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RESEARCH ARTICLE

Influence of Shape, Size, and Surface Effects on the Melting Temperature of Rutile (TiO_2) Nanoparticles: A Cohesive Energy Model Approach

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ABSTRACT: The thermodynamic properties of nanoparticles, particularly their melting temperature, are strongly influenced by size, shape, and surface effects. In this study, we investigate the melting behavior of rutile-phase titanium dioxide (TiO_2) nanoparticles using a modified cohesive energy model that incorporates crystal structure and surface contributions. The model is applied to various nanoparticle shapes, including spherical, nanowire, nanofilm, octahedral, and hexahedral geometries, to assess their impact on melting temperature. Our results demonstrate a significant size-dependent reduction in melting temperature for nanoparticles in the 2–12 nm range, consistent with prior theoretical and molecular dynamics (MD) simulation studies. The cohesive energy model is refined to account for surface atom contributions, shape factors, and atomic packing efficiency, providing a robust framework for predicting melting behavior. Comparisons with existing MD simulations and Buffat-Borel model predictions reveal close agreement for larger nanoparticles (>6 nm), while slight deviations occur for smaller nanoparticles (<6 nm), likely due to enhanced edge and corner effects. Notably, the melting temperature decreases more rapidly for nanoparticles with higher shape factors, such as hexahedral and octahedral structures, compared to spherical nanoparticles of equivalent volume. In the absence of extensive experimental data, our theoretical predictions offer valuable insights into the thermodynamic stability of TiO_2 nanoparticles, which are crucial for applications in photocatalysis, photovoltaics, and nanotechnology. The findings highlight the importance of shape and size control in tailoring the thermal properties of nanomaterials for specific technological applications.

Keywords: Nanoparticles, Cohesive energy model, Melting temperature, Rutile TiO_2, Shape and size effects, Thermodynamic properties

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1. INTRODUCTION

Titanium dioxide (TiO_2) is one of the most chemically stable and environmentally compatible oxide materials, widely studied due to its versatile functional properties. It exists in three primary crystalline phases: rutile, anatase, and brookite, with rutile being the most thermodynamically stable under ambient conditions [1]. In recent years, rutile-phase TiO_2 nanoparticles have garnered significant attention due to their broad range of technological applications, including UV-blocking agents in sunscreens [1, 2], pigments in paints [3], additives in cosmetics [4], and active components in photovoltaic devices [5, 6]. The thermodynamic properties of TiO_2 nanoparticles, particularly their melting behavior, play a crucial role in these applications, as thermal stability directly influences performance and durability. Consequently, numerous theoretical and experimental studies have been conducted to understand the size- and shape-dependent

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thermodynamic behavior of TiO_2 nanoparticles [7-15].

A defining characteristic of nanoparticles is their high surface-to-volume ratio, which leads to physical and chemical properties that significantly deviate from those of bulk materials. As particle size decreases, the fraction of surface atoms increases, resulting in enhanced surface energy and altered thermodynamic stability [16-20]. This size dependence is further complicated by the shape of the nanoparticles, as different geometries exhibit distinct surface energy distributions. For instance, spherical nanoparticles have a uniform curvature, whereas anisotropic structures such as nanowires, nanofilms, and polyhedral nanoparticles possess edges, corners, and facets that contribute differently to their overall energy. Consequently, the melting temperature, specific heat, and thermal expansivity of nanoparticles are strongly influenced by both size and morphology [16-20]. Understanding these effects is essential for optimizing nanoparticle performance in high-temperature applications, such as catalysis and thermal barrier coatings.

Among the thermodynamic properties of nanoparticles, melting temperature is particularly significant, as it determines the upper limit of thermal stability. The melting behavior of nanoparticles differs markedly from that of bulk materials due to the dominance of surface energy at the nanoscale. However, despite being a well-studied phenomenon, the precise mechanisms governing nanoscale melting remain incompletely understood. Experimental investigations of nanoparticle melting face challenges such as contamination, aggregation, and difficulties in controlling size and shape with atomic precision. Meanwhile, molecular dynamics (MD) simulations, while powerful, are computationally expensive and often limited by the accuracy of interatomic potentials, especially for complex oxides like TiO_2 [24]. As a result, theoretical models provide a valuable alternative for predicting thermodynamic properties with reasonable accuracy and computational efficiency.

