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DYNAMICS OF NANOMETER SiO2 PARTICLES AND THEIR COALESCENCE CHARACTERISTICS

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ABSTRACT

Various mechanisms of glassy transformations involving computational annealing were investigated by Molecular Dynamics simulations. Large clusters of silicon dioxide ranging from sub to nanometer size regime were considered. Silica is both a prototype ceramics and glassy material. Silica particles are fabricated in flow and flame reactors to design novel granular materials which depend strongly on the heating and cooling processes. During these processes extensive thermally driven relaxation in growing clusters allow for configurational changes from a liquid-like cluster to a glassy cluster. Crystal-like structures were investigated as well. Cooling rates comparable to experimental rates were achieved in these simulations. We find that the glass transition temperature decreases with decreasing cluster size. Calculations were performed by implementing a massively parallel particle decomposition schema of Molecular Dynamics with an excellent speedup and a significant decrease of complexity.

INTRODUCTION

Formation of ceramic particles from the products of combustion mechanisms in flow and flame reactors is one of the novel techniques used to fabricate granular thin films and coatings.[1-5] The building blocks of these films are particles in the nanometer size regime fabricated with the aim to enhance and control their properties.[6] In the gas phase solid cluster structures are formed at temperatures characteristic of the flame or above (2000K to 3000K) and later deposited on surfaces undergoing a fast cooling process. Both mechanisms, particle growth in the gas phase and cluster deposition to yield a final thin film are not fully understood. In this arena the atomistic approaches are very scarce.[6] The aim of this work is to build understanding in this direction by investigating some mechanisms by which either crystalline, polycrystalline or glassy particles may be obtained from the liquid-like state.

A number of Molecular Dynamics simulations have been performed to simulate bulk related properties of crystalline and glassy SiO_2 using effective pairwise additive interatomic potentials.[7-13] Recently Tsuneyuki et al[7,10] have developed an optimized two-body potential fitted on ab initio calculations of tetrahedral SiO_4^{4-} clusters including long range Coulomb interactions between localized effective charges. This potential has been used in crystalline and glassy bulk simulations in recent years.[10,13] In this work we use this potential to model the interactions of Si-Si, Si-O and O-O in clusters containing tens to hundreds of SiO_2. Results presented here on the liquid glass transition and structural properties of silica particles are our first attempts in the study of the agglomeration and coalescence mechanisms of particle deposition.

MODEL POTENTIAL

The atomic interactions are modeled through a sum of pairwise additive terms, each of them containing a Born-Mayer-type repulsion, Coulomb interaction and a dispersion term[7] between every pair of atoms:

$$U=\sum_{i<j}\{f_0(b_i+b_j)\exp[(a_i+a_j-r_{ij})/(b_i+b_j)]+u_{ij}^{Coulomb}(r_{ij})-c_ic_j/r_{ij}^6\}$$

Here r_{ij} is the distance between atoms and a_i (b_i) are the effective radius (softness parameter) of the ith atom and f_0=1 kcal/A/mol. Molecular Dynamics is used to follow the time evolution of the system by solving the classical equations of motion of every atom in the cluster. Due to the nature of the proposed potential, these equations are second order ordinary differential equations containing highly non-linear terms. These ode's are solved numerically by third order finite difference methods and a time step of 3.5 fs to ensure conservation of energy.[14] The initial configurations are spherical structures of SiO_2 arranged in the positions of the α-quartz crystal at room temperature. Typical runs to bring the system to equilibrium were conducted over several tens of thousands of time steps.

