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Molecular Dynamics Study of the Thermal Conductivity of Graphene Coated Copper

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Abstract **-** In this study, the thermal conductivity of various size of pure copper, pure graphene and, different number of layer graphene coated copper models are studied using non-equilibrium molecular dynamics (NEMD) simulations. Our findings show that the thermal conductivity of graphene coated copper is higher than the uncoated ones. Furthermore, results also indicate that single layer graphene (SLG) model has the highest thermal conductivity as compared to the other model. Even though multiple layer graphene (MLG) has lower thermal conductivity value compare to SLG, this study shows that the thermal conductivity of MLG coated copper has higher thermal conductivity than SLG coated one. The most important finding in this study suggests that the thermal conductivity of copper can be improved using high thermal conductivity materials like graphene.

Keywords**:** Thermal conductivity, Molecular dynamics, Copper, Graphene.

1. Introduction

The developments in technology and science enable shrinking the size of electronic devices to micro- and nano- sizes. As the sizes reduce, the heat dissipation problem has become a very important issue. Overheating that is the locally generated heat cannot be removed from the material or transferred fast enough to the corresponding heatsink is always a crucial problem for all area of thermal applications. Thus, many studies have been done in the literature to solve this problem since overheating affects material structures and mechanical and physical properties badly. In the field of nano-electronics and among the electronic components, one of the most widely used materials as a heat sink is copper [1]. Therefore, it is important to enhance thermal conductivity of copper for dissipating heat rapidly and protect the material from the high temperatures. At this point, using high thermal conductivity materials helps copper to dissipate the heat quickly [2], [3].

In 2004, new carbon-based material is discovered which extract layer by layer from graphite and that single layers are called graphene layers [4]. This discovery has dazzled researchers to study graphene widely. Graphene is one of the basic carbon-based materials including graphite, carbon nanotubes and fullerenes [2]. It is the lightest, strongest, transparent, flexible, and a conductive material which is known [2], [5]–[7]. Among all of these properties, this study interest improving the thermal conductivity of copper using graphene [2], [8]. Heat transport in graphene dominated by phonons and affected by the length of phonon mean free path (PMFP) that is about ~600nm near room temperature [9]. Thus, it gives graphene unique thermal properties. The thermal conductivity of graphene calculated according to the Boltzmann transport equation is about ~3000 W/m.K [10]. As a result of that graphene-coated copper and calculate thermal conductivity of graphene-coated materials become a hot topic. Thus, researchers have studied graphene synthesis on copper to show the applicability of the new material [9]–[12]. After the graphene synthesis is obtained as a single layer/multilayer or coated on copper, some works have done to calculate thermal conductivity experimentally [2], [13]–[21]. There have been some numerical studies done to investigate the thermal conductivity of the pure graphene and graphene-coated different materials. Molecular dynamics (MD) simulation is one of those numerical calculation methods. MD provides an atomistic level understanding of materials properties and it is widely used in chemical physics, materials science and molecular-scale modelling [6]. Basically, it is a simulation program, which computes the physical movements of atoms by using Newton's equation of motion to obtain

detailed information of behaviour of atoms and molecules with the calculating physical and chemical properties together [22].

Researchers have found that the thermal conductivity of graphene increases with its length. This is called strong size dependence because of the graphene long PMFP and converge the thermal conductivity values near it [3,7,23–27]. Also, it is demonstrated that the thermal conductivity of graphene affected by the increment in the width direction [3,24,28]. This is because the reduction of edge localized phonon effect. In addition to the length effect, the boundary scattering effect will decrease as the width increases and it leads to enhancement the thermal conductivity. Furthermore, the phonon scattering increases with the system temperature and it reduces the thermal conductivity of graphene [24], [28].

In this study, a C++ code is initially generated to create the lattice models of pure graphene, pure copper, and graphene-coated copper. After obtaining these models, the non-equilibrium MD (NEMD) simulation code is generated to investigate the thermal conductivity of these materials. The effect of temperatures, lengths (x direction), width (y direction), and height (z direction) on the graphene, the copper, and the graphene-coated copper materials analyzed.

