Nika et al. [60] to determine temperature effect in graphene thermal conductivity. We have used this theory to see the effects of lateral dimension and thermal interface resistance of μm sized graphene-MLG in composite thermal conductivity; now it has been used to identify the temperature effect of μm sized flakes on composite thermal conductivity. Here, μm sized SLG will be considered as particles for which theoretical thermal conductivity vs. temperature data are available. Thermal interface resistance and filler volume fraction is considered as 10\*10-9 m2KW-1 and 0.1 (10%) respectively.

280

300

320

340

360

380

400

420

440

460

5

10

15

20

25

30

Temperature ( K )

Thermal conductivity Kc (W/mK)

L=5 μm

L=4 μm

L=3 μm

L=2 μm

L=1 μm

Figure 6.13: Thermal conductivity of composite vs. temperature for different μm sized SLG fillers.

IN the figure-6.13 we see the variation of composite thermal conductivity with volume fraction of fillers for different μm sized length of single layer graphene. The variation is also negligible here.

**Combination of nm and μm sized filler particle:**

Now, temperature effect in composite thermal conductivity is analyzed for a combination of both nano and micrometer sized graphene-MLG flakes. We have taken samples of combinations of nm and μm ranged lateral size and seen how composite thermal conductivity varies with temperature. We have considered 3 samples where combination is made with the available data:

Sample1:

1. 10% SLG with average length L=100 nm( figure-3.9(a) and Eq. 3.5 for thermal conductivity with λ=500 nm)
2. 75% MLG (n=3) with average lateral size L=400nm (figure-3.9(a) and Eq. 3.5 for thermal conductivity with λ=300 nm)
3. 15% SLG with lateral size L=3 μm (figure-3.7 for thermal conductivity, Ref. [60])

Sample2:

1. 10% SLG with average length L=100 nm
2. 70% MLG (n=3) with average lateral size L=400nm
3. 20% SLG with lateral size L=3 μm

Sample3:

1. 10% SLG with average length L=100 nm
2. 65% MLG (n=3) with average lateral size L=400nm
3. 25% SLG with lateral size L=3 μm

Thermal interface resistance is considered as 10\*10-9 m2KW-1 and filler volume fraction is considered as 0.1 (10%). Composite thermal conductivity variation of these samples is shown in the next plot.

300

310

320

330

340

350

360

370

380

390

400

4

4.5

5

5.5

6

6.5

7

Temperature (K)

Thermal conductivity Kc (W/mK)

Sample 3

Sample 2

Sample 1

Figure 6.14: Thermal conductivity of composite vs. temperature for 3 samples each with a combination of nm and μm sized fillers.

As theoretical prediction considers increase in thermal conductivity of graphene flakes with temperature, composite thermal conductivity also increases with temperature but the change is small.

**6.3.5 Matrix thermal conductivity variation**

Most of the base polymers have thermal conductivity around 0.2- 0.3 Wm-1K-1. In table-3 we have seen thermal conductivity of some polymers. Now we will see how composite thermal conductivity is varied with matrix thermal conductivity variation. For analysis, we vary matrix thermal conductivity as km= 0.10, 0.2, 0.3, 0.4 and 0.5 Wm-1K-1. We will see the result separately for three cases - nm, μm and a combination of both sized particles.

**Particle sized in nm range:**

We consider MLG (n=3) with average lateral length L= 500 nm with mean free path λ=300nm. Thermal conductivity of graphene is considered as 1030 Wm-1K-1 from figure-1(a) (with the relation and =3.7 X109Wm-2K-1); R is considered as 10\*10-9 m2KW-1. For different matrix thermal conductivity we get the composite thermal conductivity variation like this:

0

1

2

3

4

5

6

7

8

9

10

0

0.5

1

1.5

2

2.5

3

3.5

Volume fraction f (%)

Thermal conductivity kc (W/mK)

km= 0.5 Wm-1K-1,

0.4 Wm-1K-1,

0.3 Wm-1K-1,

km = 0.2Wm-1K-1,

0.1 Wm-1K-1

Figure 6.15:Thermal conductivity of composite vs. volume fraction for different matrix thermal conductivity with avg. filler length 500nm.