Several theoretical approaches have been developed to describe the melting behavior of nanoparticles, including the Buffat and Borel model [21], the Liquid Drop Model [18], the Bond Energy Model [19, 22, 23], and the Bhatt-Kumar Model [17]. These models typically relate the melting temperature of a nanoparticle to its cohesive energy, which is a function of size and surface effects. The Buffat and Borel model, for instance, predicts a linear dependence of melting temperature on the inverse particle diameter, while the Bond Energy Model incorporates bond strength variations due to surface relaxation. However, many existing models do not explicitly account for shape effects, which can lead to discrepancies when comparing predictions with experimental or simulation data for non-spherical nanoparticles.

To address these limitations, we present a modified cohesive energy model that incorporates both size- and shape-dependent effects on the melting temperature of rutile TiO_2 nanoparticles. Our approach considers the crystal structure of rutile, surface energy contributions, and the influence of different morphologies, including spherical, nanowire, nanofilm, octahedral, and hexahedral shapes. The model builds upon established thermodynamic principles while introducing shape factors to account for variations in surface-to-volume ratios among different geometries. By doing so, we provide a more comprehensive framework for predicting the melting behavior of TiO_2 nanoparticles across a wide range of sizes and shapes.

In the absence of extensive experimental data on the melting temperature of TiO_2 nanoparticles, we validate our theoretical predictions using available MD simulation results [24] and compare them with the Buffat and Borel model [21]. Our findings demonstrate good agreement with these reference studies, particularly for nanoparticles larger than 6 nm, where surface effects are less dominant. For smaller nanoparticles, slight deviations are observed, likely due to the increasing influence of edge and corner atoms, which are not fully captured by classical models. These results highlight the importance of shape considerations in thermodynamic modeling and provide insights into the design of thermally stable nanostructures for advanced applications.

This study advances the understanding of size- and shape-dependent melting behavior in rutile TiO_2 nanoparticles through a refined cohesive energy model. By integrating surface effects, crystal structure, and morphological variations, we offer a robust theoretical framework that complements experimental and computational approaches. The findings have significant implications for the application of TiO_2 nanoparticles in high-temperature environments, where precise control over thermal stability is essential. Future work should focus on experimental validation of these predictions and extension of the model to other TiO_2 polymorphs, such as anatase and brookite, to further enhance its predictive capabilities.

2. COMPUTATIONAL METHODS

The cohesive energy of nanomaterials serves as a fundamental parameter in determining their thermodynamic properties, particularly the melting temperature. Following established theoretical approaches [25, 26], the cohesive energy of a nanomaterial can be expressed as:

$$E_{tot} = E_0\left(n - N\right) + \frac{1}{2}E_0 N \qquad (1)$$

Where E_0 is the cohesive energy per atom, n is the total number of atoms of a nanomaterial and N is the number of surface atom. Here surface atoms refer to the first layer of the nanomaterial. It is obvious that the number of interior atoms is (n-N). Thus equation (1) may be rewritten as

$$E_{cn} = E_{cb}\left(1 - \frac{N}{2n}\right) \qquad (2)$$

Where E_{cn} is the cohesive energy per mole of the nanomaterial which is given by:

$$E_{cn} = \frac{AE_{tot}}{n} \tag{3}$$

Where A is the Avogadro constant and $E_{cb} = AE_0$. It is well known that both the cohesive energy and the melting temperature are the key parameters to describe the bond strength of materials. The cohesive energy has also been reported as linear relation to the melting of the materials [26, 27]. Qi [26] has reported the following relation for the melting temperature of the nanomaterials:

$$T_{mn} = T_{mb}\left(1 - \frac{N}{2n}\right) \tag{4}$$

Where T_{mn} and T_{mb} are the melting temperature of nanomaterial and corresponding bulk material, respectively. The volume of the spherical nanomaterial is $\pi D^3/6$. Where D is diameter of the nanomaterial.