2. Model and Simulation Details

All the simulations are performed with the MD simulation code that is created in C++ language using MPI library in this study. In the molecular model, molecules consist of atoms and bonds between them. Figure 1 presents the simulation models with their sizes in three-dimensional coordinate systems. The rectangular box represents for copper and rectangular plane stand for graphene layers. The length of the models is increased in the x-direction from 3 nm to 12 nm with constant size in y- and z- directions that is 3 nm and 2 nm respectively to investigate the length effect on the thermal conductivity. In the same way, width is changed from 1.5 nm to 6 nm with constant size in x- and z-direction that is 10 nm and 3 nm respectively for width effect. After that, height is extended in the z-direction from 1 nm to 4 nm to search the effect on the thermal conductivity with constant size in x- and y-direction which is 6 nm and 3 nm respectively.

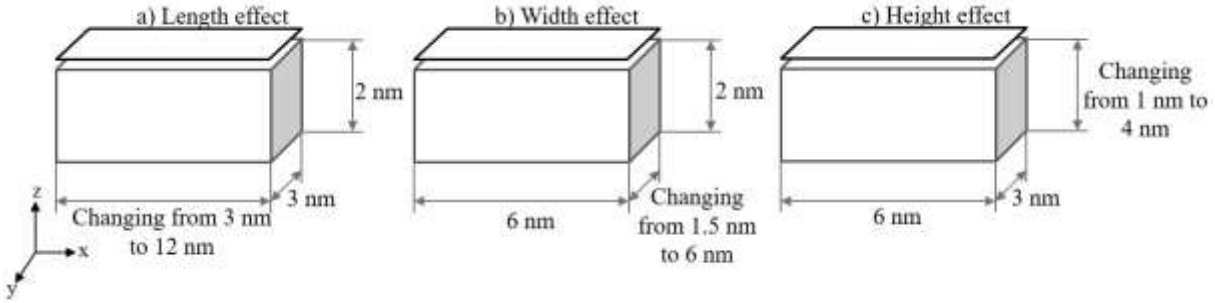

Fig. 1: A schematic presentation of the simulation model
a) Length, b) Width, c) Height.

Since the thermal conductivity of graphene along the zigzag direction takes a higher value than along the armchair direction in the literature, zigzag graphene structure (ZGNR) is selected [3,7]. The distance between the graphene layers takes 0.335 nm in multilayer graphene structures [26]. The face-centered cubic structure is chosen for copper lattice model (100) and the distance between copper atoms is 0.365 nm. Furthermore, the distance between the closest layer of graphene and the copper is set to 0.34 nm. The interatomic forces in graphene layer between carbon atoms is calculated with Tersoff Potential [29]. The metallic interactions between copper atoms, EAM Potential with Sutton-Chen parameters is selected [31]. For the weak Van der Waals interactions, Lennard-Jones (LJ) potential is applied to the non-bonding interactions among the graphene layers, and between graphene and copper [32]. Between the copper and the graphene layer interactions, Lennard-Jones parameters define as, σ=0.30825 nm, and ε=0.2578 eV and cutoff distance of r_c take as 2.5σ at truncated [1]. The velocity Verlet algorithm is used to calculate new positions and velocities of the atoms for the next iterations from t to $t + dt$ with time step of 0.05 femtosecond (fs).

Figure 2 shows the molecular model of the simulation model with its zones. The copper atoms with minimum and maximum -x position fixed in all directions, and free boundary conditions are applied to rest of the models. Next to the fixed atoms, error slabs are located to diminish the edge effects. The temperature profile is obtained using the thermostat

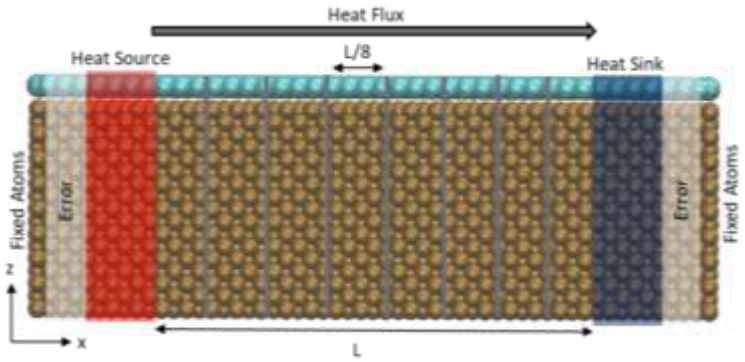

Fig. 2: Molecular model of graphene-coated copper.

to the following two error slabs as a heat source at 320 K and heat sink at 280 K. System temperature is controlled by the the Nosé-Hoover Thermostat [1].

