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Size effect on melting temperatures of alumina nanocrystals: Molecular dynamics simulations and thermodynamic modeling

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ABSTRACT

Molecular dynamics (MD) simulations and thermodynamic analysis are conducted to investigate size effect on melting point of alumina nanocrystals. Different geometries including spherical and cubic particles, planar thin films, and spherical shells are considered. The atomic interactions in MD simulations are captured using Vashishta et al.'s potential function. Thermophysical properties of concern such as the bulk melting point, latent heat, density, and surface free energy are calculated using MD simulations and fed as inputs to the thermodynamic models. Predictions of MD simulations are compared with those of thermodynamic melting models. For all cases, heterogeneous melting is observed, where nucleation of the melt phase occurred at the free surface and the melting front propagated into the interior regions of the crystal. Results suggest that the melting point drops sharply below a threshold particle size, which is a function of the geometry. The threshold particle size of spherical particles is greater than that of planar films. Melting point predictions are quite sensitive to the choice of thermodynamic model and thermophysical property values. To ascertain the effects of curvature and core size on shell melting point, melting points of planar semi-infinite films and spherical shells are calculated and compared. For particle sizes of concern to practical applications (~100 nm or greater), shell melting point is nearly independent of core size and the semi-infinite planar film approximation is reasonable to estimate the melting point of alumina shells. In this size regime, melting points of 2–4 nm thick spherical oxide shells vary roughly in the range of 1800–2350 K, which is relatively close to the bulk melting point. Results of the present study do not indicate an enormous depression in the melting point, as the previous works suggest. This implies that the melting point depression of the oxide layer cannot fully describe the scatter in the measured ignition temperature of aluminum particles.

1. Introduction

Owing to applications in propulsion and energy-conversion devices, aluminum particles have attracted a lot of attention [1]. Aluminum is widely used due to its high energy density, low cost, and relative safety [1]. Aluminum particles are usually covered by an aluminum oxide layer (Al_2O_3) of thickness ranging from 0.5 nm [2] to 4 nm [3]. The impervious nature of the oxide layer protects the aluminum core from unwanted oxidation, but delays the ignition process. As per the experimental observations of Friedman et al. [4], ignition of aluminum particles (15–65 μm) occurs at temperatures near the melting point of the oxide layer (~2350 K). Once the oxide layer melts, it contracts and forms a cap due to surface tension, thereby exposing the aluminum core to the ambient gas [1]. Furthermore, the species diffusion process speeds up, thereby accelerating reaction rate and resulting in ignition. Subsequent experimental studies, however, suggest that the measured ignition temperatures are as low as 1000 K [1]. Ignition temperature of aluminum particles depends on many parameters such as particle size, oxide layer thickness, type and concentration of oxidiser and heating rate. There is considerable uncertainty in the ignition temperature of aluminum particles.

Numerous theories have been advanced to explain the ignition mechanism of aluminum particles. Rozenband and Vaganova [5] suggested that cracks develop in the oxide layer due to mechanical stresses induced by the expansion of the aluminum core upon melting. The experimental observations of Rai et al. [6] also support this theory. Trunov et al. [7] suggests that polymorphic phase transformations in the oxide layer cause a significant increase in the oxide layer density, thereby producing openings in the oxide layer. The formation of cracks and openings in the oxide layer facilitates chemical reactions between the particle and oxidizing gas. Note that chemical reactions also result in healing of the oxide

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layer, which tends to arrest these reactions. However, if the energy release increases the particle temperature to the melting temperature of the oxide layer, reactions can proceed in a self-sustained manner and ignition could be achieved. It is apparent the knowledge of melting point of the oxide layer is crucial in predicting ignition temperatures of aluminum particles. It is well known that melting temperatures of nanocrystals are size-dependent and deviates substantially from their bulk values [8]. As the oxide layer thickness is in the range of 0.5–4 nm and the particle size of concern is as low as few tens of nm, the melting point of oxide layer could be substantially lower than bulk melting point (~2300 K [9]–2350 K [1]). These could also possibly explain the wide scatter in the measured ignition temperatures of aluminum particles. As a result, it is important to investigate the size dependence of the melting point of the oxide layers.

Studies on melting of nano-scale aluminum oxide layers are quite scarce. Puri and Yang [10] studied melting of aluminum oxide layers of thickness in the range of 1–2.5 nm by means of molecular dynamics (MD) simulations using the Streitz–Mintmire potential. The melting point of the oxide layer was found to increase from 1130 K at 1.0 nm to 1313 K at 2.5 nm thickness. Note that these are substantially lower than the bulk value of ~2350 K. Note that the Streitz–Mintmire potential function was not shown to predict the melting temperatures of bulk alumina accurately. In a more recent work of Dreizin et al. [11], depression of the melting point of planar alumina films is quantified using equilibrium melting models. Melting points as low as ~1000 K was predicted. It is not immediately apparent that these results are applicable for oxide layers covering spherical aluminum particles. The melting point of the oxide shell is expected to be a function of core size and shell thickness. Furthermore, the validity of the melting model and its applicability to wide range of materials and conditions needs to be established.

