



Non-equilibrium Molecular Dynamics for Calculating the Thermal Conductivity of Graphene-Coated Aluminum

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Abstract

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Non-equilibrium Molecular Dynamics (NEMD) simulations have been created in C++ using Message Passing Interface (MPI) library to calculate the phonon thermal conductivity of bare graphene, aluminum, and graphene-coated aluminum. This study focuses on how graphene can alter the thermal conductivity of graphene-coated aluminum. The effect of length, graphene, and the number of graphene layers are analyzed. Even though electrons are dominant on thermal conductivity of aluminum, the effect of graphene coating can be seen in the results. The results show that the thermal conductivity of aluminum increases by up to 149% by graphene coating. When the number of layers increases to two layers, the thermal conductivity increases by up to 261%. Moreover, the results increase with the length of all models.

1. Introduction

The development in computer and materials sciences enable us to create new devices in many areas including automotive and aerospace. At the same time, these new devices must work under heavily loaded operations. These operations generate heat as a by the production of operation. Among metals, aluminum has been adopted in these devices owing to its high thermal conductivity value among metals. However, higher thermal conductivity materials are needed for these advanced applications to keep them under the required working conditions [1]. In the literature, there have been various materials including Carbon Nanotubes (CNTs), diamond, graphite, and graphene used to obtain the need for thermal management.

Graphene is one of the materials that has the highest thermal conductivity value among carbon allotropes. It also has lightweight, high mechanical, and electrical properties [2–5]. These properties make graphene attractive material among thermal applications [6].

Researchers have been working on graphene to use in many areas. It has been used as pure graphene and reinforcing or coating material to enhance material properties.

Many attempts have been done for producing graphene reinforced Aluminum Metal Matrix Composites (AMMCs). For instance, graphene reinforced AMMCs are produced with Friction Stir Processing (FSP) [7], powder synthesis [8–10], vacuum hot pressing [11], and Chemical Vapor Decomposition (CVD) methods [12]. Jeon et al. [7] studied graphene reinforced AMMC fabrication by FSP and the results showed that the thermal conductivity was 15% higher than the bare aluminum. Another research showed that a 15.4% enhancement in thermal conductivity can be achieved by adding graphene into pure Al by powder metallurgy technique [13]. Zheng et al. [12] synthesized graphene-coated aluminum alloy by transferring the CVD grown graphene on aluminum alloy. Aluminum alloy's anti-corrosion property enhanced via graphene coating. The corrosion resistance of aluminum studies has been done by other researchers in the literature and it was also found that the graphene layer protects the aluminum against corrosion [14]. Moreover, Han et al. [15] were fabricated nanotube@Cu/Ag@graphite/Al composite.

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The results showed that 0.1 mm graphite enables composite to have 48.8% higher thermal conductivity, stable coefficient of thermal expansion at a high temperature, and 126% higher bending strength compared to without graphite film. Abhinav et al. [16] made up of an aluminum box and a graphene-coated aluminum box to compare heat transfer and electrical resistance. The results showed that the temperature of the inside graphene-coated aluminum box is 36% higher than the uncoated one. The electrical resistance value was also decreased by 33%.

The studies on graphene are not limited to experimental ones; the numerical calculation has been done in the literature. One of the most widespread methods of Molecular Dynamics (MD) is an atomistic simulation technique to study the properties of nano-sized materials. Zhang et al. [17] studied the length effect on the thermal conductivity of supported graphene and achieved that TC increases with the length. Cao [18] studied MD simulation to show the temperature effect of graphene on the TC. The

results showed that the TC decreases from $1600 \text{ Wm}^{-1}\text{K}^{-1}$ to $400 \text{ Wm}^{-1}\text{K}^{-1}$ as the temperature increases from 300 K to 1000 K. In addition to pure graphene, the mechanical behavior of graphene-coated aluminum is investigated. The Young modulus of aluminum increases with graphene coating by 88% [19].

NEMD simulation code is created in the C++ programming language using Message Passing Interface (MPI) library and the code is used to investigate the length dependence and graphene coating effect on the phonon thermal conductivity (κ_{ph}) of aluminum.

2. Method

A zig-zag structure graphene-coated aluminum that has a Face-centered Cubic (FCC) structure with a lattice constant of 4.04 \AA models is created. Figure 1 illustrates the schematic model of graphene-coated aluminum with calculation zones.