Before the thermal conductivity calculation, the system temperature is equilibrated at 300 K and relaxes with NVT (canonical) ensemble which takes 0.05 ns. After the first part of the simulation, NEMD simulation performed in NVE (microcanonical) ensemble that runs up to final time step which is 1.5 ns. The simulation model divided into eight slabs to obtain a temperature profile excluding the error slabs and the thermostat slabs. The temperature of each slab calculated using equipartition theorem. After the system relaxed to the steady state, the imposed thermostat source and sink method is applied along the in-plane direction (x- direction) of the simulation model to calculate thermal conductivity [30]. In this method, the energy changes are calculated from kinetic energies in the thermostat parts before (old) and after (new) applying the thermostat with following the equations;

$$\Delta\varepsilon_{source} = \sum \frac{m}{2}\left(\sum_{Heat\ source} v_{new}^2 - \sum_{Heat\ source} v_{old}^2 \right) \tag{1}$$

$$\Delta\varepsilon_{sink} = \sum \frac{m}{2}\left(\sum_{Heat\ sink} v_{new}^2 - \sum_{Heat\ sink} v_{old}^2 \right) \tag{2}$$

From the calculated kinetic energy, the average energy changing is computed as following equation;

$$\Delta\varepsilon_{ave} = \frac{\Delta\varepsilon_{source} + \Delta\varepsilon_{sink}}{2} \tag{3}$$

From this equation, thermal conductivity is calculated based on Fourier Law as;

$$k = -\frac{\Delta\varepsilon_{ave}}{A\tau(dT/dx)} \tag{4}$$

In the above formula, k is the thermal conductivity of the system, $\Delta\varepsilon$ describes the change in average energy per unit time which is constant heat flux (J), τ describes the duration of time when the thermostats are active, dT/dx is the temperature gradient, and A defines the cross-sectional area of the simulation model to the heat flux direction. After the simulation time finalized, the linear regression method is used to obtain the temperature gradient dT/dx in the x-direction. All simulations were run for 1.5 nano-seconds.

All simulations are performed with MPI library in C++ to obtain less simulation time. MPI is a communication protocol for programming parallel computers which enables to solve algorithms by communicating between cores and it shares calculated results by sending and receiving.

3. Results

The thermal conductivity of pure SLG and MLG (2-layer and 4-layer graphene) plotted as a function of length from 6 nm to 48 nm at 300 K as shown in Figure 3. The results show that the thermal conductivity of the SLG is higher than the MLG. The thermal conductivity decreases with the number of graphene layers increase as it has been obtained in the literature [25]–[27]. The simulations of thermal conductivity 2-layer graphene and 4-layer graphene are still running. Figure 3 shows that the bonding strength between neighboring layers cause reduces the thermal conductivity. Moreover, the

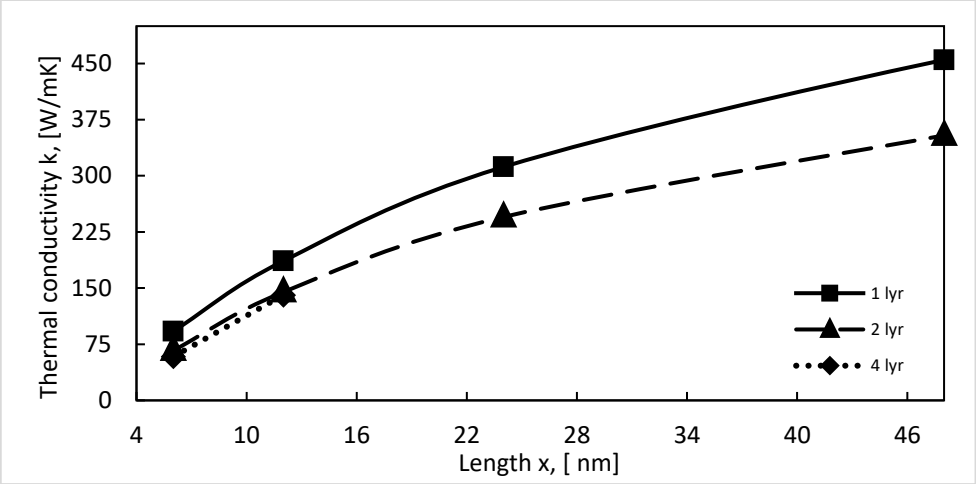

Fig. 3: Thermal conductivity of graphene for different number of layers (width: 3 nm, height: 2 nm).

