Sintering Rate and Mechanism of TiO$_2$ Nanoparticles by Molecular Dynamics

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Titania is the dominant white pigment and photocatalytic material, a key component of sunscreens and has promising applications in photovoltaics and sensors of organic vapors. Here[1], the growth of TiO$_2$ nanoparticles by sintering, the critical step during their large scale manufacture and processing, is elucidated and quantified by molecular dynamics. Highly mobile ions from the particle surface fill in the initially concave space between nanoparticles (surface diffusion) forming the final, fully-coalesced, spherical-like particle with minimal displacement of inner Ti and O ions (grain boundary diffusion) revealing also the significance and sequence of these two sintering mechanisms of TiO$_2$. A sintering rate for TiO$_2$ nanoparticles is extracted that is much faster than that in the literature[2,3] but nicely converges to it for increasing particle size.

The simulations have been run on a common graphics card (NVIDIA GeForce GTX 295) and a desktop workstation (Dell Precision T3400, Ubuntu 9.10, CUDA Version 2.3). Some issues between central (CPU) and graphics processing unit (GPU) simulations have to be considered[4], especially for single precision floating point operations to achieve quite good energy conservation[5]. The open source MD code HOOMD-blue 0.8.2[6] was modified to simulate the TiO$_2$ pairwise potential of Matsui and Akaogi[7]. The original code running on one GPU attains a performance of around 34 CPUs in parallel on a distributed memory cluster for Lennard-Jones liquids with $r_{cut} = 3\sigma$[6]. There, significant computational time was used on updating the neighbor lists of the ions, but here to account for the long range interactions of the TiO$_2$ force field all ions have been included in the neighbor lists and therefore it was not updated during the simulations. The implemented TiO$_2$ potentials have been optimized with

single precision runtime math operations and benchmarking the code for different block sizes[8]. Figure 1 compares the timesteps per second at the beginning of a sintering simulation of two TiO_2 nanoparticles with diameter between 2 – 5 nm (804 – 12582 ions) obtained with the MD code LAMMPS[9] on a single CPU (triangles) and the modified HOOMD-blue (circles) on a CPU/GPU combination. The required memory for the real and "ghost" ions limited the sintering simulations to particles with initial diameters between 5 and 6 nm on the utilized GPU chip.
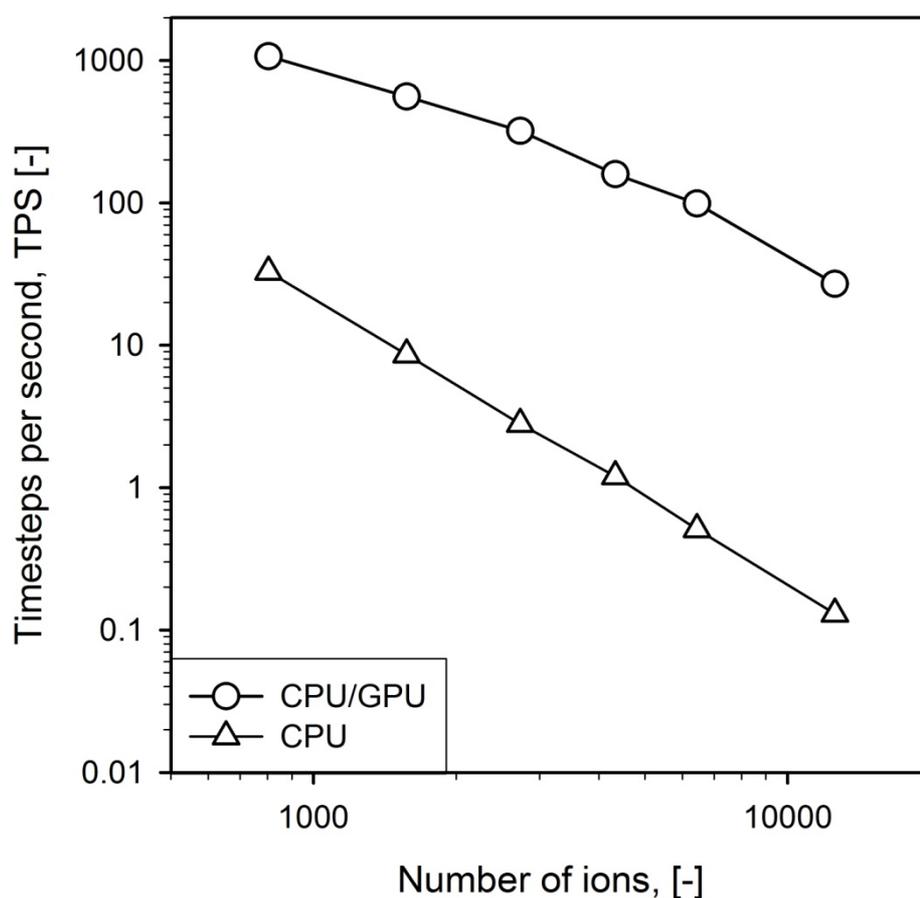

Figure 1 Time steps per second of MD simulation of two sintering TiO_2 nanoparticles (d_p = 2 – 5 nm) on one CPU (triangles, LAMMPS) and CPU/GPU (circles, HOOMD-blue) as function of number of ions.