With the increase of matrix thermal conductivity, composite thermal conductivity also increases. For 10% volume fraction of fillers, matrix thermal conductivity of 0.1, 0.2, 0.3, 0.4 and 0.5 Wm-1K-1 leads to composite thermal conductivity of around 2.18, 2.84, 3.15, 3.31 and 3.42 Wm-1K-1 respectively. But this variation of composite thermal conductivity is low. But from the figure we see that for very small thermal conductivity values, composite thermal conductivity variation is more significant (in the figure for km =0.2 and 0.1 Wm-1K-1) than larger thermal conductivity.

**Particle sized in μm range:**

Now, we shall see the variation of composite thermal conductivity with volume fraction for different matrix thermal conductivity considering μm sized particle. We consider MLG (n=4) with average lateral length L= 5μm for which thermal conductivity of graphene is used from figure-6.1(c) (kp = 1300 Wm-1K-1); R is considered as 10\*10-9 m2KW-1.

0

1

2

3

4

5

6

7

8

9

10

0

5

10

15

20

25

Volume fraction f (%)

Thermal conductivity of composite kc (W/mK)

km= 0.5 Wm-1K-1,

0.4 Wm-1K-1,

0.3 Wm-1K-1

0.2 Wm-1K-1,

0.1 Wm-1K-1

Figure 6.16: Thermal conductivity of composite vs. volume fraction for different matrix with avg. filler length of 5μm and thickness H = 4\*0.35 nm.

Here again we see the same result as for nm sized fillers. For low matrix thermal conductivity, difference between composite thermal conductivity is significant but as matrix thermal conductivity increases, composite thermal conductivity change becomes negligible considering same difference between two matrix thermal conductivity.

**Composition with both nm and μm ranged fillers:**

We again take a sample of different combinations of nm and μm sized particle. The sample is taken like this--

1. 10% SLG with average length L=100 nm,

(ii) 70% MLG (n=3) with average lateral size L=250nm,

(iii) 20% MLG (n=3) with average lateral size L=5 μm.

For these lateral sizes, particle thermal conductivity is used from figure- 6.1.

With 4 values of matrix thermal conductivity-km= 0.10, 0.2, 0.3 and 0.4 Wm-1K-1 and for R = 10\*10-9 m2KW-1 we can see the variation of composite thermal conductivity.

The result is shown below:

0

1

2

3

4

5

6

7

8

9

10

0

1

2

3

4

5

6

7

Volume fraction f (%)

Thermal conductivity of composite kc (W/mK)

km= 0.5 Wm-1K-1,

0.4 Wm-1K-1,

0.3 Wm-1K-1

0.2 Wm-1K-1,

0.1Wm-1K-1

Figure 6.17: Thermal conductivity of composite vs. volume fraction for different matrix thermal conductivity for a sample of nm and μm sized filler combination.

In the same way, Composite thermal conductivity of the composition increases with base matrix but difference in the change of composite thermal conductivity is more significant for lower matrix thermal conductivity values. As base matrix k moves to higher values composite thermal conductivity difference from the previous stage becomes less prominent gradually.

**6.3.6 Effect of graphene-MLG flakes on commercial TIMs**

Here, we will see the effect of change in thermal conductivity of a composite of commercial TIMs of silicone oil and graphene-MLG by EMA theory proposed by Nan.

Goyal et al. [9] conducted an experiment to see the effect of graphene inclusion on silver epoxy composite and found 500% increase in thermal conductivity with 5% graphene inclusion. They mentioned that in their graphene-FLG solution, amount of the single layer graphene (SLG) and bilayer graphene (BLG) content were 27% and 48%, respectively. Though no information is available for lateral size, we have observed composite thermal conductivity for different combinations and found that experimental result can still be achieved by Effective medium theory (EMT) approximation. The temperature effect has also been observed and we have got theoretical result which is close to experimental data. These results are shown in figure 6.18 and 6.19.

0

0.5

1

1.5

2

2.5

3

3.5

4

4.5

5

1

2

3

4

5

6

7

8

9

10

11

Volume fraction f (%)

Thermal conductivity kc(W/mK)

Figure 6.18: Thermal conductivity vs. volume fraction for hybrid graphene-FLG-silver epoxy composite: theoretical result from EMA for a combination & experimental result from [9]

270

280

290

300

310

320

330

340

350

360

6

6.5

7

7.5

8

8.5

9

9.5

10

10.5

11

Temperature (K)

Thermal conductivity Kc (W/mK)

5% volume fraction

3% volume fraction

Figure 6.19: Thermal conductivity vs. temperature of hybrid graphene-FLG-silver epoxy composite for 2 volume fraction: theoretical result from EMA for a combination & experimental result ( Ref. [9] )

Thermal interface materials made by silicone oil compounds, which are mainly greases, consist of silicone oil as a base matrix with filers like silica or metals. Varying the amount of fillers, many TIMs are available which have thermal conductivity value in the range of 0.7-4.0 Wm-1K-1. As graphene has been used as fillers in many metal-polymers, we can also make compounds of graphene and commercial silicone oil TIMs and see what the result is in thermal conductivity of the compound. We consider a commercial silicone rubber compound of thermal conductivity 1.5 Wm-1K-1 where filler volume is not very high and graphene flakes can also be included.

