Theoretical Investigation of Nano Fluid Heat Transfer Enhancement Considering the Effects of Melting Point Depression

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ABSTRACT Melting point depression is the phenomenon of reduction of the melting point of materials with reduction of its size. This phenomenon is very prominent in Nano scale materials, which melt at temperatures hundreds of degrees lower than bulk materials. Melting point depression is most evident in nanowire, nanotube and Nano particles, which all melt lower temperature than the bulk amount as same materials. Changes in melting point occur because Nano scale materials have a much large surface to volume ratio than bulk materials, drastically altering thermodynamics and thermal properties.

Introduction
The melting temperature of a bulk material is not dependent on its size. However as the dimensions of a material decrease towards the atomic scale, the melting temperature scales with material dimension. The decrease melting temperature can be on the order of tens to hundreds of degrees for metal with Nano meter dimension.

In this paper focuses on nanoparticle because researchers have compiled a large amount size-dependant melting date for near spherical nanoparticle. Nanoparticle are easiest to study due their ease of fabrication and simplified condition for theoretical modelling. The melting temperature of Nano particle decreases sharply as the particle reaches critical diameter, usually less than 50 nm for common engineering metals. Figure 1 shows the shape of typical melting curve for a metal nanoparticle as a metal nanoparticle as a function of its diameter.

Fig 1: Experimental melting curve for near spherical metal nanoparticle exhibits a similarly shaped curve

Measuring technology
Two technologies allow measurement of the melting point of nanoparticle. As described above the electron beam of the transmission electron microscope (TEM) cab be used to melt nanoparticles. The melting temperature is estimated from the beam intensity, while changes in the diffraction conditions to indicate phase transition from solid to liquid. This method allows direct viewing of nanoparticles as they melt, making it possible to test and characterize samples with a wider distribution of particle sizes. The TEM limits the pressure range at which melting point depression can be tested.

More recently, researchers developed Nano calorimeters that directly measure the enthalpy and melting temperature of nanoparticles. Nano calorimeters provide the same data as bulk calorimeters, however additional calculations must account for the presence of the substrate supporting the particles. A narrow size distribution of nanoparticles is required since the procedure does not allow users to view the sample during the melting process. There is no way to characterize the exact size of melted particles during experiment.

Physics
Nanoparticles have a much greater surface to volume ratio than bulk materials. The increased surface to volume ratio means surface atoms have a much greater effect on chemical and physical properties of a nanoparticle. Surface atoms bind in the solid phase with less cohesive energy because they have fewer neighbouring atoms in close proximity compared to atoms in the build of the solid. Each chemical bond an atom shares with a neighbouring atom provides cohesive energy, so atoms with fewer bonds and neighbouring atoms have lower cohesive energy. The average cohesive energy per atom of a nanoparticle has been theoretically calculated as a function of particle size according to Equation.1

\[ E = E_b (1 - (d/D)) \]  

Where: \( D = \) nanoparticle size  
\( d = \) atomic size  
\( E_b = \) cohesive energy of bulk.

As Equation 1 shows the effective cohesive energy of a nanoparticle approaches that of the bulk material as the material extends beyond atomic size range (\( D >> d \))
Atoms located at or near the surface of the nanoparticle have reduced cohesive energy due to a reduced number of cohesive bonds. An atom experiences an attractive force with nearly all nearby atoms according to the Lennar-Jones potential. The Lennard-Jones pair-potential shown in Figure 2 models the cohesive energy between atoms as a function of separation distance.

**Figure 2. A Lennard-Jones potential energy curve**

The model shows the interactive energy between 2 atoms at a normalized distance, \(d/d_0\), where \(d_0=\) Atomic diameter. The interaction energy is attractive where the curve is negative, and the magnitude of the energy represents the cohesive energy between a pair of atoms. Note that the attractive potential extends over a long range beyond the length of a chemical bond, so atoms experience cohesive energy with atoms further than their nearest neighbours.

The cohesive energy of an atom is directly related to the thermal energy required to free the atom from the solid. According to Lindeman’s criterion, the melting temperature of a material is proportional to its cohesive energy \(av(T_m=C_u)\). Since atoms near the surface have fewer bonds and reduced cohesive energy they require less energy to free from the solid phase. Melting point depression of high surface to volume ratio materials results from this effect. For the same reason, surfaces of bulk materials can melt at lower temperatures than the bulk materials.

The theoretical size-dependent melting point of a material can be calculated through classical thermodynamic analysis. The result is the Gibbs-Thomson equation shown in Equation 2.

\[
T_m(d) = T_{M_B}(1-\frac{4S_l}{H_f d})^{2/3}
\]

Equation 2 gives the condition at which an entire nanoparticle melts according to the LSN model. The liquid shell nucleation model (LSN) predicts that a surface layer of atoms melts prior to the bulk of the particle. The melting temperature of a nanoparticle is a function of its radius of curvature according to the LSN. Large nanoparticles melt at greater temperatures as a result of their larger radius of curvature.

The model calculates melting conditions as a function of two competing order parameters using Landau potentials. One order parameter represents a solid nanoparticle, while the other represents the liquid phase. Each of the order parameters is a function of particle radius.

