Molecular Dynamics Simulation Studies on Melting of Silver Nano-Clusters

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ABSTRACT: Metal nano-clusters (NCs) exhibit unique and interesting thermodynamic behaviour as compared to single molecule as well as bulk materials. Classical Molecular Dynamics (MD) simulations with Modified Embedded Atom Method (MEAM) model has been carried out in order to study the melting phenomena of Silver (Ag) NCs. Two NCs consisting of 108 and 1372 Ag atoms are chosen. The melting point temperature of these NCs has been estimated from various analyses techniques, such as: variation of potential energy per atom, mean square displacement of atoms, self-diffusion coefficients of atoms with temperature. The jump in the data corresponds to phase transition marking the starting of melting phenomena. From all these analyses, the melting point temperature of 108 atoms NC is found to be 380K and that of 1372 atoms NC is 730K, where the phase transition is marked. It is concluded that the melting point temperature of NCs are much smaller than the bulk (~1200K) and also the melting point of NCs are size dependent. The smaller the size, smaller is the melting point temperature.

KEYWORDS: Nano-cluster, MD simulations, melting phenomena, size dependency.

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1. INTRODUCTION

nano-particle Currently systems attract considerable interest from both academia and industry because of their interesting and diverse properties, which deviate from those of the bulk. Owing to the change of the properties, the fabrication of nano structural materials and devices with unique properties in atomic scale has become an emerging inter disciplinary field involving solid-state physics, chemistry, biology and materials science [1]. For example silver nano-particles can be applied in various widespread bases such as optical sensors, biosensor materials [2], cryogenic superconducting materials [3], and antibacterial applications [4]. The deviation of the corresponding conventional bulk thermodynamic behaviour is probably the lowering of the melting point of small particles of metallic species. The first experimental investigation of melting temperature dependence on particle size was conducted more than 50 years ago [5]. The term nano-clusters simply refer to large clusters whose dimensions are most conveniently measured in nanometres. In the last two decades many microscopic, thermodynamic analysis has been carried out on the physical properties of nanoparticles. Among the properties, melting is one of the best characterized processes of nano-particles. In nano-particles surface and core atoms are not distinct and solid-liquid phases are not in coexistence, but they are in dynamic equilibrium. In between the fusion temperature and the melting temperature, nano-particles fluctuate between solid and liquid state like equilibrium between two chemical isomers [6, 7]. As early as 1909, Pawlow [8] predicted the melting point of argon nano- particles

would reduce with size. A relation between the radius of nano-particles and melting temperature was first established. The results reveal that the melting temperature of the nano-particles is much lower as compared to bulk materials. This physical phenomenon is originated because the ratio of number of surface to volume atoms is enormous and liquid/vapour interface energy is generally lower than average solid/vapour interface energy. Hence, as the particle size decreases, its surface to volume atom ratio increases and melting temperature decreases due to improved free energy at particle [8,9].Melting behaviour surfaces and thermodynamics properties of free silver nanoclusters have been investigated and found that the melting point of nano-clusters decreases with decreasing cluster size [10-13].

Based on nonmaterial, nanotechnology has stimulated unprecedented innovation and breakthrough in science and technology, including brand-new concepts emerged from micro level of molecules or atoms within 1-100 nm and new functions due to micro formations. As the initial form of condensed matter, nano-particles consisted of several to hundreds or even thousands of atoms are essential in the development from atoms or molecules to bulk materials. The physical and chemical properties of this non-dimensional material are different from single atom as well as bulk material. Later Takagi [5] first observed small size effect of thin films of Pb, Sn, and Bi in experiments. So since a long time there is a fundamental interest in knowing the melting process of metal crystals among experimentalists. theoreticians and Different thermodynamic models assumed the nano-particles

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as spherical particles with homogeneous surfaces and yield the conclusion that the melting point decreases linearly with decrease in cluster diameter r[14,15]. Some breath taking studies have been done on the melting and crystallization behavior of iron (Fe) nano-particles by Sibutta and Suzukii [16].They showed crystal growth in liquid Fe and influence of the cooling rate all through solidification [17].

A linear relationship was observed between the thermodynamic property and particle's size in nanoparticles. Ding et al [18] observed amalgamation and melting of Fe nano-clusters, which consisted of 10,000 atoms. Wu et al. have examined melting of FCC Fe nano-particles [19] and observed that a quite high proportion of surface atoms were advantageous to the phase transition of the FCCFe nano-particles. C. Cao and group have worked on Ag NCs having diameters in the range of 2.4-5 nms using MD simulations [20]. Various researchers have analysed the thermal behaviour of the Ag NCs by using experimental techniques like, Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). These works demonstrated that clusters of sintered nano-particles exhibit a high melting point than a single one but still it is much lesser than the corresponding bulk materials.