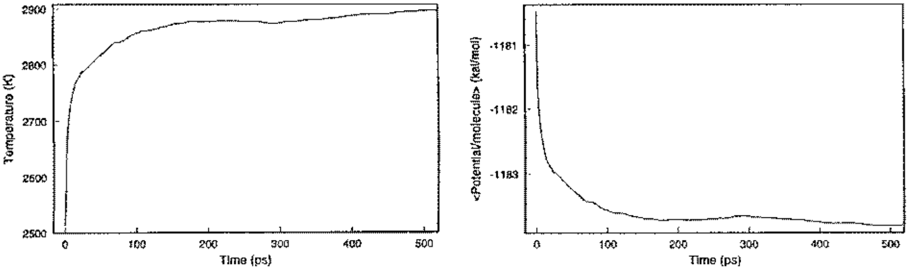

Fig. 1 Temperature (left) and average potential energy (right) as a function of time after the collision of two 64-molecule clusters that coalesce into a large 124-molecule cluster. The temperature of the colliding clusters and the collision energy was 2500K.

THE GLASSY STATE

Our search of the glass transition in these silica particles was based on two pre-cooling strategies to reach the liquid state. In the first the particles were grown larger by previous collision between smaller particles.[6] The small particles stick together and give rise to larger particles at higher temperatures.[6,15] Results from a typical collision between two 64 SiO_2 is depicted in Fig. 1. The temperature increases after the collision (1a) whereas the potential energy (1b) decreases accommodating the collision energy. The collision process was continued until reaching temperatures of about 2600K to ensure that particles are liquid-like. The second heating strategy was based on the scaling of the atomic velocities of a cluster previously equilibrated at a lower temperature until the 2600K were attained.

Once the particles are hot and in the liquid state they were subjected to an annealing process that initiates by cooling the liquid particles in a step-like manner with a scaling of the particle velocities. The first 10,000 steps of each cooling step were used to reach equilibrium whereas energy averages were calculated on the last 5,000 steps. A cooling rate of 200K/ns was achieved. Fig. 2 shows the cooling curves for three cluster sizes. The liquid to glass transition is identified at the point where the slope of the energy versus temperature presents a change. This change in the slope is however small and takes place in a smooth fashion around the transition temperature. More noticeable are the fluctuations that become smoother as temperature decreases. Cooling processes starting from clusters heated in the two different fashions gave rise to almost indistinguishable curves for internal energy as a function of temperature indicating that the history behind the liquid state is not important in the formation of the glass.

The transition temperature depends strongly on the size of the cluster. Small clusters with

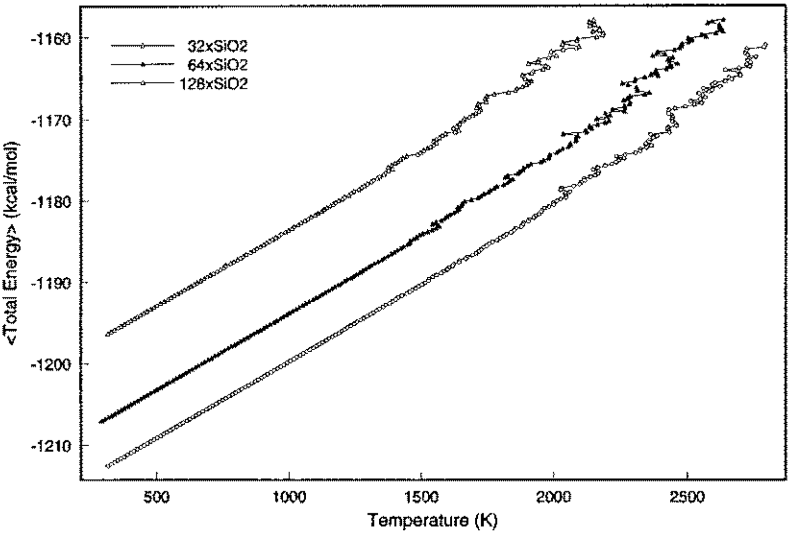

FIG.2 Total cluster energy as a function of temperature for clusters with 32 (top), 64 and 128 (bottom) SiO_2 molecules.

tens to one hundred SiO_2 molecules exhibit the glass transition at temperatures up to 20% below the equivalent bulk transition temperature of 2200K. When the cluster reaches a size of 128 molecules, the discrepancy is of only 5%. In Table I we report the region of temperatures around the glass transition for particles containing 32, 64 and 128 SiO_2 molecules. We arbitrarily estimated the glass transition temperatures as the center of that region. Below the transition temperature region the atoms are oscillating about fixed positions indicating that the molecules are locked into a solid-like configuration. The constant volume heat capacity $C_v = 0.0185 \pm 0.0008$ kcal/mol K was obtained from the low temperature portion of the curves in Fig.1 for all the cluster sizes investigated in this work This value is consistent with $9k_B$,the classical limit of a harmonic solid.