The parabolic Landau potentials for the liquid and solid phases are calculated at a given temperature, with the lesser Landau potential assumed to be the equilibrium state at any point in the particle. In the temperature range of surface melting, the results show that the Landau curve of the ordered state is favoured near the centre of the particle while the Landau curve of the disordered state is smaller near the surface of the particle.

The specific melting process for nanoparticles is currently unknown. The scientific community currently accepts several mechanisms as possible models of nanoparticle melting. Each of the corresponding models effectively matches experimental data for melting of nanoparticles. Three of the four models detailed based on classical thermodynamics.

**Proposed mechanisms**

**Liquid drop model**

The liquid drop model (LDM) assumes that an entire nanoparticle transitions from solid to liquid at a single temperature. This feature distinguishes the model, as the other models predict melting of the nanoparticle surface prior to the greater temperature range than other models predict. The LDM assumes that the surface atoms of a nanoparticle dominate the properties of all atoms in the particle. The cohesive energy of the particle is identical for all atoms in the nanoparticle.

The LDM represents the binding energy of nanoparticles as function of the free energies of the volume and surface. Equation 4 gives the normalized, size dependent melting temperature of a material according the liquid-drop model.

\[
T_m(d) = (\frac{4T_{M_B}}{H_f d})^{2/3}
\]

**Liquid shell nucleation model**

The liquid shell nucleation model (LSN) predicts that a surface layer of atoms melts prior to the bulk of the particle. The exact thickness of the liquid layer at a given temperature is the equilibrium point between the competing Landau potentials.

Equation 5 gives the condition at which an entire nanoparticle melts according to the LSN model.
The liquid nucleation and growth model (LNG) treats nanoparticle melting as a surface initiated process. The surface melts initially and the liquid-solid interface quickly advances through the entire nanoparticle. The LNG defines melting conditions through the Gibb-Duhem relations, yielding a melting temperature function dependent on the interfacial energies between the solid and liquid phases, volumes and surface areas of each phase, and size of the nanoparticle. The model calculations show that the liquid phase forms at lower temperatures for smaller nanoparticles. Once the liquid phase forms, the free energy conditions quickly change and favour melting. Equation 6 gives the melting conditions for a spherical nanoparticle according to the LNG model.

\[ T_M(d) = \left( \frac{4T_M}{H_f d} \right)^{1/2} \]

where: liquid vapour interface energy, \( H_f \) = Bulk heat of diffusion, Density of solid, Density of liquid, \( d \) = Particle diameter

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**Bond-order-length-strength (BOLS) model**

The bond-order-length-strength (BOLS) model employs an atomistic approach to explain melting point depression. The model focuses on the cohesive energy of individual atoms rather than a classical thermodynamic approach. The BOLS model calculates the melting temperature for individual atoms from the sum of their cohesive bonds. As a result, the BOLS predicts the surface layers of a nanoparticle melt at lower temperatures than the bulk of the nanoparticle.

The BOLS mechanisms state that if one bond breaks the remaining neighbouring ones become shorter and stronger. The cohesive energy or the sum of bond energy of the less coordinated atoms determines the thermal stability including melting, evaporating and other phase transition. The lowered CN changes the equilibrium bond length between atoms near the surface of the nanoparticle. The bonds relax towards equilibrium lengths, increasing the cohesive energy per bond between atoms, independent of the exact form of the specific interatomic potential. However, the integrated cohesive energy for surface atoms is much lower than bulk atoms due to the reduced coordination number and overall decrease in cohesive energy.

Using a core-shell structure have been applied to other size dependency of nanostructures such as the mechanical strength, chemical and thermal stability, lattice dynamics (optical and acoustic phonons), Photon emission and absorption electronic coeval shift and work function modulation, magnetism at various temperatures, and dielectrics due to electron polarization etc. Reproduction of experimental observations in the information such as the energy level of an isolated atom and the vibration frequency of individual dimer have been obtained by matching the BOLS predictions to the measured size dependency.

**Particle shape**

Nanoparticle shape impacts the melting point of a nanoparticle. Facets, edges and deviations from a perfect sphere all change the magnitude of melting point depression. These shape changes affect the surface to volume ratio, which affects the cohesive energy and thermal properties of a nanostructure. Equation 7 gives a general shape corrected formula for the theoretical melting of a point of a nanoparticle based on its size and shape.

\[ T_M(d) = T_M(1-\frac{d}{d_0}) \]  

where: \( C \) = material constant, \( Z \) = shape parameter of particle

The shape parameter is 1 for sphere and 3/2 for a very long wire, indicating that melting-point depression is suppressed in nanowires compared to nanoparticles. Past experimental data show that Nano scale tin platelets melt within a narrow range of 10°C of the bulk melting temperature.

**Conclusion**

This paper shows that melting point is important for heat transfer enhancement of Nanofluid, because nanoparticle surface molecule is not having that much of bond strength compare with inside the molecules of nanoparticle. The number of molecule is less compared with bulk material and it possess less number of bonds attachment, so less energy enough to remove surface molecule from the neighbouring molecule. At low-temperature, the surface of nanoparticle will melt, hence this time of collision two particles get together and the weight of this particle increases and get settled quickly. At nanoparticle-wall collision the nanoparticle attached in the surface of wall. So decreases the heat transfer co-efficient of nanoparticle. Low melting point nanoparticles decompose easily within its bulk metal.

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