We take two samples of graphene-MLG like this –

Sample 1

1. 10% SLG with average length L=100 nm,
2. 70% MLG (n=3) with average lateral size L=400nm,
3. 20% SLG with average lateral size L=4μm.

Sample 2

1. 10% SLG with average length L=100 nm,
2. 60% MLG (n=3) with average lateral size L=400nm,
3. 30% SLG (n=3) with average lateral size L=4μm.

Graphene thermal conductivity is measured accordingly from figure- for corresponding sizes. R is assumed as 10\*10-9 m2KW-1 .

For the sample filler inclusion up to 5%, we find the composite thermal conductivity variation like this-

0

0.5

1

1.5

2

2.5

3

3.5

4

4.5

5

1

1.5

2

2.5

3

3.5

4

4.5

5

Volume fraction f (%)

Thermal conductivity kc (W/mK)

Sample 2

Sample 1

Figure 6.20: Thermal conductivity vs. volume fraction for graphene-commercial silicone oil composite predicted by EMA.

Now, for the combination of sample 2 mentioned in previous section, we will see the temperature effect. According to the mentioned properties of commercial silicone oil compounds, its thermal conductivity does not change very much with temperature. So we will see the effect of composite thermal conductivity with temperature for temperature variation of graphene fillers. The analysis of graphene thermal conductivity variation with temperature was discussed before. Using that analysis, we have calculated composite thermal conductivity and got the result shown below for 2 different volume fraction of graphene-MLG (f = 5% and f=3%) .

300

310

320

330

340

350

360

370

380

390

400

3.5

4

4.5

5

5.5

Temperature (T)

Thermal conductivity Kc (W/mK)

f = 5 %

f =3 %

Figure 6.21: Thermal conductivity vs. temperature for graphene-commercial silicone oil composite predicted by EMA for 2 different volume fraction f=0.05 (5%) and f=0.03 (3%).

As usual, we get negligible change of composite thermal conductivity with temperature.

**6.3.7 Particle Orientation:**

In previous cases, we have used EMA for randomly oriented particle fillers. This is the general case as fillers in the composite will be dispersed randomly. But we can see the effect of composite thermal conductivity for particles oriented in the heat transport direction. For this case, we have used EMA equation of Nan for aligned continuous fiber oriented in the heat transport direction. The composite thermal conductivity for completely oriented and randomly oriented for a graphene-MLG filler combination is shown in the next figure. For silicone oil matrix, a sample of graphene-MLG is taken such as- (i)10% SLG with average length L=100 nm, (ii) 75% MLG (n=3) with average lateral size L=400nm, (iii) 15% MLG(n=3) with average lateral size L=5 μm. The outcome is shown below-

0

1

2

3

4

5

6

7

8

9

10

0

10

20

30

40

50

60

70

80

90

Volume fraction f (%)

Thermal conductivity kc (W/mK)

Completely Oriented

Randomly Oriented

Figure 6.22: thermal conductivity of composite a silicone oil for a graphene-MLG composition for particle orientation of completely oriented and randomly oriented.

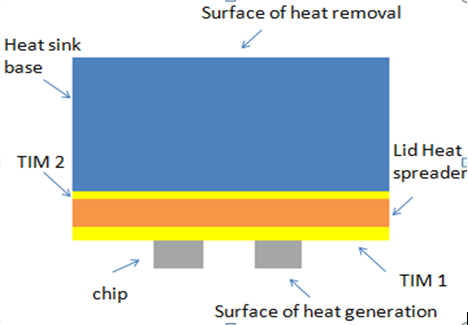
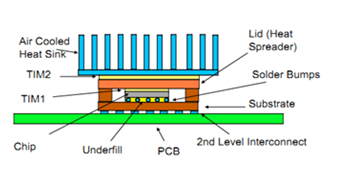
We see there is a huge difference for these two cases. Composite thermal conductivity increases approximately 17 times greater for completely oriented particles comparing randomly oriented particles. For completely oriented particles in the heat propagation direction, all particles contribute to transfer heat in a particular direction. So, thermal conductivity increases in a large amount.

