Glass transition and thermodynamics of liquid and amorphous TiO$_2$ nanoparticles
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Abstract

Glass transition and thermodynamics of liquid TiO$_2$ spherical nanoparticles have been studied in a model with different sizes ranged from 2 nm to 5 nm under non-periodic boundary conditions. We use the pairwise interatomic potentials proposed by Matsui and Akaogi. Models have been obtained by cooling from the melt via molecular dynamics (MD) simulation. Structural properties of liquid nanoparticles at 3500 K have been analyzed in details through the partial radial distribution functions (PRDFs), coordination number distributions, bond-angle distributions and interatomic distances. Moreover, we also show the radial density profile in nanoparticles. Calculations show that size effects on structure of a model are significant and that liquid TiO$_2$ nanoparticles have a distorted pentahedral network structure with the mean coordination number $Z_{n-o} \approx 5.0$ and $Z_{o-n} \approx 2.5$ while amorphous TiO$_2$ nanoparticles have an octahedral network structure. Temperature dependence of surface structure and surface energy of nanoparticles has been obtained and presented. In addition, size dependence of glass transition temperature and temperature dependence of diffusion constant of atomic species have been found and discussed.

Keywords: amorphous TiO$_2$ nanoparticles, surface structure, glass transition.
PACS numbers: 61.46.-w, 61.20.Ja, 78.55.Qr; 61.43.Bn.

I. INTRODUCTION

Nanosized TiO$_2$ has been under intensive investigation for recent years by experiments [1-27] or computer simulations [28-31] due to its technological importance, i.e. it is a strategic material for the production of photo-electrochemical cells, optical filters, chemical sensors, the systems with enhanced catalytic activity [1,9-11] or as an effective UV-B radiation skin-protective compound in sunscreens [19]. Nanosized TiO$_2$ exists in several polymorphic forms, including amorphous, anatase or rutile depending on fabricating conditions and further heat treatment [3,6,7,12,14,21,23,24,26,27]. Nanosized TiO$_2$ is usually produced by sol-gel, hydrolysis methods or by gas condensation [1,4,5,8,11]. Particularly, sol-gel TiO$_2$ nanoparticles with different phases such as amorphous, anatase and rutile were investigated in details by optical techniques, by systematically varying synthesis, sample handling, and annealing variables [6]. And, it was found annealing-induced phase transformation from amorphous nanosized-TiO$_2$ to anatase and to rutile via Raman scattering, infrared reflectivity, infrared absorption, x-ray diffraction, and electron energy-loss spectroscopy [6]. Heat treatment induced transformation from amorphous nanosized-TiO$_2$ to different crystalline forms also can be found in other works [7,16,21,23,24]. Generally, structure and properties of nanoparticles greatly depend on their size. It was found that the amorphous to anatase transformation in nanosized TiO$_2$ was also size dependent [6]. Moreover, size effects on photocatalytic activity, Raman spectrum or on the pressure-induced amorphization in nanoscaled TiO$_2$ have been found [12,20,25,27]. On the other hand, although amorphous TiO$_2$ nanoparticles have been obtained in practice our understanding of their structure and properties is limited up to now. The fact, effects of amorphous content on the photocatalytic properties of TiO$_2$ nanoparticles have been observed in that for
nanoparticles mainly in the anatase phases and mixed-phases, their photocatalytic activities increase significantly with decreasing amorphous content. This indicates that due to specific short-range order structure of amorphous phase, differed from those of crystalline ones, properties of TiO$_2$ nanoparticles can be changed by varying amorphous content in the samples [12].

However, more detailed information on an atomistic level about structure and properties of nanoparticles can be provided by computer simulation. And up to now one can find a few works related to the simulation of TiO$_2$ nanoparticles. Ground state structure and properties of small nanoparticles including crystalline TiO$_2$ ones have been calculated by using Density Functional Theory (DFT) [28]. DFT was also used for determining the surface energy and surface tensions of crystalline TiO$_2$ nanoparticles and it was found that surface passivation has an important impact on nanocrystalline morphology and phase stability of TiO$_2$ nanoparticles [30]. On the other hand, MD simulation of crystalline TiO$_2$ nanoparticle sintering was done by using the Matsui-Akaogi interatomic potentials [31], the validity of which for the TiO$_2$ surfaces has been tested by ab initio calculations [29]. And, although amorphous form of TiO$_2$ nanoparticles is an important one, much attention was spent for investigation of crystalline TiO$_2$ nanoparticles. Therefore, our knowledge of microstructure and thermodynamics of liquid and amorphous TiO$_2$ nanoparticles is limited. It motivates us to carry out the study in this direction.