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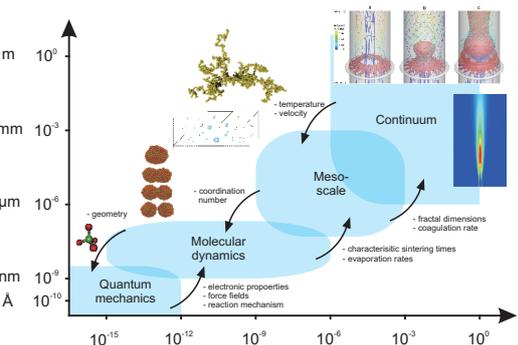
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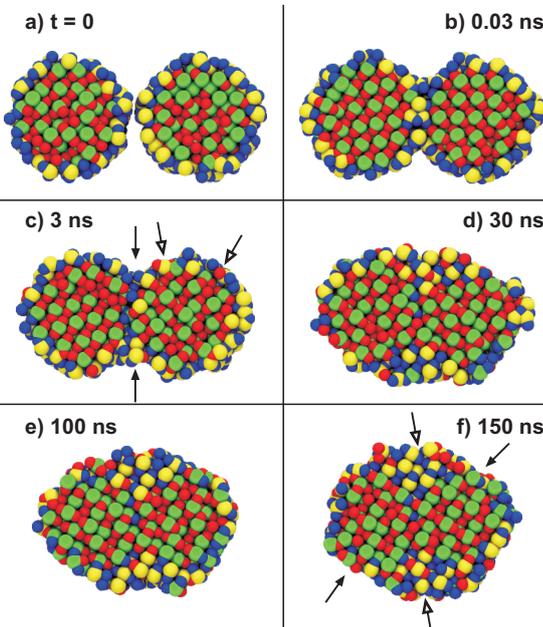Particle Technology Laboratory

Motivation

Titania (TiO$_2$) nanoparticles have many attractive applications in photovoltaic and photocatalytic processes. The performance of TiO$_2$ nanoparticles depends on their size which is determined by their sintering rate during their synthesis.

Here, the complete sintering of rutile TiO$_2$ nanoparticles is investigated by GPU-accelerated MD from adhesion and neck growth to full coalescence over several hundred nanoseconds in residence time. The sintering mechanism of TiO$_2$ is unraveled and the sintering rate is quantified by analyzing the evolution of the surface area.

Molecular Dynamics, in the multiscale simulations framwork focusing on aerosol synthesis of materials, provides sintering times as input for mesoscale/continuum simulations for reactor design or atomic structures as input for QM.

Characteristic Sintering Time, τ

Characteristic sintering time obtained by MD (symbols) along with that of Kobata *et al.* (2) (solid lines) and Seto *et al.* (3) (dashed lines) as function of $d_{p,0}$ at a) T = 1800 K and b) 1900/2000 K. The τ_{MD} are fitted by equation 3 (dotted line).

Sintering Mechanism

a) t = 0.0 ns: Ti/O ions are colored yellow/blue (surface) and green/red (bulk), respectively and shown as cross-section of the particles.

b) t = 0.03 ns: The particles have formed a sinter neck mostly by adhesion without much ion relocation leading to the surface area reduction of the first sintering stage.
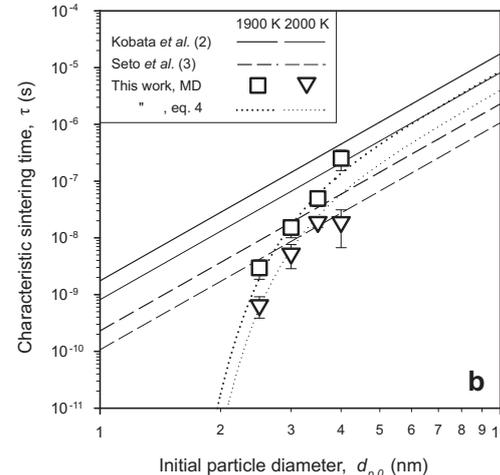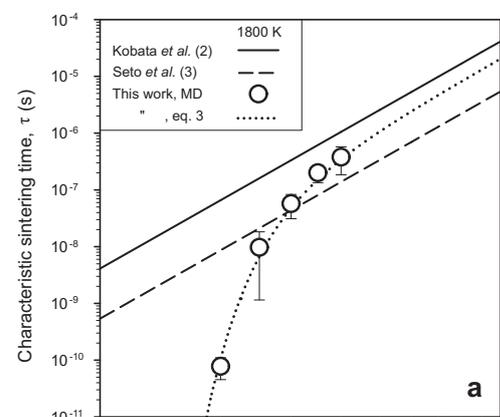
c) t = 3 ns: The sinter neck diameter has increased mostly by surface ions (yellow/blue) that have moved over the particle surface and found energetically favorable positions beginning to fill the initially concave region between the nanoparticles (surface diffusion, filled arrows). Bulk ions emerge to the particle surface (open arrows).