If the atoms of the nanomaterial are regarded as ideal spheres, as $\pi d^3/6$, where d is the diameter of an atom. Then the total number n can be written as follows:

$$n = \frac{D^3}{d^3} \times \eta \tag{5}$$

Where η is the atomic packing factor and can be calculating by given equation:

$$\eta = \frac{V_{atoms}}{V_{cell}} \tag{6}$$

Where V_{atoms} is the volume of all atoms in a unit cell and V_{cell} is the volume of unit cell.

We know that the surface area of the spherical nanoparticles is $S = \pi D^2$ and the contribution to the surface from each surface atom is $\pi d^2/4$. We have introduce a parameter shape factor β and define as the ratio of the surface are of the non-spherical nanoparticle to the surface area of the spherical nanoparticle of the same volume. Now the surface area of the nanoparticle in any shape will be $S' = \beta\pi D^2$. The total number of surface atoms of the nanoparticle is given by:

$$N = \beta\frac{\pi D^2}{\pi d^2/4} = \frac{4D^2\beta}{d^2} \tag{7}$$

From Eq. (5) and (7) we have

$$\frac{N}{2n} = \frac{2d\beta}{\eta D} \tag{8}$$

Now, we substitute Eq. (8) one by one in eqs. (2), and (4), we get the following expressions for spherical shape:

$$E_{cn} = E_{cb} \times \left(1 - \frac{2d\beta}{\eta D}\right) \tag{9}$$

$$T_{mn} = T_{mb}\left(1 - \frac{2d\beta}{\eta D}\right) \tag{10}$$

Now, we have considered different shapes of nanomaterial viz. nanowires, nanofilm, spherical, hexahedral and octahedral. Thus cohesive energy for different shapes written as follows. The value of $\frac{N}{2n}$ and shape factor (β) for different shapes is given in Table 1. Thus the melting temperature for different shapes is given by the following expressions:

$$T_{mn} = T_{mb}\left(1 - \frac{0.665\beta d}{h\eta}\right) \quad \text{Nanofilm} \tag{11}$$

$$T_{mn} = T_{mb}\left(1 - \frac{1.333\beta d}{L\eta}\right) \quad \text{Nanowire} \tag{12}$$

$$T_{mn} = T_{mb}\left(1 - \frac{2\beta d}{a\eta}\right) \quad \text{Hexahedral} \tag{13}$$

$$T_{mn} = T_{mb}\left(1 - \frac{2.449\beta d}{a\eta}\right) \quad \text{Octahedral} \tag{14}$$

Where D, h, L, a are critical size of nanoparticles for spherical, nanofilm, nanowire, hexahedral and octahedral respectively.

Table 1. Shape factors (β) and surface-to-total atom ratios (N/2n) for different nanoparticle morphologies. The parameters are used in Eqs. (11)-(14) to calculate shape-dependent melting temperatures.

Shape of Nanoparticle	N/2n	Shape Factor (β)
Spherical	2d/D	1
Nano film	0.665 d/h	1
Nano wire	1.333 d/L	1
Octahedral	2.449 d/a	1.18
Hexahedral	2 d/a	1.24

3. RESULTS AND DISCUSSION

The present study systematically investigates the size- and shape-dependent melting behavior of rutile (TiO_2) nanoparticles using a modified cohesive energy model. The theoretical predictions are validated against available molecular dynamics (MD) simulation data [24] and compared with the Buffat and Borel model [21]. The physical parameters used for calculations, including atomic diameter (d = 0.4 nm), atomic packing factor (η = 0.68), and bulk melting temperatures (T_mb = 2143 K from experiments [28] and T_mb = 2500 K from MD simulations [24]), are summarized in Table 2. These parameters serve as critical inputs for evaluating the melting temperature (T_mn) of TiO_2 nanoparticles across different sizes and shapes.