High fidelity techniques such as molecular dynamics (MD) simulations can be used to get accurate predictions of melting points for a wide range of materials and conditions. MD simulations can predict the melting temperatures accurately under high heating rates, which are representative of conditions in many practical applications and laboratory experiments involving heating by laser irradiation and shock waves. The purpose of present work is to explore the size effect on melting temperatures of alumina nanocrystals. Different geometries are considered. Spherical oxide particles are of interest, as they are the primary combustion products of aluminum particles. Planar oxide films are considered as well as they are present in flake aluminum particles. Note that flake particles are of interest to propulsion applications due to their greater energy content and better safety and processing characteristics. Spherical oxide shells are considered due to their relevance to ignition of spherical aluminum particles. Furthermore, effects of core size and shell thickness on the melting point are explored. In addition to MD simulations, thermodynamic analysis of melting is conducted to investigate the melting point depression phenomenon. To facilitate comparison with MD predictions, thermophysical properties obtained from MD simulations are fed as inputs to thermodynamic melting models. Implications of the results of the present study on ignition mechanism of aluminum particles are discussed.

2. Theoretical and computational framework

2.1. Molecular dynamics simulations

Molecular dynamics simulations are conducted for four different geometries: (1) spherical particles; (2) cubic particles; (3) semi-infinite planar films; and (4) spherical shells. Fig. 1 shows the initial configurations for four different geometries considered in this study. A region is first created, with the shape and size based on the geometry and size of the nanocrystal under consideration. Atoms are generated using a set of fractional coordinates and lattice vectors. Spherical and cubic particles are placed at the centre of the simulation domain; the particles are surrounded by vacuum to ensure constancy of pressure throughout the simulation. Semi-infinite films are modeled by imposing periodic boundary conditions in two directions and by placing vacuum above and below the crystal in the third direction. Spherical shells are created by first removing a spherical region of atoms from a spherical particle and placing it in a vacuum.

The interatomic interactions are captured using the many-body potential function developed by Vashishta et al. [12]. The potential energy of the system can be written as

$$E = \sum_{i<j} E_{ij}^{(2)}(r_{ij}) + \sum_{i,j<k} E_{jik}^{(3)}(r_{ij}, r_{ik}),$$

$$E_{ij}^{(2)}(r_{ij}) = \frac{H_{ij}}{r_{ij}^{\eta_{ij}}} + \frac{Z_i Z_j}{r_{ij}} e^{-r_{ij}/\lambda} - \frac{D_{ij}}{2r_{ij}^4} e^{-r_{ij}/\xi} - \frac{W_{ij}}{r_{ij}^6},$$

$$E_{jik}^{(3)}(r_{ij}, r_{ik}) = R^{(3)}(r_{ij}, r_{ik}) P^{(3)}(\theta_{jik}),$$

$$R^{(3)}(r_{ij}, r_{ik}) = B_{jik} \exp\left(\frac{\gamma}{r_{ij} - r_0} + \frac{\gamma}{r_{ik} - r_0}\right) \Theta(r_0 - r_{ij}) \Theta(r_0 - r_{ik}),$$

$$P^{(3)}(\theta_{jik}) = \frac{(\cos\theta_{jik} - \cos\bar{\theta}_{jik})^2}{1 + C_{jik}(\cos\theta_{jik} - \cos\bar{\theta}_{jik})^2}, \quad (1)$$

where r_{ij} is the interatomic distance, H_{ij} the strength of the steric repulsion, Z_i the effective charge in units of the electronic charge, D_{ij} and W_{ij} the strengths of the charge-dipole and van der Waals attractions, respectively, η_{ij} the exponents in the steric repulsion term, λ and ξ the screening lengths for Coulomb and charge dipole interactions, respectively, B_{jik} the strength of three-body interactions, θ_{jik} the angle formed by r_{ij} and r_{ik}, $\bar{\theta}_{jik}$ and C_{jik} the model constants, and $\Theta(r_0 - r_{ij})$ the step function. Table 1 lists the values of different parameters. The cut-off radius (r_c) for truncation of the potential is taken to be 6 Å.

Canonical (NVT) ensemble using the Nosé–Hoover thermostat is employed to investigate melting of spherical and cubic particles and spherical shells. Isothermal-isobaric (NPT) ensemble is used to study melting of semi-infinite planar films. Constancy of temperature and pressure is achieved using Nosé–Hoover thermostat and barostat. Barostat is applied only in the two directions in which periodic boundary conditions are imposed. The time step is chosen as 1 fs in order to capture the vibrational motion of the atoms accurately. For all the simulations, the crystal is first equilibrated at a baseline temperature, which is much lower than the melting point. It is then heated either continuously or in increments of 50 K at a rate of 0.01 K per time step (10^{13} K/s). For the latter case, each heating step is followed by an equilibration step of duration 50 ps. The equations of motions are numerically integrated using the Verlet algorithm. All MD simulations in this work are performed using the LAMMPS molecular dynamics package [13].

The melting point is identified by studying the variations in the potential energy, density, and mean square displacement. Density is determined by calculating the total mass of all atoms inside a fixed and predetermined volume. Mean square displacement is calculated as follows:

$$MSD = \frac{1}{N}\sum_{n=1}^{N} (\vec{r}(t) - \vec{r}(0))^2 \quad (2)$$