Chapter 7

Conclusions and future directions

7.1 Conclusions

The thermal transport study is important for the technologies such as thermoelectric generators and coolers, thermal barriers and heat management in the nanoelectronic devices. The performances of these nano-devices and the advancements in the technologies depend on the nanoscale thermal transport in their constituting materials. However, the thermal transport in nano-materials differ drastically as compared to the bulk. Moreover, different effects of a particular nanostructuring are seen on different materials. Therefore, a prior understanding of thermal transport in these nano-materials would be convenient to tailor their thermal properties, with particular nanostructuring, according to the application. This is achieved by theoretically investigating the thermal transport in materials.

However, the thermal conductivity simulations for nanostructured materials are unfeasible with *ab initio* because of the required large simulation cells due to lack of symmetry. Use of simplified potentials provides an efficient way of calculating thermal conductivity of a material at larger length scales. However, the existing short ranged empirical models exhibit deviations of up to an order of magnitude for the thermal conductivity of pure materials, as compared to experiments, Fig. 2.1.[1] Furthermore, not much work has been done on extending these potentials to alloys and nanostructures.

In this thesis, we developed simplified potentials for simulation of thermal properties of nanostructures. Furthermore, we also studied the effect of nanostructuring
on thermal conductivity of materials from first principles. For the determination of thermal conductivity, Boltzmann Transport Equation (BTE) for phonons was solved in relaxation time approximation (RTA). In RTA, the scattering rate for a phonon mode is considered to be independent of the perturbations to other phonon modes. Within this framework, precise understanding of scattering of each phonon mode is obtained. The effect of different scattering channels, due to nanostructuring, on the scattering rate of each phonon mode can also be calculated separately. Such a study provides important insights of the thermal transport behaviour of a material with particular nanostructuring, which could be beneficial to engineer material with desired thermal conductivity. The theory of this framework to calculate thermal conductivity is discussed in Chapter 3.

In Chapter 4, we developed a short ranged force constant model for the precise determination of the thermal properties of \( \text{Si}_x\text{Ge}_{1-x} \) random alloys.\(^4\) The parameters for our force constant model were extracted from DFT calculations with the effective contributions of long ranged interactions in our short ranged model parameters. Capturing long ranged interactions in our model helped to reproduce correct acoustic phonons which significantly contribute to the thermal properties. The model was tested for the thermal properties as thermal expansion, Grüneisen parameters and heat capacity for pure Si, Ge, and ordered structure of \( \text{Si}_{0.5}\text{Ge}_{0.5} \) using PHONOPY package.\(^{116} \) A good reproduction of anharmonic properties as Grüneisen parameters and thermal expansion was obtained with our model, which indicates that thermal conductivity can also be calculated accurately with a short ranged model, Fig. 4.5. Furthermore, a good transferability of our model was confirmed by applying it to the different compositions of \( \text{Si}_x\text{Ge}_{1-x} \) random alloys, Fig. 4.7. This simple model thus confirms the possibility of having a short ranged potential for calculating the long ranged interactions to correctly reproduce the thermal properties of complex structures.

For the thermal conductivity determination based on the BTE-RTA formalism, we used a new computer program as an extension to PHONOPY, developed in collaboration with Prof. Atsushi Togo. We studied the thermal transport in nanostructured zinc-chalcogenides which crystallise in the similar structure as Si and Ge, presented in Chapter 5.\(^9\) Furthermore, zinc-chalcogenides show interesting thermal conductivity cross-over at nanoscale.\(^{135} \) We carried out full \textit{ab initio} study to understand this cross-over behaviour in detail. The isotope and grain boundary, along with anharmonic scattering, were considered in our calculations and the
effect of nanostructuring on thermal conductivity was studied by understanding the contributions of different mean free path (MFP) phonons at nanoscale in zinc-chalcogenides. We found that origin of both the thermal conductivity cross-over for ZnS and ZnSe at nanoscale and higher bulk thermal conductivity of ZnS is the large contribution of long MFP phonons in ZnS which are scattered strongly with nanostructuring, Fig. 5.6. The acoustic-optic phonon gap in ZnS, which arises due to mass difference of constituting elements, gives birth to these long MFP phonons in ZnS, in contrast to ZnSe and ZnTe. Moreover, our ab initio study showed the thermal conductivity cross-over at larger grain size of \( \sim 100-200 \text{ nm} \) as compared to 30 nm predicted by earlier model, Fig. 5.6.[135] We also found the thermal conductivity to be half of the earlier model predictions for ZnS at 100nm grain size which could be technologically important.