neighboring layer creates an obstacle to phonon transport because it restricts the atom's movement. Thus, this demonstrates that the thermal conductivity of the SLG will be reduced when coated or bonded with other materials. As another outcome

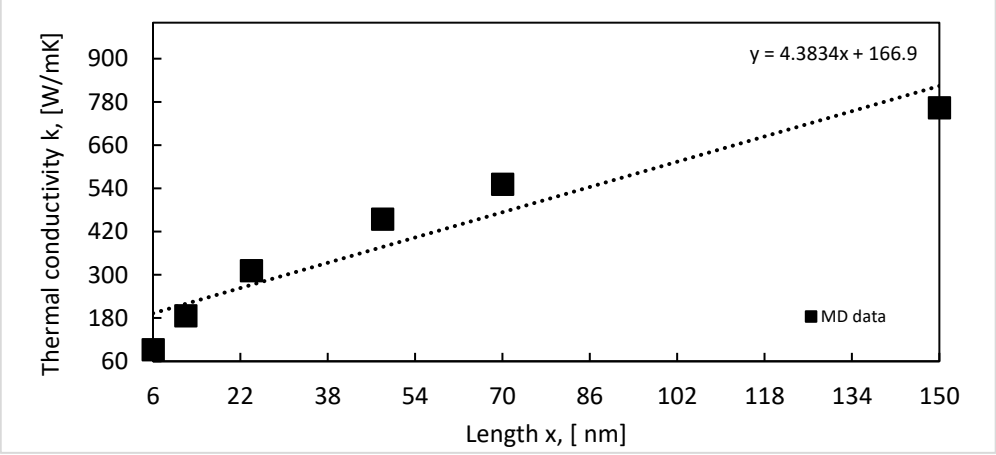

Fig. 4: The thermal conductivity of single layer graphene linear curve prediction according to the power law.

from these results is that the thermal conductivity changes with the length. The reason is that the heat conduction in graphene dominates by phonons and it is affected by the phonon mean free path (PMFP). When the thermal conductivity of graphene increases until the length reaches to the PMFP. This shows that graphene has a strong size dependence. According to the power law which is $k \sim L^{\beta}$ the thermal conductivity can be predicted unknown length under the PMFP. β calculated by the least-squares fit method as 0.43 as shown in Figure 4, in the literature it varies from 0.3 to 0.49 [3], [24].

In a similar way, the thermal conductivity of pure copper and graphene-coated copper systems investigated. Figure 5 shows the thermal conductivity changing by the length dependence with the same width (3 nm) and height (2 nm) in Cu, SLG-Cu, and MLG-Cu models.