II. CALCULATION

We perform the simulations in a spherical model with different diameters ranged from 2nm to 5 nm at the fixed density of 3.80 g/cm$^3$, which corresponding to the real density of amorphous TiO$_2$ obtained in practice [32]. Each model contains the number of Ti and O atoms in accordance to the TiO$_2$ stoichiometry. We first placed randomly N atoms in a sphere of fixed radius and the configuration has been relaxed for 50000 MD steps at 7000 K under non-periodic boundary conditions. The MD time step is of 1.6 fs and the system was cooling down from the melt at constant volume corresponding to the system density of 3.80 g/cm$^3$. Temperature of the system was decreased linearly in time as $T = T_0 - \gamma t$, here $\gamma$ is a cooling rate of $4.2945 \times 10^{13}$ K/s and $T_0$ is the initial temperature of 7000 K. There were several interatomic potentials for the bulk crystalline TiO$_2$ [33-42]. Via detailed analysis of the different force fields for TiO$_2$, Collins et al. concluded that the force field developed for crystalline TiO$_2$ proposed by Matsui and Akaogi is the most suitable for MD simulating the bulk TiO$_2$ [33,43]. For convenience we call these potentials the MA ones. The MA potentials are composed of the pairwise additive Coulomb, dispersion and repulsion interactions. The energy parameters of MA potentials were determined to reproduce the crystal structures of rutile, anatase and brookite, and the measured elastic constants of rutile. By using such potentials they successfully reproduced a wide range of properties of the different polymorphs of TiO$_2$ crystals mentioned above including the crystal structures, volume compressibility, volume thermal expansivity and enthalpy relationships between them [33]. After intensive testing we found that MA potentials are good for simulating liquid and amorphous TiO$_2$, i.e. amorphous TiO$_2$ models have a distorted octahedral network structure with the mean coordination number $Z_{\text{N-O}} \approx 6.0$ and $Z_{\text{O-N}} \approx 3.0$ like those observed by experiments [44]. Moreover, TiO$_2$ is an ionic-covalent system and it must be considered in simulation. Numerous experimental studies of oxide systems indicate a substantial contribution of ionic bonding to interaction due to high electronegativity of the oxygen atoms [45], while covalent bonding is also important. The covalent interaction is described in terms of three-particle potentials, which significantly increase the computation time. Since ionic
contribution cannot be neglected for oxides, the Coulomb interactions have to be considered. Simulation of oxide systems with mixed ionic and covalent bonds requires too many force parameters that it is very difficult to carry out. Therefore, the models have to be simplified and the choice of model based on the ionic interactions has significant advantages. Simulation results for oxide systems by using ionic model for the past three decades including our recent simulation for liquid and amorphous TiO$_2$ by using MA potentials confirmed this point. Therefore, one can infer that MA interatomic potentials describe well both the bulk and the surface properties of crystalline or amorphous TiO$_2$ and we use them again here for simulating amorphous TiO$_2$ nanoparticles, the MA potentials have the following form:

$$U_y(r) = Z_i Z_j \frac{e^2}{r} + f(B_i + B_j)\exp[(A_i + A_j - r)/(B_i + B_j)] - \frac{C_i C_j}{r^6}$$  \hspace{1cm} (1)

with $i, j = \text{Ti, O}$. Here $r$ is the interatomic distance and $Z_i, Z_j$ are the charges of ions: $Z_{\text{Ti}} = +2.196$ and $Z_{\text{O}} = -1.098$. The quantity $f$ is a standard force of $4.184$ kJÅ$^{-1}$mol$^{-1}$. Other parameters of potentials are shown in Table 1. More details about the MA potentials can be found in [33].

Coulomb interactions were taken into account by means of Ewald-Hansen method [46]. In order to calculate the coordination number and bond-angle distributions in amorphous TiO$_2$ nanoparticles, we adopt the fixed values $R_{\text{Ni-Ti}} = 4.00$ Å, $R_{\text{Ni-O}} = 2.50$ Å and $R_{\text{O-O}} = 3.50$ Å. Here $R$ denotes a cutoff radius, which is chosen as the position of the minimum after the first peak in PRDFs for the amorphous bulk at 350 K. The models at different temperatures have been relaxed for 50000 MD steps before evaluating static quantities. In order to improve the statistics of the simulation, the results have been averaged over two independent runs for nanoparticles with the size of 2 nm, 3 nm and 4 nm. Due to large number of atoms in the model with the size of 5 nm (i.e. 5626 atoms) single run was done for this size. In order to compare, we also show the results of liquid TiO$_2$ models under periodic boundary conditions containing 3000 atoms which would be considered as the bulk counterparts.