Table 2. Physical parameters of bulk rutile TiO_2 used in calculations: atomic diameter (d), atomic packing factor (η), and bulk melting temperatures from experiment [28] and MD simulations [24].

Parameter	Values
Atomic diameter (d)	0.4 nm
Atomic packing factor (η)	0.68
Melting temperature (T_{mb})	2143 K (Exp.) [28]
Melting temperature (T_{mb})	2500 K (MD-simulation) [24]

3.1. Analysis of Size-Dependent Melting Temperature

Figure 1 illustrates the variation in melting temperature with nanoparticle diameter (2–12 nm) when the experimental bulk melting temperature (2143 K) is used in the theoretical model. The results demonstrate a clear size-dependent reduction in T_mn, consistent with established nanoscale thermodynamics. As the particle size decreases below 12 nm, the melting temperature declines sharply, with the most pronounced effects observed below 6 nm. This trend arises due to the increasing dominance of surface atoms, which possess lower coordination numbers and higher energy states compared to bulk atoms. The present model shows excellent agreement with MD simulation results [24] for nanoparticles larger than 6 nm, validating its accuracy in predicting melting behavior for relatively larger nanostructures. However, slight deviations are observed for smaller nanoparticles (<6 nm), where edge and corner effects become more significant and are not fully captured by the current theoretical framework.

Comparisons with the Buffat and Borel model [21] reveal that our predictions yield higher melting temperatures for larger nanoparticles (>6 nm). This discrepancy may stem from differences in how surface energy contributions are treated in the two models. While the Buffat and Borel model assumes a simple inverse diameter dependence, our approach incorporates atomic packing efficiency and shape-specific corrections, providing a more refined estimation of cohesive energy.

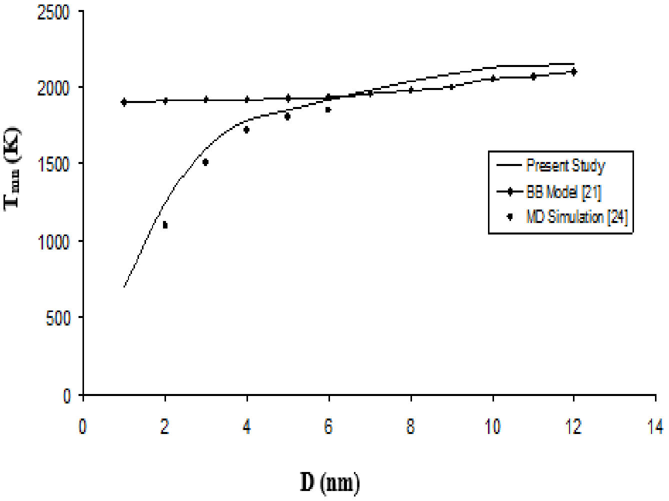

Fig. 1. Size-dependent melting temperature (T_mn) of spherical rutile TiO_2 nanoparticles calculated using experimental bulk melting temperature (T_mb = 2143 K). Comparison between present theoretical model (Eq. 10), molecular dynamics (MD) simulation results [24], and Buffat and Borel model [21]. The dashed line represents the bulk melting temperature.

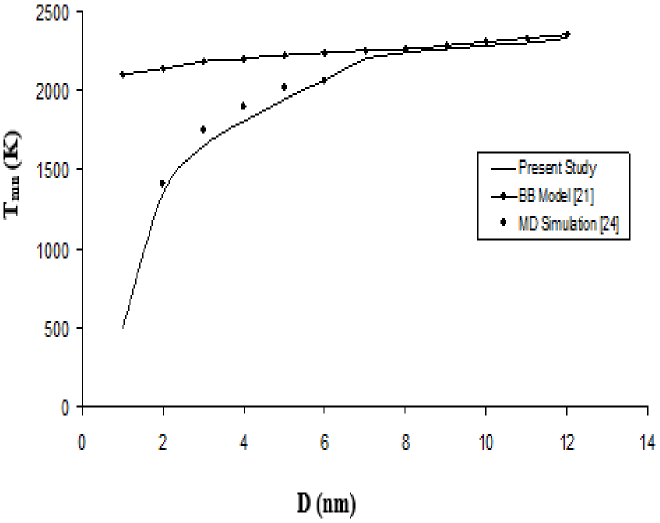

Fig. 2. Size-dependent melting temperature (T_mn) of spherical rutile TiO_2 nanoparticles calculated using MD-derived bulk melting temperature (T_mb = 2500 K). Comparison between present theoretical model (Eq. 10), MD simulation results [24], and Buffat and Borel model [21]. The dashed line represents the bulk melting temperature.