**Chapter 7**

**Comparison of Performance of TIMs with a Simplified Model of High Power Package and Heat Sink**

A typical configuration for a high power microprocessor or ASIC (Application-Specific Integrated Circuit) package attached to a heat sink is depicted in Figure 1a. This sort of flip-chip design lends itself to effective routing of power and signals between the chip and the PCB (Printed Circuit Board) below and to the efficient transfer of heat to the heat sink above. The package has a lid that is usually fabricated of copper to promote heat spreading. Thermal interface materials (TIMs) assist in the transfer of heat between the die and the lid (TIM1) and the lid and the heat sink base (TIM2).

Finite element analysis was conducted on a simplified solid model of the package and board as depicted in Figure 1b, using a commercial software tool COMSOL Multiphysics 3.5. The model represents only the chip-to-heat sink thermal path. Regarding the heat sink, only its base is explicitly represented in the model.



(b)

(a)

Figure 7.1: Diagrams of high power package attached to a heat sink. (a) a typical system application; (b) simplified geometry as represented in the model.(figure courtesy- Electronics Cooling, Volume-16, Number-4, Winter 2010).

Important features of the high power package include-

* The fin structure is accounted for by the use of an effective heat transfer coefficient applied to the top surface of the heat sink base.
* All other surfaces are assumed to be adiabatic.
* This analysis ignores the presence of a secondary heat flow path to the ambient air through the PCB. This path is usually negligible for high-power packages because of the very low thermal resistance of the primary path to air via the heat sink.

Following table lists the specific dimensions and material properties assumed for the package and heat sink for Finite Element Analysis. We consider four equal sized chips uniformly placed over the PCB.

Table 7.1 : Specific dimensions and material properties assumed for the package and heat sink for Finite Element Analysis.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Layer No | Component | Thickness  (mm) | Length\*Width  (mm)\*(mm) | Material | Thermal Conductivity (W mK-1) |
| 1 | Die | 0.5 | 15\*15 | Si | 111 |
| 2 | TIM 1 | 0.1 | 100\*100 |  |  |
| 3 | Lid | 0.5 | 100\*100 | Cu | 390 |
| 4 | TIM2 | 0.05 | 100\*100 |  |  |
| 5 | Heat Sink Base | 6 | 100\*100 | Cu | 390 |

Power of 80 W is uniformly distributed in the volume of 15mm\*15mm\*0.5mm of every chip. For the outer boundary of heat base sink,heat transfer coefficient h considered 2000 W/m2-K. External and ambient temperature both are considered as 0⁰ C.

Thermal conductivity of silicone oil is 0.1 WmK-1. For a particular graphene-MLG sample we have got composite thermal conductivity as 5.8 WmK-1. Thus heat transfer efficiency between microprocessor and heat sink base increases considerably.

To compare how heat transfer efficiency depends on TIM material we have considered four cases. They are:

* Case 1: silicone oil as TIM 1 and TIM 2.
* Case 2: Silicone oil as TIM 1 and Silicone oil-graphene nanocomposite as TIM 2.
* Case 3: Silicone oil-graphene nanocomposite as TIM 1 and silicone oil as TIM 2.
* Case 4: Silicone oil-graphene nanocomposite as TIM 1 and TIM 2.

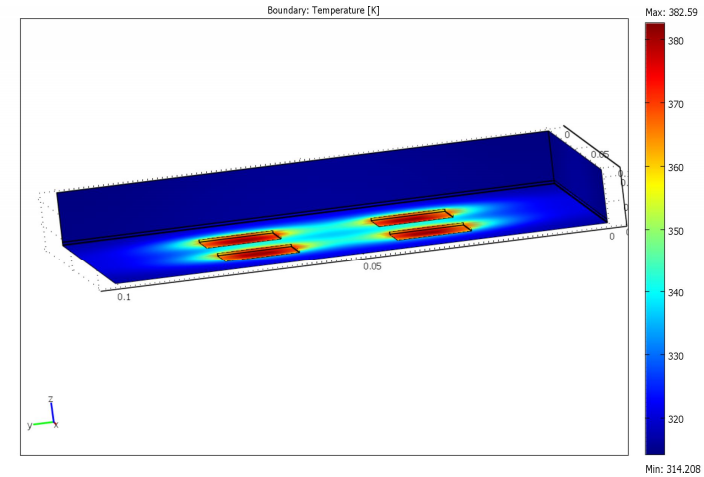
****

Figure 7.2 : Finite Element Analysis output figure for case 3. Here, we use silicone oil-graphene nanocomposite as TIM 1 and silicone oil as TIM 2.