### III. RESULTS AND DISCUSSIONS

#### A. Structural properties of liquid TiO$_2$ nanoparticles at 3500 K

Structural properties of liquid TiO$_2$ nanoparticles obtained at 3500 K have been studied in details compared with those observed in the bulk model at the same temperature. Table 2 shows that structural properties of TiO$_2$ nanoparticles are closer to those for the bulk if their size increases. Particularly, mean coordination number for all atomic pairs in nanoparticles increases with their size toward the value for the bulk. In contrast, no systematic changes have been found for the mean Ti-Ti and O-O interatomic distances. Noticing that due to strong Ti-O bond, the mean Ti-O interatomic distance remains constant in nanoparticles and in the bulk which is equal to 1.81 Å. Such value is much smaller than 1.96 Å observed in practice for bulk amorphous TiO$_2$ (bulk a-TiO$_2$) [47]. Like those discussed for the bulk liquid and amorphous TiO$_2$ [44], the value 1.96 Å for Ti-O interatomic distance is typical for octahedrally coordinated titanium systems meanwhile for tetrahedrally coordinated titanium system such as Ba$_2$TiO$_4$ the Ti-O bond length varies between 1.63 Å - 1.82 Å [48]. This means that the value 1.81 Å for Ti-O bond length obtained in TiO$_2$ nanoparticles reflects the
existence of undercoordinated TiO\textsubscript{n} units with \( n < 6 \). Indeed, TiO\textsubscript{n} units with \( n < 6 \) have their domination in liquid TiO\textsubscript{2} nanoparticles (see Tables 2 & 3) and their fraction is enhanced with decreasing nanoparticle size due to the surface effects. On the other hand, we found no splitting of the first peak in PRDF for Ti-Ti pair in both the liquid bulk and nanoparticles unlike those observed in the amorphous bulk [44,47] (see Table 2 and Fig. 1), i.e. the prepeak is centered at around 3.00 Å and the main peak is at 3.55 Å (see Table 2). As discussed in [47], the shorter Ti-Ti interatomic bond of 3.00 Å is related to the pairs of Ti atoms centering octahedra linking by the edge, the longer one of 3.55 Å is of pairs of Ti atoms from octahedra having a common vertex. And due to pentahedral network structure in liquid TiO\textsubscript{2} such connectivity between octahedra has not been found. Moreover, one can see in Fig. 1 that PRDFs are strongly size dependent. This shows that local and intermediate scale orders in TiO\textsubscript{2} nanoparticles are size dependent. In addition, PRDFs of nanoparticles are higher than those for the bulk indicated more inhomogeneous structure of the formers due to the surface contribution.

More details about the size dependence of TiO\textsubscript{2} nanoparticles can be found via coordination number and bond-angle distributions (Figs. 2 & 3). Fig. 2 presents that if the nanoparticle size is larger than 4 nm coordination number distributions for all atomic pairs are close with each other. The distributions for Ti-O and O-Ti pairs are similar for nanoparticles with different sizes and they are also close to those for the bulk indicated the close local structure in the systems. In contrast, the distributions for Ti-Ti and O-O pairs totally differ from each other. It ensures that intermediate scale order, i.e. the linkage between structural units TiO\textsubscript{n}, is more sensitive to the nanoparticle size compared with those for the local scale one and it strongly differs from those observed in the bulk. Concerning the bond-angles, we show only the most important ones such as Ti-O-Ti and O-Ti-O, the first one describes the connectivity between TiO\textsubscript{n} units in the system while the latter describes the local order inside them (Fig. 3). And, unlike smooth curves for the bulk one can see the occurrence of additional peaks in the curves for nanoparticles which are more pronounced for the smallest nanoparticle of 2nm. The appearance of small peaks in the bond-angle distributions for TiO\textsubscript{2} nanoparticles may be related to the existence of small membered rings at the surface of TiO\textsubscript{2} nanoparticles like those observed and discussed for amorphous SiO\textsubscript{2} nanoscaled clusters [49]. In addition, several remarks can be inferred from the coordination number distributions for Ti-O and O-Ti pairs (see Table 3). And that, while bulk amorphous TiO\textsubscript{2} has an octahedral network structure with \( Z_{\text{Ti-O}} \approx 6.0 \) and \( Z_{\text{O-Ti}} \approx 3.0 \) [44,47], bulk liquid TiO\textsubscript{2} or nanoparticles have a pentahedral network structure in that fivefold coordinated titanium (i.e. TiO\textsubscript{5}) dominates in the system. Fraction of Ti with \( Z_{\text{Ti-O}} = 6 \) and O with \( Z_{\text{O-Ti}} = 3 \) increases with nanoparticle size toward the value for the bulk, while fraction of Ti and O atoms with under-coordination decreases. This tendency indicates the growing of structural defects in nanoparticles if the size is lowered due to the enhancement of surface effects.

Radial density profile, \( \rho(R) \), is an important quantity for getting more insights into the local structure of nanoparticles and we also present it here. If the number of atoms belonging to the spherical shell with the thickness of 0.20 Å formed by two spheres with the radii of \( R - 0.10 \) Å and \( R + 0.10 \) Å is determined one can infer \( \rho(R) \). Here \( R \) is the distance from the center of nanoparticles. Like those were done in [50], we calculate directly \( \rho(R) \) for the radii just beyond finite large enough value, which is taken equal to 10.00 Å in present work. The density profile has been averaged over two different configurations. And \( R \) increases from 10.00 Å with the step of 0.20Å. As shown in Fig. 4, \( \rho(R) \) fluctuates around the value of 5.00 g/cm\textsuperscript{3}, which is higher than the density of an amorphous TiO\textsubscript{2} obtained in practice.
(i.e. it ranges from to 3.00 g/cm$^3$ to about 4.00 g/cm$^3$ depending on the fabricating method of samples [32]). We also found that oxygen atoms have a tendency to concentrate at the surface of nanoparticles like those observed at liquid SiO$_2$ or amorphous Al$_2$O$_3$ surfaces [49,51]. One can see clearly the phenomenon via the partial density profile curve for oxygen separately (Fig. 4). Like those discussed for amorphous SiO$_2$ surfaces [49], the reason is that the system is energetically favored with an oxygen atom at the surface, since only one bond has to be broken if any, whereas if a titanium is at the surface several bonds have to be broken. Due to the excess of oxygen at the surface, Ti atoms have a tendency to concentrate in the shell close to the surface in order to achieve the local charge neutrality [49,51]. And it causes a peak of the total density in the vicinity of the surface. Similar tendency has been found for TiO$_2$ nanoparticles at three different sizes (Fig. 4).