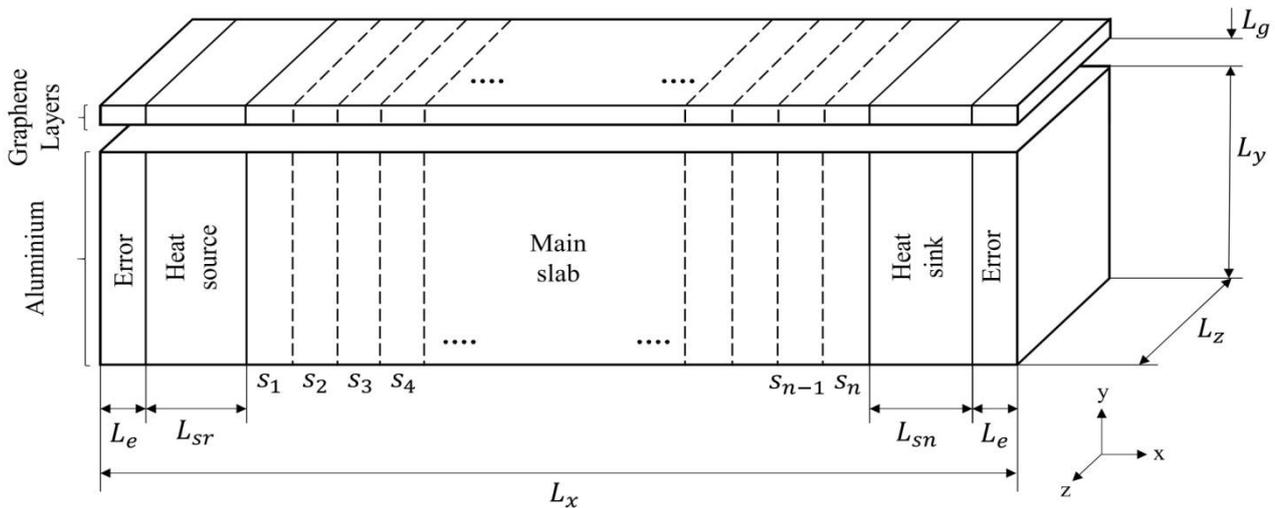


Figure 1. Schematic illustration of the simulation domain.

The height (L_y) and width (L_z) of the aluminum block are kept at 16 \AA during the simulations. The simulation models have three calculation zones; error, thermostat, and main. Two error zones are created and placed at each end of the modeled materials. Their lengths (L_e) are kept at 3 \AA . The thermostat zones have placed both edges between the main zone and error zones and kept at 320 K as a heat source and 280 K as a heat sink using the Nose-Hoover thermostat. Nose Hoover thermostat is one of the numerical methods used to control the temperature by maintaining the velocities [20]. The relaxation time of the thermostats, τ , is selected as 50 fs . The length of the heat source (L_{sr}) and sink (L_{sn}) are 8 \AA . The main zone or main slab is where the length effect is investigated. The main slab is virtually sliced into 8 sections. The length of each section is equal to each other.

The lengths of the modeled materials (L_x) are $60, 100, 200,$ and 250 \AA to predict the length effect on the phonon thermal conductivity (κ_{ph}). The length between the top of the aluminum block and the graphene layer (L_g) is 3 \AA [21]. The length between each graphene layer is 3.4 \AA for multiple layers graphene [22].

The C-C bonding interactions in graphene layers are calculated by the Tersoff potential;

$$U_{TE}(r_{ij}, r_{ik}, \Theta_{ijk}) = f_{ij}^{Ct} \left[a_{ij} A e^{-\lambda_1 r_{ij}} - b_{ij} B e^{-\lambda_2 r_{ij}} \right] \quad (1)$$

where C is the cut-off function and b_{ij} is the bond angle terms. The rest of Tersoff potential parameters are $A=1393,6 \text{ eV}$, $B=346,74 \text{ eV}$, $\lambda_1=3.4879 \text{ \AA}$, $\lambda_2=2.2119 \text{ \AA}$, $n=0.72751$, $c=38049$, $d=4.3484$, $h=-0.57058$,