The boundary scattering, in Chapter 5, was calculated within an empirical model due to the computational expenses associated with explicit ab initio calculations for nanostructures. Considering this challenge and inspired by the performance of short ranged model for thermal properties of Si\(_x\)Ge\(_{1-x}\) random alloys in Chapter 4, we have developed a tight binding (TB) model for Si, presented in Chapter 6. TB models take into account the quantum bonding information of a material by modelling its orbital interactions. We reviewed earlier short and long ranged orthogonal TB models for Si and analysed their performances for calculating thermal expansion and thermal conductivity. These earlier TB models were fitted for the correct determination of energetics and showed some deviations for thermal properties.

Hence we modelled a new short ranged and simple orthogonal TB model for thermal properties of Si. The bond integrals were derived from DFT using a downfolding procedure.[89] Furthermore, a simple functional form, as proposed by Goodwin et al.[145], was used for bonding and repulsive terms. The model parameters were obtained by fitting only to potential energy for diamond Si. The model calculated Si thermal expansion, Fig. 6.11, and thermal conductivity, Fig. 6.12, gave a good agreement with DFT results and showed improvement over the earlier orthogonal TB models for Si. Our model also exhibited transferability to electronic properties of different structures of Si, Fig. 6.13. Deviations from DFT for the binding energy curves of different structures of Si were found with our model which would indicate the need to further optimise our model. However, the phonons for 2D structure of Si (silicene) calculated with our model showed a very good agreement
with DFT, Fig. 6.18. Thus our short ranged model fitted to small dataset reproduces the energetics and thermal properties of diamond Si. Moreover, it also exhibits transferability to some other structures of Si.

7.2 Future directions

The future directions of this thesis includes the application of our developed models for materials simulations at larger length scales. Furthermore, our models could also be extended for improving their performances. The force constant modelling scheme, presented in Chapter 4, parameterised the second order force constant matrices which are used to obtained the thermal properties in harmonic and quasi-harmonic approximations. However, the calculation of thermal conductivity requires determination of higher order force constants which needs to be modelled. Considering the sparseness of third order force constants matrix, a new mathematical algorithm called Compressive Sensing (CS), could serve beneficial. CS is a recently developed algorithm in the field of signal processing and is finding interest in material science field as it requires few number of samples to reproduce a signal correctly. Thus the short ranged models, based on CS technique, can be developed to reproduce anharmonic force constants for the efficient and accurate calculations of the thermal conductivity of different nanostructures.

For the case of our TB model for Si, presented in Chapter 6, our model could be extended to correctly predict the energetics of other structures of Si. This includes the prediction of stable phase of $\beta$-tin Si with our model. Thus the next step would be to try out different strategies for fitting our model to the energetics of different structures of Si and testing it for stable Si structures as $\beta$-tin and clathrates.

The molecular dynamics (MD) studies at larger length scales can also be performed efficiently for bulk Si as well as silicene with our model. Furthermore, with the improvement in transferability of our model to other structures, one can do MD studies for thermal conductivity of different nanostructures.

One more future perspective would be to develop an orthogonal TB model for Ge following the similar modelling strategy as used for Si TB model, presented in Chapter 6. This will help to study the thermal transport in Si-Ge random alloys as well as in various other Si-Ge nanostructures at larger length scales.