B. Surface and core structures of liquid TiO$_2$ nanoparticles

Due to mixing of ionic and covalent bonds in metal oxides such as TiO$_2$, surface structure has a strong influence on local surface chemistry compared to pure metals or elemental semiconductors [52]. Therefore, it needs a good knowledge of surface structure and properties of TiO$_2$. Indeed, TiO$_2$ is the most investigated single-crystalline system in the surface science of metal oxides because of its technological importance like those discussed in the Introduction (good review related to the surface science of crystalline TiO$_2$ can be seen in [53]). However, better understanding and improvement of catalytic reactions are one main driving force for surface study on TiO$_2$ [53]. On the other hand, much attention has been paid for research of photoelectric and photochemical properties of TiO$_2$ and it was suggested that surface defects may play a role in the decomposition of water into H$_2$ and O$_2$ [53]. However, while it was spent much attention to the surface of crystalline TiO$_2$ our understanding of liquid and amorphous surfaces of TiO$_2$ is limited. Therefore, it is worth to carry out the study in this direction. Because of the lack of long range order in structure, it is difficult to separate the surface shell from the core of amorphous nanoparticles compared with those for crystalline nanoparticles. In order to investigate the surface of TiO$_2$ liquid and amorphous nanoparticles we need a criterion to decide which atoms belonging to the surface and which ones belonging to the core of nanoparticles. There is no common principle for such choice of surface or core of the amorphous substances. One can find several choices in literature. For amorphous SiO$_2$, all atoms that were within 5.0 Å of the hull just touched the exterior of droplet were defined belong to the surface, atoms that had the distance between 5.0 Å and 8.0 Å from the hull belong to the transition zone and remaining atoms belong to the interior [49]. In contrast, for amorphous Al$_2$O$_3$ thin film they simply used the top 1.0 Å or 3.0 Å layer of the amorphous thin film for surface structural studies [51]. From structure point of view it can be considered that atoms belonging to the surface if in principle they could not have full coordination for all atomic pairs and in contrast, atoms belonging to the core if in principle they can have full coordination for all atomic pairs like those in the bulk (i.e. the model with the periodic boundary conditions). Therefore, for simplicity we assume that atoms located in the outer shell of TiO$_2$ spherical nanoparticle with thickness of 4.0 Å (i.e. the largest radius of the coordination spheres used in the system) belong to the surface and remaining atoms belong to the core of nanoparticle. Coordination number distributions for all atomic pairs in surface shell and in the core of TiO$_2$ nanoparticles at 3500 K have been presented in Figs. 5 & 6 and in Table 4. One can see that such distributions are size dependent in that the size effects are more pronounced for structure of surface compared with those in the core of nanoparticles. Mean coordination number for all atomic pairs in the surface shell increases with increasing nanoparticle size (Table 4).
In order to get more insights into the structure of TiO$_2$ nanoparticles we show temperature dependence of coordination number distribution for the Ti-O pair in 4 nm TiO$_2$ nanoparticles and in their surface shells also. One can find that upon cooling from the melt, percentage of sixfold coordinated Ti atoms to oxygen in nanoparticles strongly increases and it reaches the value of around 61% at 350 K (i.e. it becomes the most dominant in the amorphous phase, see Fig. 7). The same tendency has been found for the fraction of TiO$_7$ units, however, their fraction is small. In contrast, percentage of Ti atoms with $Z_{Ti-O} = 3$ and 4 decreases with decreasing temperature while fraction of TiO$_5$ units reaches a maximum at around 3500 K and then it decreases. This means that amorphous TiO$_2$ nanoparticles also have a distorted octahedral network structure with the mean coordination number $Z_{Ti-O} \approx 6$ and $Z_{O-Ti} \approx 3$ like those observed in the bulk amorphous TiO$_2$ [44,47]. Hence, one can assume that Ti sites with $Z_{Ti-O} \neq 6$ and O sites with $Z_{O-Ti} \neq 3$ are the structural point defects in amorphous TiO$_2$ nanoparticles. And, we found that concentration of such defects is much higher in the surface shells compared with those in the core of nanoparticles (see Figs. 7 & 8, the data for the core is not shown). Additionally, due to lack of periodic order structure there is a possible large amount of another type of point defects in amorphous TiO$_2$ nanoparticles, i.e. vacancy like defects. Interstitial large pores in amorphous TiO$_2$ can change their position with neighboring atoms and act as vacancy in diffusion process like those found and discussed previously for amorphous Al$_2$O$_3$ [46,54]. It seems that due to small dimension and specific amorphous structure there is an existence of only typical structural point defects in the surface shells of amorphous TiO$_2$ nanoparticles just discussed. It is unlike different types of structural defects observed in crystalline TiO$_2$ surfaces such as step edges, line defects, crystallographic shear planes etc. in addition to the point defects [53]. Existence of structural defects at the surfaces of amorphous nanoparticles might enhance diffusion of atomic species and it is an origin of different surface properties of TiO$_2$ nanoparticles [53]. It is essential to notice that strong red photoluminescence of amorphous SiO$_2$ nanoparticles has been attributed to the defects at their inner surfaces or it was pointed out that the intrinsic point defects are the origin of optical band gap narrowing in fumed silica nanoparticles [55,56]. The same role of point defects for similar phenomena of TiO$_2$ nanoparticles can be suggested.