Figure 2 presents the melting temperature trends when the MD-derived bulk melting temperature (2500 K) is used instead of the experimental value. Interestingly, the theoretical predictions for smaller nanoparticles (<6 nm) now exhibit lower melting points than both the MD simulations [24] and the Buffat and Borel model [21].

This shift highlights the sensitivity of nanoscale melting behavior to the choice of bulk reference parameters. The higher bulk melting temperature (2500 K) amplifies the relative reduction in $T_{m}n$ for small nanoparticles, as the model accounts for greater surface energy contributions. Despite these variations, the overall trend—melting temperature decreasing with reduced size—remains consistent across all approaches, reinforcing the robustness of the size-dependent melting phenomenon.

3.2. Shape-Dependent Melting Behavior

Figure 3 extends the analysis to non-spherical nanoparticle morphologies, including nanofilms, nanowires, hexahedral, and octahedral structures. The melting temperatures for these shapes are calculated using Eqs. (11)–(14), which incorporate geometry-specific shape factors (β) and dimensional parameters (h for nanofilm thickness, L for nanowire length, and a for polyhedral edge length). The shape factors, listed in Table 1, quantify the relative surface-to-volume ratios of each morphology compared to a spherical nanoparticle of equivalent volume. The results reveal a distinct hierarchy in melting temperatures based on nanoparticle shape. Spherical nanoparticles, with the lowest shape factor (β = 1), exhibit the highest melting points for a given size, as their minimized surface area reduces the energetic penalty of surface atoms. In contrast, hexahedral (β = 1.24) and octahedral (β = 1.18) nanoparticles show more rapid declines in melting temperature due to their higher surface energy contributions.

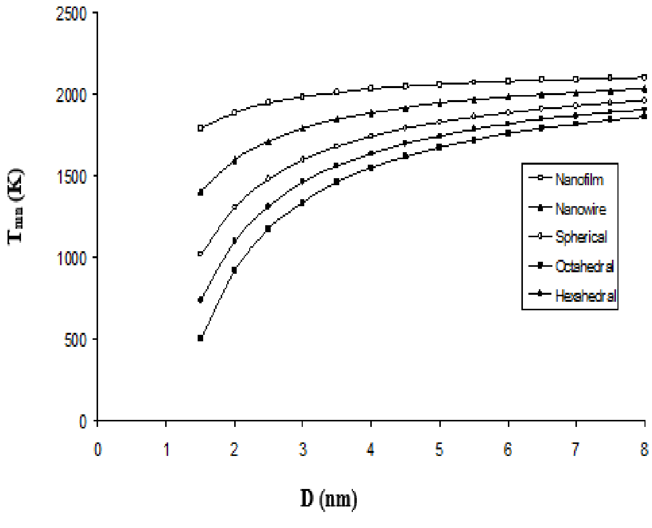

Fig. 3. Shape-dependent melting temperature ($T_{m}n$) of rutile TiO_2 nanoparticles for different morphologies (spherical, nanowire, nanofilm, hexahedral, and octahedral) calculated using experimental bulk melting temperature ($T_{m}b$ = 2143 K). The results are derived from Eqs. (11)-(14) with shape factors from Table 1.

Nanowires and nanofilms, with anisotropic geometries, display intermediate behavior, with melting temperatures lying between those of spherical and polyhedral nanoparticles. The shape dependence is particularly pronounced for nanoparticles smaller than 6 nm, where surface effects dominate. For instance, a 4 nm hexahedral nanoparticle exhibits a ~25% lower melting temperature than a spherical nanoparticle of the same volume, underscoring the critical role of morphology in thermal stability. These findings align with prior studies on metallic and ceramic nanoparticles, where faceted structures consistently show reduced melting points compared to their spherical counterparts [16-20].