TABLE I. Glass transition temperature and temperature regions within which the glass transition is located as a function of the cluster size

No. of SiO_2 Molecules in Cluster	Transition Temperature Region (K)	Glass Transition Temperature (K)
32	1400-1750	1550
64	1550-1850	1700
128	2000-2200	2100

CLUSTER STRUCTURE

Glass and liquid structure are best visualized through the radial distribution functions. Since a number of equilibration processes were investigated, for each of them we calculated the pair distribution functions $g_{Si\text{-}Si}$, $g_{Si\text{-}O}$ and $g_{O\text{-}O}$ as a function of size and temperature. In Fig 3 the pair distribution functions of two sets of simulations are shown and compared to the crystal-like ones for the 32-molecule cluster. Figures on the top of Fig. 3 show g_{Si-Si} (left), g_{O-O} (center) and g_{Si-O} (right) for a spherical cluster in the α-quartz configuration, whereas the other figures show the changes to the structure when the clusters are equilibrated at 300K before (middle) and after annealing (bottom).

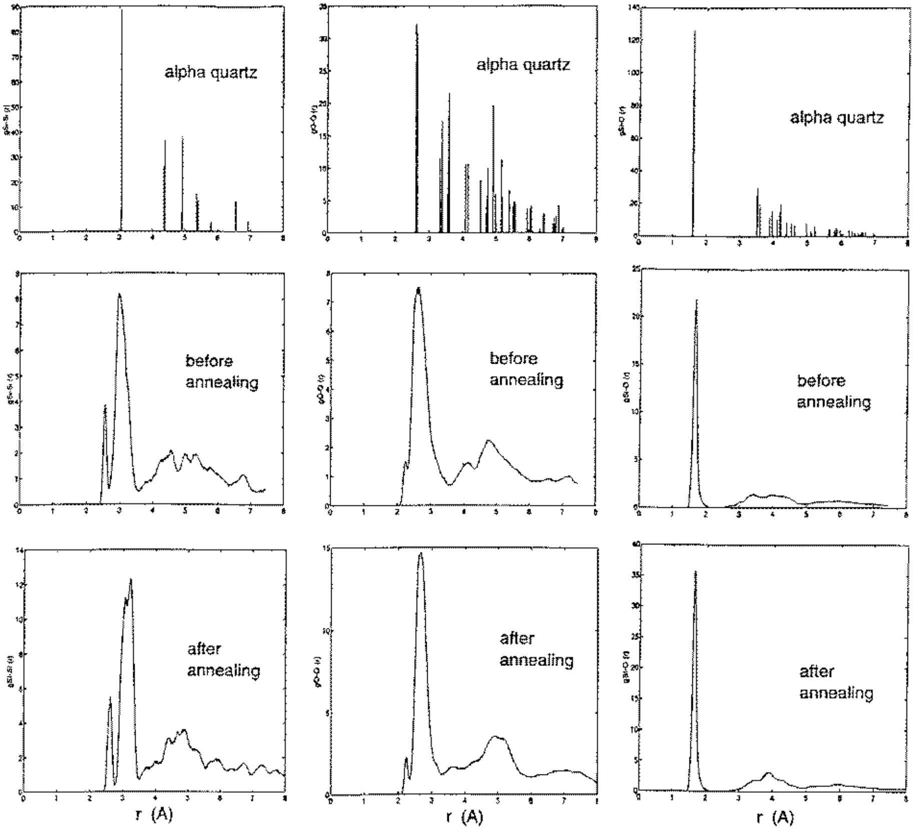

FIG 3. Pair distribution functions g_{Si-Si} (left), g_{O-O} (center) and g_{Si-O} (right) for 32-molecule clusters in the α-quartz configuration (top) and at 300K before annealing (center) and after annealing (bottom).