In addition, we found that upon cooling from the melt toward glass transition total number of atoms (both Ti and O together) in the core of TiO$_2$ nanoparticles increases while it decreases in the surface shell. The phenomenon reflects the corresponding change not only in the mass density but also in concentration of defects in two parts of nanoparticles (Fig. 9). And may be it also causes the change in the stoichiometry (Fig. 10). At high temperatures, fluctuation of stoichiometry in the core and in the surface shell of TiO$_2$ nanoparticles has been found (see Fig. 10). However, at lower temperatures (at $T \leq 4900$ K) clear discrepancy in more stable stoichiometry of the core and surface of nanoparticles has been found, i.e. while surface has a positive deviation from the TiO$_2$ stoichiometry the core has a negative deviation. This means that oxygen-deficiency defects mainly exist in the core of nanoparticles rather than at the surface. And, in contrast one can find the existence of ‘oxygen-excess defects’ in the surface shell. The discrepancy in stoichiometries of the core and surface of TiO$_2$ nanoparticles might be related to the different electronic structure of the surface compared with those in the core or to the so called oxygen-deficiency defects in the core of TiO$_2$ nanoparticles [53]. Perhaps, electronic structure of crystalline TiO$_2$ has been calculated by using different theoretical methods and it was found that surface electronic structure is not too different from that of the bulk, except for non-stoichiometric surfaces (see Refs. [53,57-59] and references therein). Moreover, the iono-covalent character of the TiO$_2$ surface and of Ti$_x$O$_m$ clusters with different sizes and charges has been studied [60]. In average, the Ti charge is close to +1.7 (while for the formal oxidation it is of +4) and O
charge is close to -0.85 (compared with -2 for the formal oxidation) [60]. There is no work related to the stoichiometry of amorphous TiO₂ surfaces and therefore, our results give additional understanding of such important problem. The fact, the influence of stoichiometry on Raman spectroscopy of crystalline TiO₂ nanoparticles has been found and discussed [25].

C. Surface energy and glass transition temperature of liquid TiO₂ nanoparticles

Surface energy (\(E_s\)) or glass transition temperature (\(T_g\)) attract great interest. It was pointed out the role played by the surface energy in determining the cluster structure [61]. However, several subsequent works showed that such statement needs serious reconsideration when it was found a key role of surface structure in determining nanoparticle structure [13]. Moreover, surface energy is one of quantities using to test the validity of different interatomic potentials for describing surface properties of simulated nanoscaled systems [49]. On the other hand, glass transition in nanoscaled systems including in nanoparticles, in thin films and those of liquids in confined geometry has been under intensive investigation (see [62-68] and references therein). While the glass transition temperature is typically lower in the confined geometry, experiments also found the cases where \(T_g\) increases as well [67,68]. Glass transition temperature of TiO₂ nanoparticles has not been found yet and we try to get some insights into the problem in present work. In order to calculate surface energy of nanoparticles we firstly determine the potential energy per atom, \(E_{pot}\). Temperature dependence of \(E_{pot}\) for TiO₂ nanoparticles with three different sizes together with one for the bulk has been presented in Fig. 11. One can see that \(E_{pot}\) for nanoparticles is significantly higher than that for the bulk due to the surface energy of the formers and we found clearly size effects on potential energy of nanoparticles, i.e. it is higher if the nanoparticle size is smaller due to the enhancement of surface effects. Thus we can suggest the relation:

\[
E_{pot}^{nano} - E_{pot}^{bulk} = E_s / N
\]

here, \(E_s\) is the surface energy of nanoparticle and \(N\) is the total number of atoms in a model. Fig. 12 shows that \(E_s\) decreases linearly with decreasing temperature and no systematic changes in \(E_s\) with nanoparticle size have been found. Small deviations of \(E_s\) from the linearity may be related to the not good statistics of the calculations rather than they have a physical meaning. On the other hand, the value of \(E_s\) for 5 nm TiO₂ nanoparticle ranges from about 0.80 J/m² to 1.60 J/m², while it ranges from about 0.50 J/m² to 1.00 J/m² for nanoparticles with smaller size over the temperature range from 350 K to 7000 K. This means that temperature dependence of \(E_s\) is significant. There are no experimental data for temperature dependence of \(E_s\) of liquid and amorphous TiO₂ nanoparticles to compare. However, at 350 K \(E_s\) is of around 0.50 J/m² - 0.80 J/m² which is close to those calculated for the low index surfaces of anatase, i.e. it is equal to 0.35 J/m² - 0.81 J/m², or those for rutile, i.e. it is equal to 0.47 J/m² - 0.95 J/m² [30]. Moreover, \(E_s\) obtained in present work at 350 K is also close to the experimental data for low indexed surfaces of anatase or rutile, i.e. it ranges from 0.44 J/m² to 1.09 J/m² for anatase [69] or from 0.31 J/m² to 1.65 J/m² for rutile [57]. One can consider that the calculated \(E_s\) has a reasonable value, which is close to those
for crystalline ones. This means that MA interatomic potentials are suitable for representing both the bulk and surface properties of amorphous TiO$_2$.