$\beta=1.5724*10^{-7}$, $R_{ij}=1.8 \text{ \AA}$, $S_{ij}=2.1 \text{ \AA}$, and $a_{ij}=1$ [23]. The Al-Al interactions are described as the Sutton-Chen potential which is on the Embedded Atom Method (EAM) potential;

$$U_{SC}(r_{ij}) = \left[\sum_{j \neq i}^N \epsilon \frac{1}{2} \left(\frac{\sigma}{r_{ij}} \right)^n - c \sqrt{\sum_{j \neq i}^N \left(\frac{\sigma}{r_{ij}} \right)^m} \right] \quad (2)$$

where $\epsilon_{Al-Al} = 0.033147 \text{ eV}$, $m=6$, $n=7$, $c=16,399$ [24]. The nonbonding interactions between the aluminum block and graphene layer which is Al-C and between each graphene layer which is C-C are assumed as the Lennard-Jones potential;

$$U_{LJ}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (3)$$

where $\epsilon_{Al-C} = 0.035078 \text{ eV}$ and $\sigma_{Al-C} = 3.0135 \text{ \AA}$ for Al-C interactions [21] and $\epsilon_{C-C} = 0.002168 \text{ eV}$ and $\sigma_{C-C} = 3.36 \text{ \AA}$ for C-C interactions [25]. The numerical integrations are calculated using the Velocity-Verlet integration algorithm with 0.5 fs timestep [26].

The molecular model of a single layer graphene-coated aluminum block is seen in Figure 2.

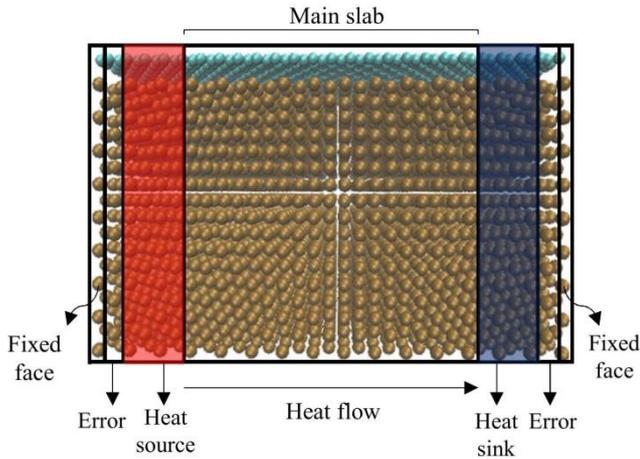


Figure 2. Single-layer graphene-coated aluminum.

A single atomic layer of aluminum is fixed at both the left and right ends of the models. The simulations are first to run 0.125 ns to equilibrate the system temperature at 300 K. Following the system reaches the temperature of 300 K, the heat source at 320 K and heat sink at 280 K are applied to the model for 14.875 ns. After the temperature differences, the simulations are continued for 5 ns where the thermal conductivity is calculated. During the last period, the temperature gradients and thermostat energy change data are collected. Using the Fourier law approach and the simulation data, the thermal conductivity is

calculated as follows [27];

$$\kappa_{ph} = \frac{\Delta E_{avg}}{A \Delta t \frac{\Delta T}{\Delta x}} \quad (4)$$

where Δt is the simulation time, $\Delta T/\Delta x$ is the temperature gradient of the main slab, A is the cross-sectional area, and ΔE_{avg} is the average energy changes in the heat source and sink. It is the mean energy that is added and subtracted in thermostat regions. It is calculated from the energy differences between before and after thermostats applied to both heat source and heat sink parts.

3. Results

The phonon thermal conductivity of pure graphene, uncoated aluminum, and graphene-coated aluminum was predicted. For comparison, the length effect on the thermal conductivity was calculated for each model. The length effect on the suspended graphene in the range from 60 to 250 \AA is calculated and shown together with the results by Wei et al. [22] in Figure 3. Single-layer graphene with a thickness of 3.4 \AA was used during pure graphene simulations. As seen in the results, the length dependence of bare graphene shows similar results and increases with length.