Both g_{Si-Si} and g_{O-O} pair distribution functions show a distinct peak at short distances which is absent in the crystalline configuration. The novel short distance features prevail in the 64 and 128-molecule clusters. We attribute this new feature to re-arrangements of Si-O bonds into 4-member rings. These peculiar rings, absent in the α-quartz, are primarily formed at the surface of the clusters. It is important to note that these novel ring formations are also present in the glassy clusters (bottom figures). The g_{Si-O} function for any cluster size does not present major changes when passing from crystal to glass (see left column in Fig. 3). This fact indicates that the first-neighbor bonding structure is not significantly affected by either the annealing process nor the thermal surface reconstruction.

At the glass transition temperature (or above) the short distance peaks of the pair distribution functions are smeared out into one broad first peak with a prominent tail at short distances. In Fig. 4 the three pair distribution functions at 2200K for a large 128-molecule cluster are reported. The position of the first peak in the three cases is remarkably close to the calculated[13] and experimental[16,17] values reported for bulk silica. On this basis we conclude that the mechanism of thermal surface reconstruction in small clusters is extremely strong and that glassy transformations initiate at temperatures well below the glass transition.

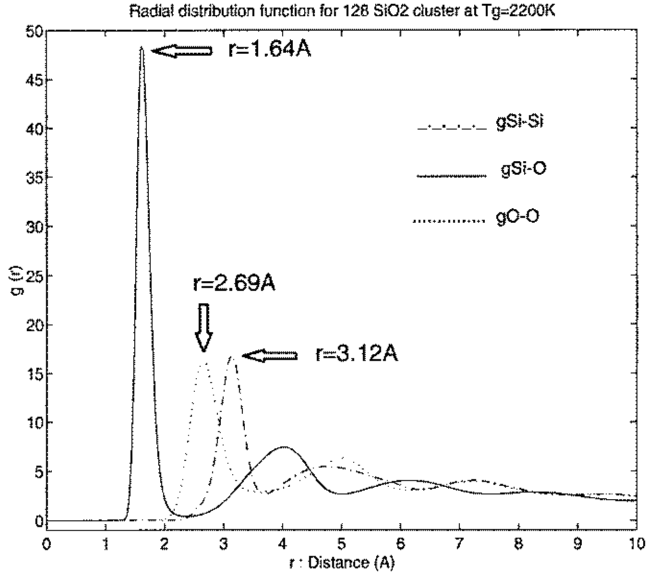

Fig. 4 Pair distribution functions $g_{Si\text{-}Si}$ (-·-·-), $g_{O\text{-}O}$ (····) and $g_{Si\text{-}O}$ (——) for the 128-molecule cluster at T=2200K.

SINTERING OF CLUSTERS

Sintering simulations were conducted to investigate the time and temperature dependence of voids created between three clusters physisorbed on a surface. Assuming that glassy particles are formed in the gas phase, during the process of surface deposition voids are inevitably generated. We have modelled simple voids at room temperature by placing three clusters of the same size radially located from the center of an empty circle of diameter d. Typically the sintering process of these simple voids lasted a few ps. The long range interactions are extremely important during the process of sintering. Due to these interactions the clusters around the void have the ability to increment their temperature by 200 to 300K in less than 10 ps. The behavior is depicted in Fig. 5a. Since the mobility of the atoms is larger, they start migrating towards the center of the void with a peculiar deformation of the cluster shape. Very fast, in just a few ps, the shape deformation is so strong that the void is filled with atoms. Si-O bonds are formed locking the structure into large agglomerates of three clusters. The rate of sintering is fast at the beginning of the process and remains a constant after the first few ps (see Fig. 5b). Sintering rates are slightly slowed down when the void is made up of crystal-like clusters.