Molecular dynamics simulations offer an effective tool to study the melting and coalescence of nanoparticles [21,22]. These atomistic simulations require accurate atomic interaction potentials to compute the total energy of the system. In the present work, the melting point temperatures of two Ag nanoclusters consisting of 108 atoms and 1372 atoms have been estimated through MD simulations by using MEAM potentials.

2. Simulation Details

The simulations are initiated by creating FCC silver crystals consisting of 108 atoms and 1372 atoms from a unit cell by replicating it along X, Y and Z

directions appropriately. The dimensions of the cubic crystals are 12.24Åand 28.56Å respectively along all three directions. After equilibrating the crystal, the nano-cluster has been achieved by removing the periodic boundary conditions (PBC) in all three dimensions. The NCs have been studied in canonical ensemble (constant NVT) at various temperatures in the range of 300K-1000K for the equilibration and then micro-canonical ensemble (constant NVE) runs are performed to obtain their melting points. MEAM potential parameters are used for the interaction among Ag atoms [23]. The MD simulations are performed by using LAMMPS program [24].The equations of motion are integrated using the velocity Verlet algorithm with a time step of 1fs [25]. The systems has been equilibrated for 1ns and production runs were for about 1ns.The functional form of the MEAM potential energy is given by

 $V(r_i) = \sum_{i=1}^{N} F(\rho_i) + \sum_{i \neq j} S_{ij} \varphi_{ij} \left(\left| r_i - r_j \right| \right) \quad (1)$ Where F_i is embedding energy function, ρ_i is electron density at the position of atom i, φ_{ij} is a pair potential and S_{ij} is the screening function.

3. RESULTS AND DISCUSSION

Figure 1depicts the snapshots of the Ag clusters at their respective melting point temperatures. Figure 1(a) is the snapshot of Ag nano-cluster consisting of 108 atoms at its melting temperature i.e at 380K and Figure 1(b) is the snapshot of the NC consisting of 1372 atoms at its melting temperature i.e at 730K. Figure 1(a) and (b) are showing the melted clusters which are almost spherical.

The most commonly used way to obtain the melting point temperature of metal clusters is by monitoring the variation potential energy versus temperature for the NCs under observation, which is shown in Figure 2.



FIG. 1. Snapshots of Ag Nano-clusters at their respective melting point temperatures (a) 108 atoms and (b) 1372 atoms.



(b) FIG.2. Potential energy per atom versus temperature (a) 108 atoms cluster (b) 1372 atoms cluster



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FIG.3MSD versus temperature (a) 108 atoms cluster (b) 1372 atoms cluster

Figure 2(a) and 2(b) show the variation of potential energy per atom versus temperature for 108 atoms and 1372 atoms Ag NCs respectively. The decrease in potential energy per atom with increase in temperature is evident from the Figures, but sudden jumps could be observed at 370K and 720K for the NCs in Figure 2(a) and 2(b), respectively. This indicated the occurrence of phase change. Hence, the melting point temperature of the Ag NC with 108 atoms is estimated to be 380K and that of 1372 atoms is 730K from the study.

We deployed another method to countercheck the result found from the first observation. This method has been successfully implemented to find melting point temperature by observing the mean square displacements (MSD) of the atoms during diffusion. The equation of MSD is given by,

$$\left\langle \left| r_{i}(t) - r_{i}(0) \right|^{2} \right\rangle = \Delta r^{2}(t)$$
 (2)

Where $r_i(t)$ is the location of the atom i at time t and the angular brackets denote averages over several initial times. The temperature dependence of MSD is illustrated in figure 3.

Figure 3 shows the plot of variation of MSDs with temperature. From Figure 3(a),it can be observed from the plot that up to 370K, the variation in MSDs is negligible. Appreciable variation in MSD could be observed at 380K indicating the melting process. Hence, the melting temperature of Ag nano-cluster with 108 atoms is estimated to be 380 K. In Figure 3(b), a clear and sudden change in the plot is observed at 710K to 730K. Hence, the melting temperature of Ag nano-cluster with 1372 atoms is 730K.

4. CONCLUSION

MD simulation runs for one nanoseconds duration have been carried out to study the melting point phenomena and to determine the melting point temperature of two silver nano-clusters consisting of 108 atoms and 1372 atoms respectively. The melting point temperatures were estimated to be 380K and 730K for the two clusters respectively from various analyses, like: variation of potential energy per atom and mean square displacements with temperature. Hence, it is inferred that as cluster size increases, melting point temperature also increases. The melting point temperature of bulk has also been calculated (data not shown). The melting point temperatures of clusters are much smaller than that of the bulk. The size dependency characteristic of melting point temperatures for Ag NCs is under study by considering NCs of different sizes.

