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MD simulation-based study on the melting and thermal expansion behaviors of nanoparticles under heat load

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ABSTRACT

Molecular dynamics simulations have been performed to determine the melting point and thermal expansion coefficient of nanoparticles under a constant heat intake rate. The melting points of Cu and Al nanoparticles are estimated to be much less compared to those of the bulk materials and are found to decrease with decrease in particle size. The coefficient of thermal expansion of Cu nanoparticles evaluated on the basis of present simulations is found to be more than that of the bulk Cu and it increases with decrease in particle size or increase in temperature. The estimated results have been compared with the data available in literatures for bulk materials and have indicated the dominant role of surface in influencing both the melting point and thermal expansion coefficient of nanoparticles.

1. Introduction

The nanosized metallic particles can be potentially used in many applications due to their promising physical, chemical and mechanical properties. The effect of surfaces and interfaces is greatly dominating in nanomaterials and enhances different properties. In a conventional bulk material the specific surface (or interface) area is so small that it has only a small effect on the overall properties of the material. However, in nanomaterials the specific surface (or interface) area is several orders of magnitude greater than that of the bulk materials. This unique feature gives rise to many unusual properties of nanomaterials compared to bulk materials. Over the past decade a considerable experimental and theoretical effort has been devoted to study the size dependent physical properties of nanoparticles. It has been established by experiments [1–5] as well as theoretical models [6–15] that the melting temperature of nanoparticles depends on the particle size and is different from that of the corresponding bulk materials.

Eckert et al. [4] observed considerable reduction in the melting point with decreasing grain size of nanocrystalline aluminum powder. The study was performed with 13–40 nm sized particles using differential scanning calorimeter (DSC). The melting point was found to increase from 840 K for 13 nm sized particles to its bulk value of 940 K for 40 nm sized particles.

In addition to experimental studies there are several theoretical works reported in literature on melting of nanoparticles. Alavi and Thompson [11] performed molecular dynamics (MD) simulations for clusters of aluminum atoms, up to a minimum size of 3 nm, using Streitz–Mintmire potential and canonical (NVT) ensembles. In their study special attention was given to the structure of the clusters and dynamic coexistence of the liquid and solid phases. They also observed an analogous melting behavior as exhibited by the experiments. Yeshcenko et al. [13] have studied the size dependent melting point of copper nanoparticles embedded into silica matrix and observed that the melting begins at a thin layer close to the surface. Thereafter, it propagates inwards until the entire particle completely melts. The surface melting generally occurs at temperatures much lower than the bulk melting point. They have reported that melting point of Cu-nanoparticles of diameter 35 nm is 450 K and it increases with increasing diameter of the particle. Wang et al. [14] have presented MD simulation-based study of the melting of copper nanoclusters with up to 8628 numbers of atoms, within the framework of embedded-atom method (EAM). Their findings have indicated that there exists an intermediate nanocrystal regime above 456 atoms. The linear relation between the cluster size and its thermodynamics properties is obeyed in this regime. Melting first occurs at the surface of the clusters and there is a drop in the melting point from the bulk value of 1360–990 K for Cu-nanoclusters containing 456 numbers of atoms. MD simulations have been performed by Puri and Yang [12] using isobaric-isoenthalpic (NPH) ensembles to predict the

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melting of nanosized aluminum particles in the range of 2–9 nm diameter. Five different potential functions, e.g., Lennard–Jones (LJ), glue, embedded atom, Streitz–Mintmire, and Sutton–Chen potentials have been implemented in their study to find the melting point of Al-nanoparticles. Their simulations with LJ potential have revealed that the melting temperature of a Al-nanoparticle increases monotonically with increasing size, from 473 K for 2 nm sized particle to the bulk value of 937 K for approximately 8 nm sized particle.

The present work reports a theoretical study on the melting point of Cu- and Al-nanoparticles using MD simulations. The size dependent melting behavior of spherical nanoparticles under non-isothermal heating conditions has been studied here using a molecular dynamics-based approach different from that adopted in the reported literatures. Moreover, size and temperature dependent thermal expansion of cubical nanoparticles has also been investigated and evaluated prior to melting. The present work focuses on the behavior of nanoparticles under specific heat flow rate using MD simulations and based on this study useful physical properties have been evaluated and compared with those of the bulk materials. This study may provide an useful guideline for assessing the suitability of nanoparticles under certain thermal loads.

2. Simulation details

2.1. Thermal equilibration

First of all, Cu-nanoparticles of diameter ranging from 3 nm to 6 nm and an Al-nanoparticle of diameter 3 nm have been generated using self developed FORTRAN code based on a crystal structure generation algorithm. Fig. 1 shows the initially generated Cu-nanoparticle of size 3 nm. The atoms have been placed at the lattice points within the specified domain.