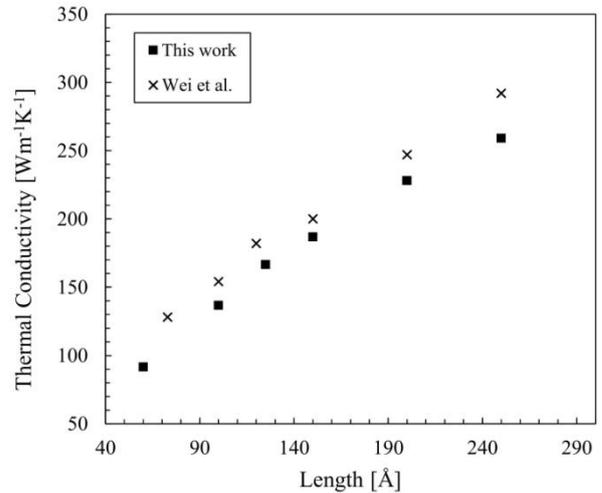


Figure 3. The phonon thermal conductivity of single layer graphene.

Even though heat transport is dominated by phonon in graphene, it is maintained by electrons in metals. Figure 4 shows the length effect on the phonon thermal conductivity of aluminum with a temperature gradient through a longitudinal direction. The results show that the thermal conductivity increases. The thermal conductivity of aluminum is 205 W/mK in the literature, however, the obtained results are much smaller since the MD simulation

results are phonon interactions. Still, the simulated results are similar to the literature [28-29].

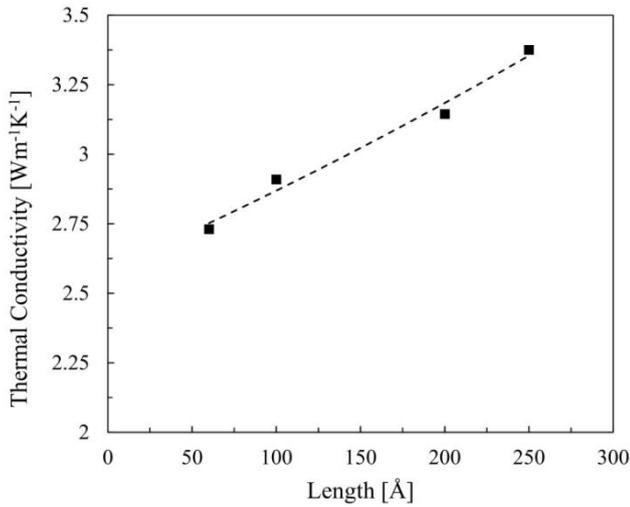


Figure 4. The length dependence of phonon thermal conductivity of aluminum.

After simulating and calculating the phonon thermal conductivity of graphene and aluminum individually, graphene-coated aluminum is modeled to investigate its results. Figure 5 shows the length and number of graphene coating layer effects on the thermal conductivity of graphene-coated aluminum.

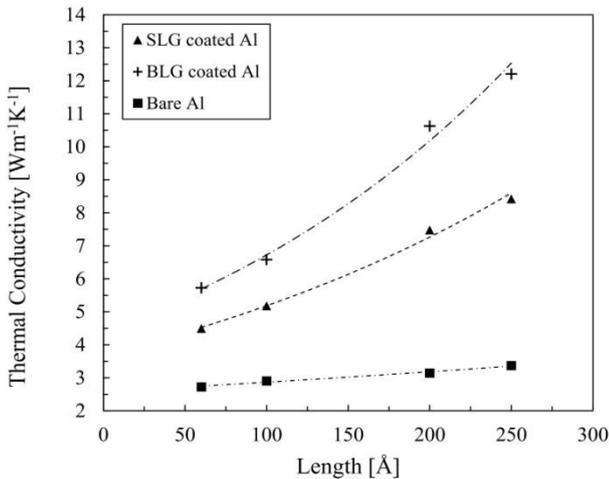


Figure 5. Phonon thermal conductivity of bare aluminum, SLG coated aluminum, and BLG coated aluminum.

As seen from the results, the thermal conductivity increases for all models with the length. There is also a significant increase in thermal conductivity with graphene coating. There is an up to 149% increase with Single-Layer Graphene (SLG) coated aluminum and up to 261% increase with two-layer graphene layers (BLG) coated aluminum. Accordingly, the C-Al interactions and the

unique properties of graphene help to increase heat transfer on the graphene-coated aluminum. This means that the thermal transport in graphene-coated aluminum is ballistic. Additionally, it is believed that increasing the number of graphene coating layers limits the phonon scattering and increases the phonon mean free path which results in increasing the thermal conductivity.