Like those discussed above, nanoparticle size dependence of glass transition temperature is of great interest. And $T_g$ in present work was found via the intersection of a linear high- and low-temperature extrapolation of the system potential energy like those was done for the bulk Al$_2$O$_3$-SiO$_2$ liquids [70] (Fig. 13). We found that $T_g$ is equal to 1292.7 K, 1279.2 K, 1271.7 K, 1247 K, 1234 K, 1228.5 K and 1222 K for 2.0 nm, 2.5 nm, 3.0 nm, 3.5 nm, 4.0 nm, 4.5 nm and 5.0 nm TiO$_2$ nanoparticles, respectively. This means that $T_g$ increases with decreasing nanoparticle size and it is contrary to those observed experimentally for organic nanoparticles [64] (see Fig. 14). However, growing of the glass transition of liquid propylene glycol and two of its oligomers inside the pores of controlled porous glasses has been found experimentally [67]. It is essential to notice that for the bulk liquid TiO$_2$ we found $T_g \approx 1300$ K, which is slightly larger than that for nanoparticles. It is essential to notice that error in determining $T_g$ of TiO$_2$ nanoparticles is smaller than the size of symbol of the curves presented in Fig. 14. On the other hand, in order to explain the increase or decrease of $T_g$ with the size of nanoscaled substances theoretical model based on boundary condition dependence of $T_g$ has been proposed [65]. Moreover, our finding highlights the finite size effects on the glass transition which affects the stability of low-dimensional materials about it recently found and discussed in literature (see [64] and references therein). The finite size effects on $T_g$ cannot be interpreted as readily as that on the melting temperature $T_m$ due to the lack of a consensus on the nature of the glass transition [71,72]. There were several attempts for interpretation of the finite size dependence of $T_g$. For example, model on the finite size effects on $T_g$ borrowing the ideas from the theory of the second-order phase transition has been developed. This model predicts a downward shift and a broadening of $T_g$ from finite size effects constraints on a correlation length defined for the glass transition [73].

**D. Diffusion in liquid TiO$_2$ nanoparticles**

While diffusion in the bulk liquids (i.e. in models under periodic boundary conditions) has been under intensive investigations by computer simulation for the past decades it was spent less attention to the diffusion in nanoscaled liquids (see Refs. [49,74,75] and references therein). It was found that close to the surface of SiO$_2$ nanoclusters the diffusion constant is somewhat larger than one in the bulk and with decreasing temperature the relative difference grows [49]. Similar trends have been observed in other works also for diffusion in nanoscaled SiO$_2$ [74,75]. However, no work related to the study on diffusion in TiO$_2$ nanoscaled has been found in literature yet. Moreover, the validity of a power law for diffusion at high temperatures in nanoscaled systems has not been tested yet, although it was found that it shows an Arrhenius law at relative not high temperature in SiO$_2$ nanoclusters [74].

One can find diffusion constant of atomic species in the system via Einstein relation:

$$\lim_{t \to \infty} \frac{\langle r^2(t) \rangle}{6t} = D,$$

where $\langle r^2(t) \rangle$ is the mean-squared displacement of atoms. The time dependence of $\langle r^2(t) \rangle$ for Ti and O in liquid TiO$_2$ nanoparticles at 2100 K can be found in Fig. 15. One can see clearly three regimes in the curves: the ballistic one at short time and diffusive one at long time with a plateau regime separated the ballistic and diffusive ones like those usually observed in the bulk liquids. However, at longer diffusion time or at higher
temperatures when the motion of atomic species is high we observe saturation in the mean-squared-displacement of atoms because the characteristic diffusion length is of the order of the cluster size like those observed previously for SiO$_2$ nanoclusters [74]. Therefore, it is enough for calculating diffusion constant in TiO$_2$ nanoparticles via relaxation over 50000 MD steps (or 80 ps) for all temperatures studied from 2100 K to 7000 K. And in order to improve statistics, the diffusion data have been averaged over three independent runs. We investigate temperature dependence of diffusion constant in liquid TiO$_2$ nanoparticles with two different sizes of 2 nm and 4 nm (Fig. 16). One can see that similar types of the curves have been observed for both sizes, i.e. it likely shows an Arrhenius law at relative not high temperatures and it deviates from this law at higher ones. However, due to small total number of atoms in 2 nm nanoparticle not smooth curves for the diffusion data have been found and it is difficult to draw the right conclusion for such case (see Fig. 16). Hence, we test the temperature dependence of diffusion constant only for 4 nm nanoparticles. We found that it shows an Arrhenius law at relative not high temperatures and at higher temperatures (i.e. at $T > 4900$ K for Ti and at $T > 4200$ K for O) it shows a power law, $D \sim (T - T_c)^\gamma$, predicted by mode coupling theory (denoted as MCT, see more details in [76]) like those observed for other network structure bulk liquid oxides such as SiO$_2$, Al$_2$O$_3$ and GeO$_2$ [77-80] (Fig. 17). Critical temperature for a power law $T_c$ was found to be 4133 K and 3867 K for Ti and O, respectively. Such values are close to those for the bulk SiO$_2$ and GeO$_2$ at the ambient pressure. Meanwhile, exponent $\gamma$ is equal to 0.789 and 0.750 for Ti and O, respectively. This means that $\gamma$ has almost the same value for both Ti and O particles and it is in good accordance with the predictions of MCT, i.e. $\gamma$ is independent for different atomic species. However, $\gamma$ obtained in present work for liquid TiO$_2$ nanoparticles is small compared with those observed for SiO$_2$ oxide [77]. For Arrhenius law, $D = D_0 \exp \left( \frac{E}{k_B T} \right)$, we found that activation energy is rather small, i.e. 0.80 eV and 0.63 eV for Ti and O, respectively. We have no experimental data for liquid TiO$_2$ to compare. However, such value for an activation energy is much smaller than that observed in practice for silica, i.e. it is equal to 4.70 eV and 6.00 eV for oxygen and silicon, respectively [81,82]. Low activation energy for diffusion in liquid TiO$_2$ nanoparticles might be related to the larger contribution of ionic bonding to the cohesive energy of the system compared with those in silica (i.e. it is worth to notice again that TiO$_2$ is an ionic-covalent system). Overall, upon cooling from the high temperatures toward glass transition we found the transition from fragile to strong liquid behaviors for liquid TiO$_2$ nanoparticles like those observed previously in other network structure oxides, and it is related to the structural changes in the system [83,84].