In order to equilibrate the nanoparticles at 298 K (room temperature) an initial velocity have been assigned to the atoms in the nanoparticle from the Maxwell–Boltzmann energy distribution [16], defined by:

$$f(E) = \frac{n(E)\mathrm{d}E}{N} = \frac{2}{\sqrt{\pi}} \frac{1}{(k_B T)^{3/2}} E^{1/2} e^{-E/k_B T} \mathrm{d}E \tag{1}$$

where, $f(E)$ is fraction of total number of atoms (N) having kinetic energy between E and $E + \mathrm{d}E$, k_B is the Boltzmann constant, and T is the absolute temperature. Fig. 2 shows the graphical representation of the initially assigned kinetic energy distribution of the atoms of a Cu-nanoparticle of 3 nm size. Using the constraint of the applied distribution function, the selection of the atom having a particular kinetic energy has been performed randomly with the help of a random number generator. Moreover, the velocity components of all the atoms in the nanoparticle have also been determined using the random number generator.

After the initial assignment of velocities to the atoms corresponding to a predetermined temperature of the nanoparticle, MD simulation for equilibration has been carried out to evaluate the phase space of the atoms with progressing time steps of 1 fs. The MD runs for thermal equilibration has been carried out using Lennard–Jones interatomic potential [17], as represented by Fig. 3. The Lennard–Jones pair potential in its truncated form as given in Eq. (2) below has been used in the present MD algorithm:

$$U(d_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{d_{ij}}\right)^{12} - \left(\frac{\sigma}{d_{ij}}\right)^{6} + \left\{2\left(\frac{\sigma}{r_c}\right)^{18} - \left(\frac{\sigma}{r_c}\right)^{12}\right\} \times \left(\frac{d_{ij}}{\sigma}\right)^{6} - 3\left(\frac{\sigma}{r_c}\right)^{12} + 2\left(\frac{\sigma}{r_c}\right)^{6}\right] \tag{2}$$

where, ε is the depth of the potential well, σ is the (finite) distance at which the interatomic potential is zero and r_c is the cut off radius. The force on any atom 'i' of the nanoparticle due to all its neighbor atoms has been calculated from the interatomic potential that controls the interactions between every pair of atoms of the object. If $U(d_{ij})$ is the interaction potential between two atoms 'i' and 'j' then force on atom 'i' due to its neighbor atom 'j' can be expressed as:

$$\vec{F}_{ij} = \frac{(\vec{r}_i - \vec{r}_j)}{|\vec{r}_i - \vec{r}_j|}\left(-\frac{\partial U(d_{ij})}{\partial d_{ij}}\right) \tag{3}$$

where, $\vec{r}_i$ and $\vec{r}_j$ are position vectors of atom 'i' and atom 'j', respectively. d_{ij} is the distance between the two atoms and it can be given as:

$$d_{ij} = \left|\vec{r}_j - \vec{r}_i\right| \tag{4}$$

To speed up the evaluation of forces on each atom and thus to minimize the computation time a specific cut off radius has been considered. When atom 'j' is beyond the cut off radius from atom 'i', the force on atom 'i' due to atom 'j' is not taken into account. In the present simulation for both Cu and Al nanoparticles the cut-off radius has been considered to be 10 Å beyond which the interatomic forces have been neglected as they become infinitesimally small. This value of the cut off radius has been decided based

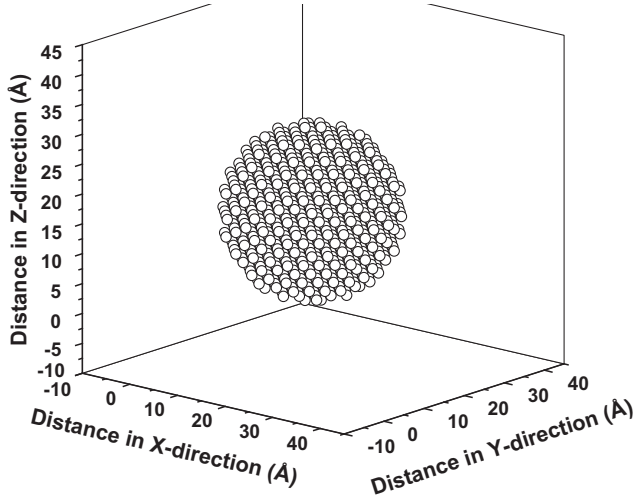

Fig. 1. Configuration of an initially generated Cu-nanoparticle of 3 nm diameter.

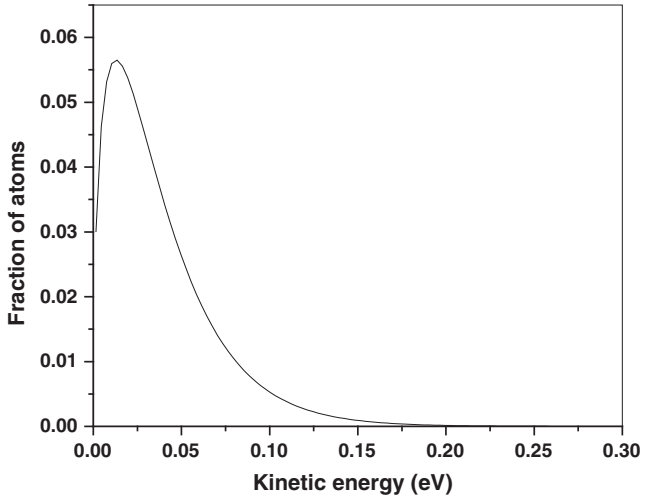

Fig. 2. Distribution of initially assigned kinetic energy of atoms of a 3 nm sized Cu-nanoparticle to be equilibrated at 298 K.