4. Conclusions

In the present study, a NEMD simulation code in C++ with MPI library was created to explore the phonon thermal conductivity of bare graphene, aluminum, and graphene-coated aluminum. Thermal conductivity of graphene-coated aluminum increases with a length which is seen similar results in bare graphene and aluminum. Due to the interaction of C-Al and C-C, the thermal conductivity of graphene coating on aluminum increases the thermal conductivity. Increasing the number of coating graphene layers shows an enhancement in the thermal conductivity for bare aluminum. Even though electrons dominate on the thermal conductivity of aluminum, the graphene coating on aluminum shows a distinctive contribution to the phonon thermal conductivity. By the results of this study, graphene coating may enable aluminum to be used in need of high thermal management.

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References

- [1] Balandin A. A., 2009. Chill Out: New Materials and Designs Keep the Chips Cool. *IEEE Spectrum*, **46**(10), pp. 28–33.
- [2] Ghosh S., Calizo I., Teweldebrhan D., Pokatilov E. P., Nika D. L., Balandin A. A., Bao W., Miao F., Lau C. N., Ghosh S., Calizo I., Teweldebrhan D., Pokatilov E. P., Nika D. L., Balandin A. A., 2008. Extremely High Thermal Conductivity of Graphene: Prospects for Thermal Management Applications in Nanoelectronic Circuits. *Applied Physics Letters*, **92**(15), p. 151911.
- [3] Balandin A. A., Ghosh S., Bao W., Calizo I., Teweldebrhan D., Miao F., Lau C. N., 2008. Superior Thermal Conductivity of Single-Layer Graphene. *Nano Letters*, **8**(3), pp. 902–907.