**IV. CONCLUSIONS**

Structure, diffusion and thermodynamics of liquid and amorphous TiO$_2$ nanoparticles have been studied in details via MD simulation over a wide temperature range by using the Matsui-Akaogi intertomic potentials. And, several conclusions can be drawn as following:

i) Our calculations show that amorphous TiO$_2$ nanoparticles have a distorted octahedral network structure, i.e. the main structural unit is TiO$_6$ with significant number of structural defects such as TiO$_4$, TiO$_5$ and TiO$_7$. On the other hand, number of undercoordinated Ti atoms to oxygen increases with growing temperature and in liquid state the TiO$_5$ units dominate in the system like those observed in bulk liquid and amorphous TiO$_2$ [44]. However, concentration of
undercoordinated structural defects in TiO\textsubscript{2} nanoparticles is significantly higher than that in the bulk counterparts due to the surface effects [85].

ii) We found that structure of TiO\textsubscript{2} nanoparticles are strongly size dependent in that mean coordination number for all atomic pairs increases with nanoparticle size toward the value observed for the bulk, in contrast, the mean interatomic distance changes not so systematic. And due to strong Ti-O bond, the mean interatomic distance for this pair remains constant with nanoparticle size.

iii) Surface structure of TiO\textsubscript{2} nanoparticles strongly differs from those in the core and in the bulk, i.e. with higher concentration of undercoordinated units or dangling bonds due to the breaking bonds at the surfaces. We found that structure of the core of nanoparticles is close to those for the bulk, and it is weak size independent. In contrast, surface structure of nanoparticles strongly size dependent and it gives the most important contribution to the size dependence of nanoparticle structure. This indicates the dominant role played by the surface structure in determining the nanoparticle structure instead of surface energy.

iv) We found significant changes in total number of atoms in surface shell and in the core of nanoparticles upon cooling from the melt toward glass transition in that it increases in the core but it decreases in the surface shell. Moreover, stoichiometry in the core and in the surface shell is also different from each other, i.e. at $T < 4900$ K the core behaves oxygen deficiency while the surface shell has oxygen excess. This phenomenon may cause the appearance of additional defects in addition to other structural point defects existed in the TiO\textsubscript{2} nanoparticles. Our finding is important while surface chemistry studies provide a link between fundamental research and applications in heterogeneous catalysis.

v) It was found that surface energy of TiO\textsubscript{2} nanoparticles decreases with decreasing temperature and at low temperatures it has a reasonable value which is close to those observed in practice for crystalline TiO\textsubscript{2} surfaces.

vi) We found that glass transition temperature of liquid TiO\textsubscript{2} nanoparticles is size dependent in that it reduces with increasing nanoparticle size.

vii) Temperature dependence of diffusion constant of atomic species in liquid TiO\textsubscript{2} nanoparticles shows an Arrhenius law at not high temperatures and it shows a power law at higher temperatures like those observed previously in several bulk oxides.

Acknowledgement

Author thanks for the financial support from Japan Society for Promotion of Science via JSPS Invitation Research Fellow. Author also thanks Prof. T. Odagaki for the hospitality during a stay at Kyushu University. Part of the calculations was done in Computational Lab of the Institute of Technology of HochiMinh City-Vietnam.

References

TABLE I. Energy parameters of MA potentials.

<table>
<thead>
<tr>
<th>A (Å)</th>
<th>B (Å)</th>
<th>(C (\text{Å}^3 \text{kJ}^2/\text{mol}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1.1823</td>
<td>0.077</td>
</tr>
<tr>
<td>O</td>
<td>1.6339</td>
<td>0.117</td>
</tr>
</tbody>
</table>

