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The behavior of the thermal conductivity near the melting temperature of copper nanoparticle

Hamid Loulijat *, Hicham Zerradi, Soufiya Mizani, El mehdi Achhal, Aouatif Dezairi, Said Ouaskit

Laboratory of Condensed Matter, Faculty of Sciences Ben M'sick (URAC.10), University Hassan II Casablanca, Morocco

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ABSTRACT

In this work, molecular dynamics simulations have been applied to calculate the thermal conductivity and the melting temperature of copper nanoparticle and its bulk, through Green–Kubo framework. Then the melting temperature was predicted by analyzing the temperature dependence of the total energy and the heat capacities, for different particles size range $47 \le N \le 2319$ and for various temperatures range $90 \le T \le 1500$ K, using Embedded Atom Method to simulate the interactions between Copper atoms. The global behavior shows that the melting temperature of Cu nanoparticles increases when their sizes increase. Moreover, the trend observed in the melting point with respect to particle size agrees with the analytical models. Likewise the melting temperature of bulk is in a good agreement with the experimental and simulations values. In overall terms, the thermal conductivity had a peak near the melting temperature, and increase with the increasing size of nanoparticle.

1. Introduction

Owing to its fundamental and pragmatic significance, during the last decades, considerable research efforts have been devoted to the study of nanoparticles, which are particles with size in the range of 1 to 100 nm, at least in one of the three possible dimensions. In this size range, the physical, chemical and biological properties of the nanoparticle change in fundamental ways from the properties of both individual atoms/molecules and its corresponding bulk material. Nanoparticles can be produced from materials of several chemical nature, starting from the most common metals (Cu, Ag, Au), until the most complicated one (Carbon nanotube, Multi-wall Carbon nanotube) [1,2]. Obviously, Copper nanoparticles manufactured in ambient atmospheric temperature and pressure inevitably have surface oxide layers because the Cu oxide phases are thermodynamically more stable than pure Cu. Furthermore, copper nanoparticles are found to aggregate severely without proper protection. The problems of aggregation and oxidation can be circumvented by sonication or the use of various protecting agents, such as polymers and organic ligands [3–7]. Presently, synthesis methods were developed for copper nanoparticles using chemical reduction [4–7], thermal decomposition [8], polyol [9], laser ablation [10], electron beam irradiation [11,12]. Interest in copper nanoparticles arises from the useful properties of this metal such as the good thermal and electrical conductivity at a low cost. These features lead to potential application in many industrial sectors, particularly nanofluids which are used in cooling fluids for electronic systems, heating, cooling exchanger including transportation and energy production. Therefore, nanofluids containing suspended nanoparticle of copper showed large enhancement of thermal conductivity relative to those of pure fluids such as (Cu–Ar) nanofluid [13,14]. Extensive literature has been conducted in the past decade to investigate and predict various proprieties, heat transfer performance and the effective thermal conductivity of nanofluid consisting of several nanoparticles [15–21]. Some studies have used the lattice Boltzmann method (LBM) for investigating different characteristics of nanofluide these studies are listed [22–27]. The lattice Boltzmann method (LBM) is a powerful numerical technique, based on kinetic theory, for simulating fluid flows and modeling the physics of fluids.

In the numerical side a very wide number of techniques have been established to calculate the thermal conductivity of nanoparticles and one of the most important is molecular dynamics simulations using Green–Kubo framework; such as the determination of carbon nanotubes and graphene sheets thermal conductivity, and their dependence on temperature [28–30].

The melting temperature is an enigmatic point that is still under intensive investigation, and it's one of the most important phase transitions in materials science and engineering, hence predicting melting temperature for bulk material is a very hard task and obviously nontrivial for the case of nanoparticles [31]. Therefore, the standard computational method is dependent on analyzing the different properties of the solid phase (such as total energy, heat capacity and radial distribution function…etc.). Voluminous body of numerical investigations

* Corresponding author.
E-mail address: hloulijat@gmail.com (H. Loulijat).