- [4] Chen S., Moore A. L., Cai W., Suk J. W., An J., Mishra C., Amos C., Magnuson C. W., Kang J., Shi L., Ruoff R. S., 2011. Raman Measurements of Thermal Transport in Suspended Monolayer Graphene of Variable Sizes in Vacuum and Gaseous Environments. *ACS Nano*, **5**(1), pp. 321–328.
- [5] Lee C., Wei X., Kysar J. W., Hone J., 2008. Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. *Science* (New York, N.Y.) **321**(5887), pp. 385–388.
- [6] Novoselov K. S., Geim A. K., Morozov S. V., Jiang D., Zhang Y., Dubonos S. V., Grigorieva I. V., Firsov A. A., 2000. Electric Field Effect in Atomically Thin Carbon Films, doi: 10.1126/science.1102896.
- [7] Jeon C. H., Jeong Y. H., Seo J. J., Tien H. N., Hong S. T., Yum Y. J., Hur S. H., Lee K. J., 2014. Material Properties of Graphene/Aluminum Metal Matrix Composites Fabricated by Friction Stir Processing. *International Journal of Precision Engineering and Manufacturing*, **15**(6), pp. 1235-1239.
- [8] Yan S. J., Yang C., Hong Q. H., Chen J. Z., Liu D. B., Dai S. L., 2014. Research of Graphene-Reinforced Aluminum Matrix Nanocomposites. *Cailiao Gongcheng/Journal of Materials Engineering*, **0**(4), pp. 1–6.
- [9] Liu J., Khan U., Coleman J., Fernandez B., Rodriguez P., Naher S., Brabazon D., 2016. Graphene Oxide and Graphene Nanosheet Reinforced Aluminium Matrix Composites: Powder Synthesis and Prepared Composite Characteristics. *Materials & Design*, **94**, pp. 87–94.
- [10] Shin S. E., Choi H. J., Shin J. H., Bae D. H., 2015. Strengthening Behavior of Few-Layered Graphene/Aluminum Composites. *Carbon*, **82**, pp. 143-151.
- [11] Huang Y., Ouyang Q., Guo Q., Guo X., Zhang G., Zhang D., 2016. Graphite Film/Aluminum Laminate Composites with Ultrahigh Thermal Conductivity for Thermal Management Applications. *Materials & Design*, **90**, pp. 508-515.
- [12] Zheng Z., Liu Y., Bai Y., Zhang J., Han Z., Ren L., 2016. Fabrication of Biomimetic Hydrophobic Patterned Graphene Surface with Ecofriendly Anti-Corrosion Properties for Al Alloy. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **500**, pp. 64-71.
- [13] Zhang L., Hou G., Zhai W., Ai Q., Feng J., Zhang L., Si P., Ci L., 2018. Aluminum/Graphene Composites with Enhanced Heat-Dissipation Properties by in-Situ Reduction of Graphene Oxide on Aluminum Particles. *Journal of Alloys and Compounds*, **748**, pp. 854-860.
- [14] Liu J., Hua L., Li S., Yu M., 2015. Graphene Dip Coatings: An Effective Anticorrosion Barrier on Aluminum. *Applied Surface Science*, **327**, pp. 241-245.
- [15] Han X., Huang Y., Gao Q., Yu M., Chen X., 2018. High Thermal Conductivity and Mechanical Properties of Nanotube@Cu/Ag@Graphite/Aluminum Composites. *Industrial & Engineering Chemistry Research*, **57**(31), pp. 10365-10371.
- [16] Abhinav C., Reddy K. V. K., Raju G. G., Subramanyam K., 2017. Experimental Investigation of Graphene Coated Al Cuboid Crammed with PCMs for Efficient Thermal Energy Storage and Conversion. *International Research Journal of Engineering and Technology*, **4**(12), pp. 396-402.
- [17] Su R., Zhang X., 2018. Size Effect of Thermal Conductivity in Monolayer Graphene. *Applied Thermal Engineering*, **144**, pp. 488-494.
- [18] Cao A., 2012. Molecular Dynamics Simulation Study on Heat Transport in Monolayer Graphene Sheet with Various Geometries. *Journal of Applied Physics*, **111**(8), p. 083528.
- [19] Erturk A. S., Kirca M., Kirkayak L., 2018. Mechanical Enhancement of an Aluminum Layer by Graphene Coating. *Journal of Materials Research* **33**(18), pp. 2741-2751.
- [20] Nosé S., 1984. A Unified Formulation of the Constant Temperature Molecular Dynamics Methods. *The Journal of Chemical Physics*, **81**(1), pp. 511-519.
- [21] Kumar S., 2017. Graphene Engendered 2-D Structural Morphology of Aluminium Atoms: Molecular Dynamics Simulation Study. *Materials Chemistry and Physics*, **202**, pp. 329-339.
- [22] Wei Z., Ni Z., Bi K., Chen M., Chen Y., 2011. In-Plane Lattice Thermal Conductivities of Multilayer Graphene Films. *Carbon*, **49**(8), pp. 2653-2658.
- [23] Rajasekaran G., Kumar R., Parashar A., 2016. Tersoff Potential with Improved Accuracy for Simulating Graphene in Molecular Dynamics Environment. *Materials Research Express*, **3**(3), p. 035011.
- [24] Deyirmenjian V. B., Heine V., Payne M. C., Milman V., Lynden-Bell R. M., Finnis M. W., 1995. Ab Initio Atomistic Simulation of the Strength of Defective Aluminum and Tests of Empirical Force Models. *Physical Review B*, **52**(21), pp. 15191-15207.

- [25] Shibuta Y., Elliott J. A., 2011. Interaction between Two Graphene Sheets with a Turbostratic Orientational Relationship. *Chemical Physics Letters*, **512**, pp. 146-150.
- [26] Verlet L., 1967. Computer “Exyeriments” on Classical Fluids. I. Thermodynamical Properties of Lennard-Jones Molecules. *Physical Review*, **159**(2), pp. 183-195.
- [27] Anderson C. V. D. R., Tamma K. K., 2004. An Overview of Advances in Heat Conduction Models and Approaches for Prediction of Thermal Conductivity in Thin Dielectric Films. *International Journal of Numerical Methods for Heat and Fluid Flow*, **14**(1), pp. 12-65.
- [28] Jain A., McGaughey A. J. H., 2016. Thermal Transport by Phonons and Electrons in Aluminum, Silver, and Gold from First Principles. *Physical Review B*, **93**(8), p. 081206.
- [29] Chantrenne, Raynaud, Barrat, 2003. Study of Phonon Heat Transfer in Metallic Solids from Molecular Dynamics Simulations. *Microscale Thermophysical Engineering*, **7**(2), pp. 117-136.