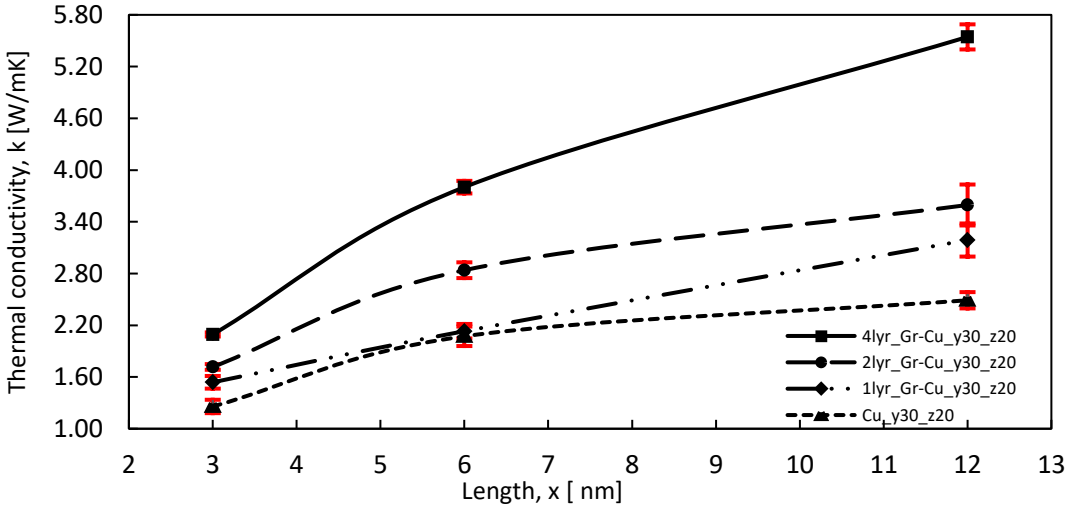

Fig. 5: Thermal conductivity of Cu, SLG-Cu, and MLG-Cu for varies lengths (width: 3 nm and height: 2 nm).

Our results indicate that when the pure copper coated with SLG is higher than the thermal conductivity of copper with average increase rate of 18%. Similarly, 2-layer and 4-layer graphene layers coated structures has higher thermal conductivity with 33% and 49% average increment rates. However, according to the results, copper's thermal conductivity is calculated up to 2.15 W/mK that is much smaller than the bulk copper's thermal conductivity which is 380 W/mK at 300K [31]. This

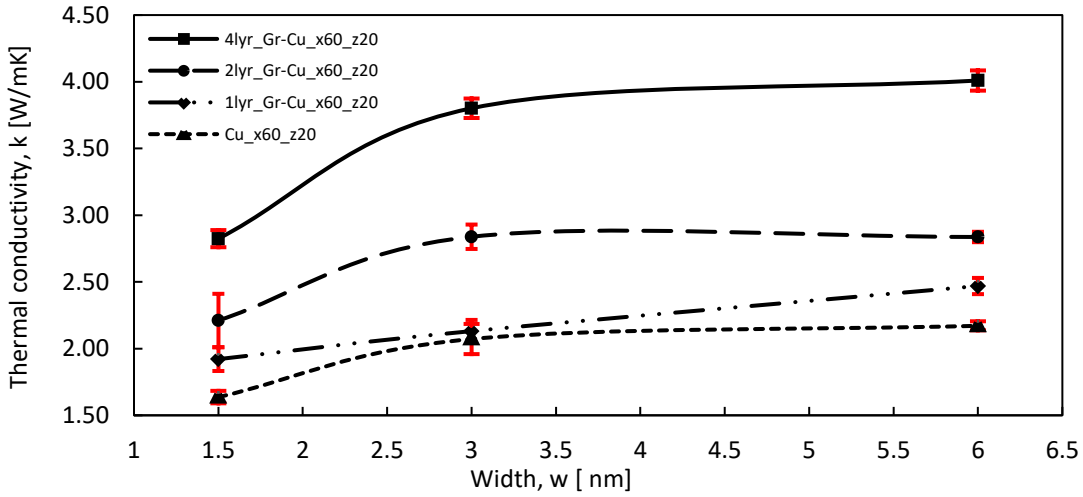

Fig. 6: Thermal conductivity of Cu, SLG-Cu, and MLG-Cu for varies widths (length: 6 nm and height: 2 nm).

is because, even though heat is carried out with phonons, and electrons in metals, MD simulations of metals underestimate the magnitude of the thermal conductivity due to lack of free electron contribution. Moreover, it is demonstrated that electron contribution on the total thermal conductivity of copper dominates about 95% whereas the phonon contribution is effected on the thermal conductivity about 5% at 200 K [28].

Fulong et al. [24] studied thermal conductivity of SLG coated Ni by using MD and they found that thermal conductivity increases with length in plane direction. Besides, Pradyumna et al. [20] experimentally demonstrated that the thermal conductivity of graphene coated copper increases compared to pure copper. They also studied the thermal conductivity of MLG-Cu. Their results give higher values than SLG-Cu so that, they interpreted this behavior as a grain size effect.