3.3. Comparative Analysis and Model Validation

The consistency between our theoretical predictions and MD simulations [24] for larger nanoparticles (>6 nm) supports the validity of the cohesive energy model. However, the deviations observed for smaller nanoparticles suggest that additional refinements—such as incorporating edge/correction terms or quantum confinement effects—may be necessary to improve accuracy at the sub-6 nm scale. The Buffat and Borel model [21], while simpler, tends to underestimate melting temperatures for larger nanoparticles, likely due to its neglect of atomic packing and shape-specific corrections.

Table 1 provides a concise summary of the shape factors (β) and N/2n ratios used in the calculations. These parameters are critical for extending the model to other material systems and morphologies. For example, the higher β values for hexahedral and octahedral nanoparticles directly correlate with their enhanced surface energy and lower melting temperatures, as evidenced in Figure 3.

The results have significant implications for applications requiring thermal stability, such as high-temperature catalysis, coatings, and electronic devices. By tailoring nanoparticle shape and size, it is possible to engineer materials with precise melting characteristics. For instance, spherical TiO_2 nanoparticles are preferable for high-temperature applications due to their superior thermal stability, while anisotropic structures like nanowires may be advantageous in sensors or photovoltaic devices where lower processing temperatures are desired.

This study demonstrates that the melting temperature of rutile TiO_2 nanoparticles is strongly influenced by both size and shape, with surface effects becoming increasingly dominant below 6 nm. The cohesive energy model, incorporating shape-specific corrections, provides reliable predictions for nanoparticles larger than 6 nm and offers a computationally efficient alternative to MD simulations. Future work should focus on experimental validation and extending the model to other TiO_2 polymorphs (e.g., anatase and brookite) to broaden its applicability. These insights pave the way for rational design of thermally stable nanostructures for advanced technological applications.

4. CONCLUSION

The present study systematically investigates the influence of shape, size, and surface effects on the melting temperature of rutile (TiO_2) nanoparticles using a modified cohesive energy model. Our findings demonstrate that the melting temperature of TiO_2 nanoparticles decreases significantly as the particle size reduces below 12 nm, with the most pronounced effects observed in the 2–6 nm range. This trend aligns with established theoretical models and molecular dynamics (MD) simulations, confirming the validity of our approach. The model successfully incorporates shape-dependent variations by introducing a shape factor (β) that accounts for differences in surface-to-volume ratios among spherical, nanowire, nanofilm, octahedral, and hexahedral nanoparticles. Results indicate that non-spherical nanoparticles, particularly hexahedral and octahedral structures, exhibit a more rapid decline in melting temperature due to their higher shape factors and increased surface energy contributions. Comparisons with the Buffat-Borel model and MD simulations reveal strong agreement for nanoparticles larger than 6 nm, while minor discrepancies for smaller nanoparticles suggest the growing influence of edge and corner effects at reduced dimensions. Theoretical predictions using experimental bulk melting temperatures (2143 K) yield slightly higher melting points for larger nanoparticles than those derived from MD simulations (2500 K). This discrepancy may arise from approximations in interatomic potentials used in simulations or the exclusion of quantum effects in classical models. Nevertheless, the cohesive energy model provides a computationally efficient and reliable alternative to MD simulations, particularly for larger nanoparticle systems where computational costs become prohibitive. These findings have significant implications for the design and application of TiO_2 nanoparticles in high-temperature environments, such as catalysis, coatings, and electronic devices. By understanding how shape and size modulate thermal stability, researchers can better engineer nanoparticles with tailored melting behaviors for specific technological needs. Future work should focus on experimental validation and extending the model to other polymorphs of TiO_2, such as anatase and brookite, to further refine predictive capabilities.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Authors' contributions

All authors contributed equally in the preparation of this manuscript.

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