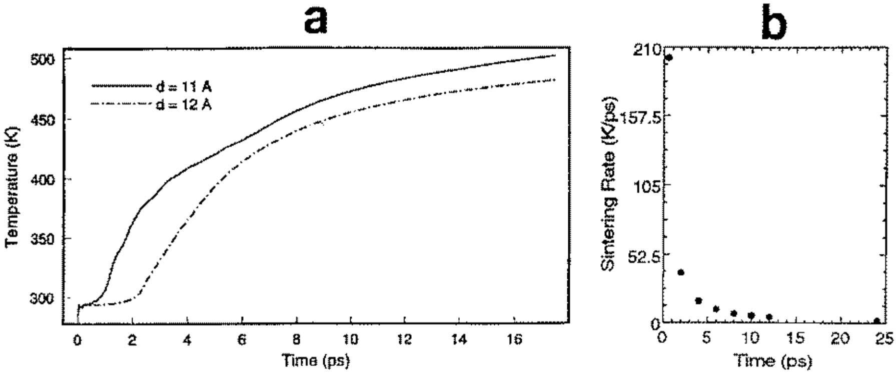

Fig. 5 Sintering of three 64-SiO_2 clusters. (a) Internal temperature of the void as a function of time. (b) Sintering rate as a function of time.

CONCLUSION

In conclusion, we have conducted Hamiltonian molecular dynamics simulations of the liquid-glass transition in silica clusters. The transition temperature decreases with the size of the silica particle up to 20% less than in the bulk material temperature. In turn this is an indication of the strong influence of that the thermal reconstruction of the cluster surface plays in the glass transition. The surface reconstruction is mainly lead by the formation of 4-member rings which are absent in the crystalline allotropes of SiO_2. The computational strategy used in the above computations allowed us to implement the particle decomposition parallel strategy in the Intel Paragon at George Mason University. This computational schema gave rise to a significant reduction in the complexity of the problem and an almost ideal speedup.

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REFERENCES

1. M. R. Zachariah and H. G. Semerjian, AIChE. J. 35, 2003 (1989).
2. S. L. Chung and J. L. Katz, Combust. Flame 61, 271 (1985).
3. F. Gelbard F.,Y. Tambour, and J. H. Seinfeld, J. Colloid Inteface Sci. 76, 541 (1980).
4. S. H. Bauer and D. J. Frurip, J. Phys. Chem. 81, 1015 (1977).
5. R. A. Dobbins and G. W. Mulholland, Combust. Sci. Technol. 40, 175 (1985).
6. E. Blaisten-Barojas and R. M. Zachariah, Phys. Rev. B 44, 4403 (1992).
7. S. Tsuneyuki, M. Tsukada, H. Aoki, and Y. Matsui, Phys. Rev. Lett 61, 869 (1988).
8. J. R. Rustand, D. A. Yuen, and F. J. Spera, Phys. Rev. A 42, 2081 (1990).
9. J. S. Tse, D. D. Klug, Y. Le Page, Phys. Rev. Lett. 69, 3647 (1992).
10. S. Tsuneyuki, H. Aoki, and M. Tsukada, Phys. Rev. Lett. 64, 776 (1990).
11. B. P. Feuston and S. H. Garofalini, J. Chem. Phys. 89, 5818 (1988).
12. G. J. Kramer et al., Phys. Rev. B 43, 5068 (1991).
13. R. G. Della Valle and H. C. Andersen, J. of Chem. Phys. 97, 2682 (1992).
14. E. Blaisten-Barojas and D. Levesque, Phys. Rev. B 34, 3910 (1986).
15. J. G. Gay and B. J. Berne, J. Colloid Interface Sci. 109, 90 (1986).
16. J. H. Konnert.and J. Karle, Acta Crystallogr. A 29, 702 (1973).
17. D. I. Grimley, A. C. Wright, and R. N. Sinclair, J. Non-Cryst. Solids 119, 49 (1990).