TABLE II. Structural characteristics of liquid TiO\(_2\) at \(T = 3500\) K; \(r_{ij}\) – Position of the first peaks in PRDFs; \(\theta_{\theta_k}\) - The main peak in bond-angle distributions; \(Z_{ij}\) - The average coordination number.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(r_{ij}) (Å)</th>
<th>(\theta_{\theta_k})</th>
<th>(Z_{ij})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Ti</td>
<td>3.34</td>
<td>76.7°</td>
<td>6.45</td>
</tr>
<tr>
<td>Ti-O</td>
<td>1.81</td>
<td>103.6°</td>
<td>4.88</td>
</tr>
<tr>
<td>O-O</td>
<td>2.53</td>
<td>10.8°</td>
<td>2.44</td>
</tr>
<tr>
<td>O-Ti-O</td>
<td>2.50</td>
<td>99.0°</td>
<td>8.41</td>
</tr>
<tr>
<td>Ti-O-Ti</td>
<td>2.50</td>
<td>82.2°</td>
<td>5.06</td>
</tr>
<tr>
<td>Ti-Ti</td>
<td>2.50</td>
<td>79.5°</td>
<td>5.06</td>
</tr>
<tr>
<td>Ti-O</td>
<td>2.50</td>
<td>79.5°</td>
<td>5.42</td>
</tr>
<tr>
<td>O-Ti</td>
<td>2.50</td>
<td>80.8°</td>
<td>2.71</td>
</tr>
<tr>
<td>O-O</td>
<td>2.50</td>
<td>76.7°</td>
<td>10.38</td>
</tr>
</tbody>
</table>

TABLE III. Fraction of Ti atoms with corresponding coordination number \(Z_{Ti-O} = 3, 4, 5, 6, 7\) and 8 and fraction of O with corresponding coordination number \(Z_{O-Ti} = 1, 2, 3\) and 4 in models obtained at \(T = 3500\) K.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(Z_{Ti-O})</th>
<th>(Z_{O-Ti})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Ti</td>
<td>1.96</td>
<td>8.80</td>
</tr>
<tr>
<td>Ti-O</td>
<td>2.67</td>
<td>5.40</td>
</tr>
<tr>
<td>O-O</td>
<td>2.67</td>
<td>2.70</td>
</tr>
<tr>
<td>O-Ti</td>
<td>2.67</td>
<td>10.50</td>
</tr>
<tr>
<td>O-O</td>
<td>2.67</td>
<td>10.50</td>
</tr>
</tbody>
</table>

TABLE IV. Mean coordination number of surface and core of liquid TiO\(_2\) nanoparticles and bulk at \(T = 3500\) K.

<table>
<thead>
<tr>
<th>Materials</th>
<th>(Z_{ij})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-Ti</td>
<td>5.505</td>
</tr>
<tr>
<td>Ti-O</td>
<td>4.526</td>
</tr>
<tr>
<td>O-Ti</td>
<td>2.305</td>
</tr>
<tr>
<td>O-O</td>
<td>7.505</td>
</tr>
<tr>
<td>Core</td>
<td>7.880</td>
</tr>
<tr>
<td>Surface</td>
<td>6.258</td>
</tr>
<tr>
<td>O-Ti</td>
<td>5.400</td>
</tr>
<tr>
<td>O-O</td>
<td>2.54</td>
</tr>
<tr>
<td>4nm</td>
<td>9.760</td>
</tr>
<tr>
<td>Surface</td>
<td>8.037</td>
</tr>
</tbody>
</table>
FIG. 1. Partial radial distribution functions in liquid TiO$_2$ nanoparticles at 3500 K compared with those observed in the bulk model at the same temperature.

FIG. 2. Coordination number distributions in liquid TiO$_2$ nanoparticles at 3500 K compared with those observed in the bulk at the same temperature.
FIG. 3. Bond-angle distributions in liquid TiO$_2$ nanoparticles at 3500 K compared with those observed in the bulk at the same temperature.

FIG. 4. Density profiles in liquid TiO$_2$ nanoparticles at 3500 K.
FIG. 5. Coordination number distributions in surface shells of TiO$_2$ nanoparticles at 3500K.

FIG. 6. Coordination number distributions in the core of liquid TiO$_2$ nanoparticles at 3500 K.

FIG. 7. Temperature dependence of coordination number distribution for the Ti-O pair in the 4 nm TiO$_2$ nanoparticles.
FIG. 8. Temperature dependence of coordination number distribution for the Ti-O pair in the surface shells of 4 nm TiO$_2$ nanoparticles.

FIG. 9. Temperature dependence of fraction of Ti and O atoms in the core and surface shell of 4nm TiO$_2$ nanoparticles.

FIG. 10. Temperature dependence of TiO$_x$ stoichiometry in the core and surface shell of 4nm TiO$_2$ nanoparticles.
FIG. 11. Temperature dependence of potential energy of TiO$_2$ nanoparticles.

FIG. 12. Temperature dependence of surface energy of TiO$_2$ nanoparticles.

FIG. 13. Determination of glass transition temperature, $T_g$, of 3 nm TiO$_2$ nanoparticle.
FIG. 14. Size dependence of glass transition temperature, $T_g$, of liquid TiO$_2$ nanoparticles.

FIG. 15. Time dependence of mean-squared displacement of atomic species in liquid TiO$_2$ nanoparticles at 2100 K. The straight lines just serve as a guide for eyes.

FIG. 16. $1/T$ dependence of diffusion constant of atomic species in liquid TiO$_2$ nanoparticles. The straight lines just serve as a guide for eyes.
FIG. 17. Fit of a power law, $D \sim (T - T_c)^\gamma$, for temperature dependence of diffusion constant of atomic species in liquid TiO$_2$ nanoparticles.