d) t = 30 ns: The two particles have transformed into an oval structured particle. The concave region between the nanoparticles is filled completely by initial surface Ti/O.

f) t = 150 ns: The particles coalesced into a spherical structure. The layer of yellow/blue surface ions became thin or disappeared (filled arrows). In the bulk, there are two regions of only green/red ions which experienced little movement. Surface ions in-between the original nanoparticles (b) were "squeezed" out into the formerly concave space between the particles (open arrows, grain boundary diffusion).

Sintering Rate

Experimental Characteristic Sintering Time, τ
Kobata *et al.* (2)

The τ is defined as the time needed to decrease the excess surface area $a_0 - a_{fc}$ by 67%.

$$\tau \Rightarrow \frac{a - a_{fc}}{a_0 - a_{fc}} = 0.33 \Rightarrow \frac{a}{a_0} = 0.86$$

$$\tau = 7.44 \times 10^{16} d_p^4 T \times \exp\left(\frac{258000}{RT}\right) \quad \text{(eq. 1)}$$
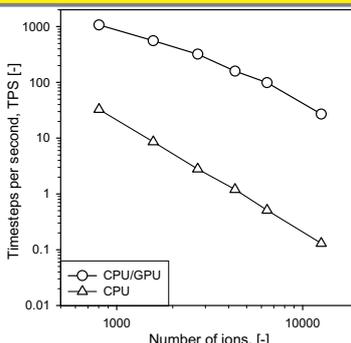
Sinter-Model
Koch and Friedlander (4)

$$\frac{da}{dt} = \frac{a - a_0}{\tau} \quad \text{(eq. 2)}$$

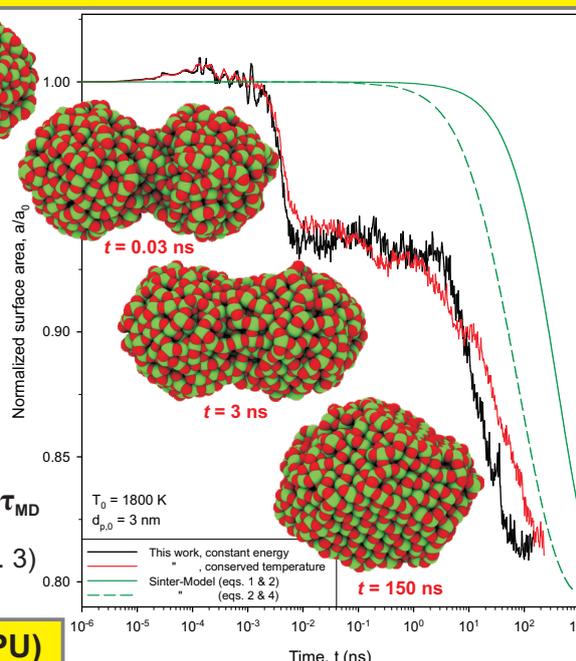### Molecular Dynamics Characteristic Sintering Time, τ_{MD}
This work

$$\tau_{MD} = 2.6 \times 10^{16} d_p^4 T \times \exp\left(\frac{258000}{RT}\left(1 - \left(\frac{2.0 \times 10^{-9}}{d_p}\frac{T}{2050}\right)^{5.8}\right)\right) \quad \text{(eq. 3)}$$

T_0 = 1800 K
$d_{p,0}$ = 3 nm

This work, constant energy
" , conserved temperature
Sinter-Model (eqs. 1 & 2)
" (eqs. 2 & 4)

t = 0 ns
t = 0.03 ns
t = 3 ns
t = 150 ns

Graphic Processing Unit (GPU)

Timesteps per second as function of total number of atoms of HOOMD-blue on one CPU/GPU (circles) along with LAMMPS on one CPU (triangles) for two particles with $d_{p,0}$ = 2, 2.5, 3, 3.5, 4 and 5 nm (1). Hardware: Dell Precision T3400, NVIDIA GeForce GTX 295. Software: Ubuntu 9.10, CUDA 2.3.

Conclusions

Molecular Dynamics reached complete coalescence of small rutile TiO$_2$ nanoparticles. Calculations accelerated by GPU reduced the simulation time considerably. Ions on the particle surface exhibit higher mobility than bulk ones. Sintering by grain boundary diffusion takes place but to a lesser extent. This reveals that surface diffusion is the dominant sintering mechanism. The sintering rate was quantified by extracting a characteristic sintering time. For the smallest particle diameters, these MD sintering times were shorter than those predicted by theory developed for larger particles, but converge around $d_{p,0}$ = 5 nm.

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