Figure 6 shows the width effect on thermal conductivity. It indicated that the thermal conductivity increases with the width. This is because, the boundary scattering effect gets weaker when the width increases so the edge localized phonon effect reduces by the width increases. Therefore, the thermal conductivity enhances. In addition, it can be said that when graphene coating on materials like copper, the interactions and phonon scattering between two materials will reduce the PMFP. It is predicted that the thermal conductivity of the graphene-coated system converges at a smaller value of PMFP according to graphene. The convergence of the thermal conductivity cannot be seen due to the simulation model size is too short. Our results show that when the width of the models changing, the thermal conductivity of copper coated with SLG, 2-layer graphene, and 4-layer graphene is higher than uncoated one with the average increment rate of 12%, 28%, and 44%, respectively. Therefore, it can be said that length dependence on the thermal conductivity in-plane direction is much more affected than the width because of the graphene long PMFP.

As it can be observed from Figure 7 that thermal conductivity of copper coated with SLG, 2-layer graphene, and 4-layer graphene is higher than the pure copper for various heights with the average rate of 6%, 21%, and 37%, respectively. It is noticeable that increasing the height does not affect the thermal conductivity that much compared to length and width.

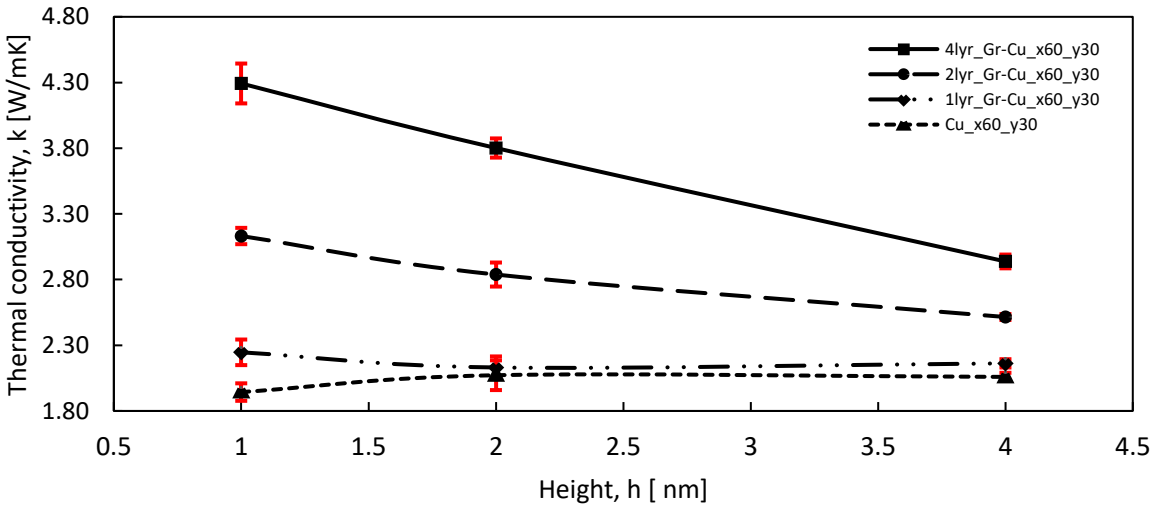

Fig. 7: Thermal conductivity of Cu, SLG-Cu, and MLG-Cu for varies heights (length: 6 nm and width: 3 nm).

4. Conclusions

The thermal conductivity of pure copper, graphene models (SLG and MLG) and graphene-coated copper models (SLG-Cu, MLG-Cu) investigated using our MD code. The thermal conductivity of the simulation model is studied with different length, width, and height to see their effect. The results indicated that the thermal conductivity increases with length. This phenomenon can explain as following; length dependence is an important factor for the low-dimensional systems and long PMFP causes a strong length dependence. Further, when the width increases then the thermal conductivity also increases because of reducing the boundary scattering effect. In addition, increasing height doesn't affect the thermal conductivity as much as length and width. Still, the thermal conductivity increases when the height increases. Another outcome is that phonon contribution effect on the thermal conductivity decreases when the temperature increases. Temperature increasing causes a problem with the movement of atoms which leads phonon scattering. Thus, thermal conductivity is reduced. Our findings support that the thermal conductivity of graphene coated model is higher than the uncoated ones. Furthermore, results also indicate that single layer graphene (SLG) model has the highest thermal conductivity as compared to the other model. However, when graphene is bonding or coated with materials, the strength between neighboring layers causes reduces the thermal conductivity. Consequently, this study suggests that the thermal conductivity of copper can be improved using high thermal conductivity materials like graphene.

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