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Nomenclature

E_i	Excess energy of atom i [J]
E_{tot}	The total energy [J]
F	The embedding energy [J]
C_V	Heat capacity[$J.K^{-1}$]
$\vec{J}$	The macroscopic heat current vector [$J.m.s^{-1}$]
$\vec{j}$	The microscopic heat current vector [$J.m.s^{-1}$]
$\vec{j}(0)$	The microscopic heat current vector at time zero [$J.m.s^{-1}$]
$\vec{j}(n)$	The microscopic heat current vector at MD time step n [$J.m.s^{-1}$]
$\vec{j}(t)$	The microscopic heat current vector at time t [$J.m.s^{-1}$]
$\vec{j}_C(t)$	The microscopic heat current vector carried by the collision energy [$J.m.s^{-1}$]
$\vec{j}^K(t)$	The microscopic heat current vector carried by the kinetic energy[$J.m.s^{-1}$]
$\vec{j}^P(t)$	The microscopic heat current vector carried by the potential energy [$J.m.s^{-1}$]
k	Thermal conductivity [$W.K^{-1}.m^{-1}$]
k_B	Boltzmann constant $k_B = 1.8.6173 \times 10^{-5}$ [$J.K^{-1}$]
L	The latent heat of fusion [$J.kg^{-1}$]
L_{el}	The mean free path of the electron[m]
m	Number of time steps or mass
M	Total number of MD time steps for averaging [−]
n	Number of time steps [−]
N	Total number of MD simulation time steps or number of atoms
r	The radius of the nanoparticle [m]
r_i	Position of atom i [m]
r_{ij}	Distance between atoms i and j [m]
T	Temperature [K]
u	Pair potential [J]
V	Volume [m^3]
v_{el}	Velocity of the electron [$m.s^{-1}$]
v_i	Velocity of atoms i[$m.s^{-1}$]

Greek symbols

γ	The surface tension [$N.m^{-1}$]
ρ	Density
τ	The relaxation time [s]
Δt	Time step[s]
$\overline{\rho}_i$	Local electron density at site i

Subscrips

B	Bulk
C	Collision
el	Electron
K	kinetic
l	Liquid
m	Melting temperature
N	Nanoparticle
P	Potential
s	Solid
tot	Total

was using classical molecular dynamics to calculate the exact melting temperature of materials in bulk form [31–33]. In this work, the MD simulation is used to calculate the melting temperature of copper bulk and copper nanoparticles, also its dependence on the size of nanoparticles. Then, through Green–Kubo method the thermal conductivity of copper nanoparticle and its bulk are examined as a function of temperature.

2. Theoretical model

2.1. Inter-atomic potentials

A number of computational disciplines were using embedded-atom method such as chemistry and computational physics. Rigorously speaking EAM is an approximation describing the energy between atoms as an interatomic potential widely used in molecular dynamics simulations, where the energy is a function of a sum of functions of the separation between an atom and its neighbors. In the present (EAM) version of Daw, Baskes, and Foiles is used to compute pairwise interactions of copper atoms [34–37]. According to many previous studies in the field [38–41] they claimed that such type of potential is applicable in the case of bulk as well as the case of smaller cluster, this suggestion is strengthened by a comparison with experimental study and first principal calculations [38]. Generally speaking this potential represent the most common model of atomic bonding in metallic systems, therefore the total energy of an elemental system is represented as [36,39].

$$E_{tot} = \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}} u(r_{ij}) + \sum_i F(\overline{\rho}_i) \tag{1}$$

Here u (r_{ij}) is a pair potential as a function of distance r_{ij} between atoms i and j, and F is the embedding energy as a function of the host electron density $\overline{\rho}_i$ induced at site i by all other atoms in the system.

$$\overline{\rho}_i = \sum_{j\neq i} \rho(r_{ij}) \tag{2}$$

Where ρ(r_{ij}) is the electron density functions.

2.2. The microscopic heat current and thermal conductivity

Several mechanisms have been used to calculate the thermal conductivity in the complex material. One of the most fascinating methods is the molecular dynamics (MD) simulation since it has been successfully employed in the past to predict solids, fluids and nanofluids thermal conductivity via Green–Kubo framework [28–30,42–44]. The thermal conductivity is defined as a linear coefficient relating the macroscopic heat current vector $\vec{J}$ to the temperature gradient (Fourier's law).

$$\vec{J} = -k.\overrightarrow{\mathrm{grad}}(T) \tag{3}$$

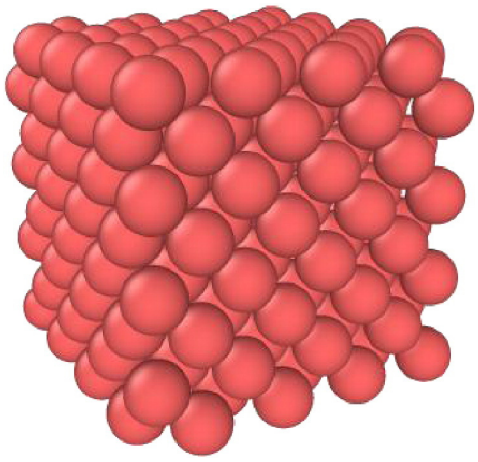

Fig. 1. Structure of Cu bulk (Periodic Boundary Condition) at 300 K is observed for Embedded Atomic Method (EAM) inter-atoms.