Following table compares heat transfer efficiency between above cases.

Table 7.2 : Input values of thermal conductivity of TIM1 and TIM2 and Output maximum temperature for performance analysis.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Case no.** | **Thermal Conductivity of TIM 1(Wm-1K-1)** | **Thermal Conductivity of TIM 2(Wm-1K-1)** | **Max temp/Die temp. (K)** | **Comment** |
| 1 | 0.1 | 0.1 | Max: 702K |  |
| 2 | 0.1 | 5.8 | Max: 657K | Maximum temperature decreased |
| 3 | 5.8 | 0.1 | Max: 382K | Maximum temperature further decreased |
| 4 | 5.8 | 5.8 | Max: 333K | Maximum temperature is the leastamong four cases. |

**Observation:**

It is beneficial to put high thermal conductivity TIM material near the chip. It is also observed that higher the value of thermal conductivity higher the heat transfer efficiency of the package.

**Chapter 8**

**Conclusion**

The demand of next generation IC technology is thermal interface materials with high thermal conductivity. Inclusion of filler particles with high thermal conductivity on matrices can increase composite thermal conductivity significantly which can be used as TIMs. Higher thermal conductivity, plane geometry, better thermal coupling thermal stability of graphene etc. have initiated promising future of graphene as fillers in TIMs. In our analysis, we have considered silicone oil as our main base matrix which has vast uses as TIMs and graphene-MLG as fillers to form a composite and used EMA model proposed by Nan to see composite thermal conductivity variation for different parameters.

Our calculation of thermal conductivity for graphene-MLG silicone elastomer composite or other composites by EMA proposed by Nan derives some aspects. With the increase of lateral size of fillers (graphene), composite thermal conductivity increases. Though we have used different relations or source of data for thermal conductivity of nanometer and micrometer sized graphene, we have got a gradual increase in composite thermal conductivity from nm to μm sized graphene fillers. Considering different samples we have got thermal conductivity enhancement of around 4000% to 5700% for 10% volume of fillers. For larger lateral sizes, the enhancement predicted by EMA increases but in practical situation, there will be a limit for the enhancement.

One of the reasons of anomalous enhancement of thermal conductivity of graphene-MLG based composites is the very small aspect ratio of graphene fillers. It is also pronounced in EMA of Nan as significant changes in composite thermal conductivity are seen for small change in aspect ratio. With the increase of no. of layers, aspect ratio () decreases for a particular lateral size. Graphene thermal conductivity also decreases with layers i.e. with the increase of aspect ratios. But in thermal conductivity calculation by EMA, aspect ratio change has more dominant effect in composite thermal conductivity than the particle thermal conductivity.

Interface resistance plays a major role in composite thermal conductivity and EMA model also indicates very large change in composite thermal conductivity with the variation of interface resistance. So interface resistance of the composite needs to be low and graphene based polymers are superior in regarding this case as these polymer composites have low interface resistance due to good coupling of graphene with base materials.

Composite thermal conductivity variation with temperature predicted by EMA model shows very small change and practical result may not be same with our theoretical prediction. Here, we are considering only particle thermal conductivity change with temperature to see the effect in composite thermal conductivity. But in real situation, many other physical effects contribute so that composite thermal conductivity may not be predicted by EMA model.

Change of base matrix thermal conductivity does not make very significant impact on composite thermal conductivity as seen by EMA model. But matrix- particle coupling needs to be considered in real situation that can separate matrices according to their superiority for TIM application. Particle orientation also makes a huge impact on composite thermal conductivity as seen by the EMA model and it will be a worth to try to change the orientation in composite materials.

In the last part of our analysis we have made a simple model of high power package to see the effect of TIMs of higher thermal conductivity over low thermal conductivity. We have observed that for high thermal conductivity of TIMs heat propagation becomes better and maximum temperature of the system reduces. This indicates clearly the importance of TIMs with high thermal conductivity.

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