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REFERENCES

- [1]. Gleiter, H., 2000. Nanostructured materials: basic concepts and microstructure. Acta Material, 48, 1-29.
- [2]. Ren, X L., Tang, F Q., 2002. Enhancement effect of Ag –Au nanoparticles on glucose biosensor sensitivity. ActaChimicaSinica,60 393–397.
- [3]. Hirano, S., Wakasa, Y., Saka, A.,Yoshizawa, S., OyaSeimiya Y., Hishinuma, Y., Nishimura, A., Matsumoto, A., Kumakura, A., 2003. Preparation of Bi-2223 bulk composed with Silver-alloy wire. Physica C, 392, 458–462.
- [4]. Jiang, H., Manolache, S., Wong, A C L., Denes, F S., 2004. Plasma-enhanced deposition of silver nanoparticles onto polymer and metal surfaces for the generation of antimicrobial characteristics. Journal of Applied Polymer Science, 93, 1411–1422.
- [5]. Takagi, M., 1954. Electron –diffraction study of liquid- solid transition of thin metal films. Journal of Physical Society of Japan, 9,359.
- [6]. Kunz, R B., Berry, R S., 1994. Multiple phase coexistence in finite systems. Physical Review E49,1895.
- [7]. Calvo, F., 2001. Thermal stability of the solid like and liquid like phases of (C₆₀)_n clusters. Journal of Physical ChemistryB, 105, 2183.

- [8]. Pawlow, P Z., 1909. The dependency of the melting point on the surface energy of a solid body. Physical Chemistry, 65(5), 545–548.
- [9]. Luo, W., Hu, W., Xiao, S., 2008. Size effect on thermodynamic properties of silver nanoparticles. Journal of Physical Chemistry C,112, 2359.
- [10]. Nanda, K K., Sahu S N., Behera, S N., 2002. Liquid-drop model for the size dependent melting of low dimensional systems. Physical Review A, 66, 013208.
- [11]. Yang, C C., Li, S., 2007. Investigation of cohesive energy effects on size dependent physical & chemical properties of nanocrystals. Physical Review B, 75, 165413.
- [12]. Luo, W H., Hu W Y., Xiao, S F., 2008. Size effect on thermodynamic properties of silver nanoparticles. Journal of Physical Chemistry C, 112, 2359
- [13]. Feng, D., Feng, Y., Yuan, S., Zhang, X., Wang, G., 2107. Melting behaviour of Ag nanoparticles and their clusters. Applied Thermal Physics, 11, 1457-1463.
- [14]. Buffat, J.,Borel, P.,1976.Size effect on the melting temperature of gold particles. Journal of Physical Review A, 13,2287.
- [15]. Yalamanchali, A., Pyfer, K. L., Jarrold, M. F., 2017. Melting of size-selected Aluminium clusters with 150-342 atoms: The transition to Thermodynamic scaling. Journal of Physical Chemistry C, 121, 10242-10248.
- [16]. Shibuta, Y., Watanabe, Y., Suzuki,T., 2009. Growth and melting of nanoparticles in liquid

iron: a molecular dynamics study. Chemical Physics Letters, 475,4-6.

- [17]. Shibuta, Y., Suzuki, T., 2011. A molecular dynamics study of cooling rate during solidification of metal nanoparticles. Chemical Physics Letters, 502, 1–3.
- [18]. Ding, F., A Rosen, A., Bolton,K., 2004. Size dependence of the coalescence and melting of iron clusters: A molecular dynamics study. Physical Review B, 70, 7.
- [19]. Shen, T., Meng, W., Wu, Y., Lu, X., 2013. Size dependence and phase transition during melting of FCC-Fe nanoparticles. Applied Surface Science, 277, 7-14.
- [20]. Feng, D., Feng, Y., Yuan, S., Zhang, X, Wang, G., 2017. Melting behaviour of Ag nanoparticles and their clusters. Applied Thermal Engineering, 111, 1457 -1463.
- [21]. Molecular dynamics investigation of Structural evolution of fcc Fe nanoparticles under heating process. Wu, L., Zhang, Y., Wen, Y H., Zhu, Z Z and Sun, S G., 2011. Chemical Physics Letters, 502 4–6.
- [22]. Kim, S G., Tomane, K D., 1994. Melting of Fullerenes: A molecular Dynamics Study. Physical Review Letters. 7,2418.
- [23]. Baskes M I., 1992. Modified embedded-atom potentials for cubic materials and impurities. Physical Review B 46, 2727.
- [24]. Plimpton, S J., 1995 Journal of Computational Physics, 11, 71.
- [25]. Frenkel, D., Smit, B., 1996. Understanding Molecular Simulations, Academic Press, San Diego, 139-160.

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