

9/28/98 9:58:58 am, Journal of Non-Crystalline Solids

MOLECULAR DYNAMICS SIMULATION OF VITREOUS SILICA STRUCTURES

Norman T. Huff*,

Owens Corning Science and Technology Center, 2790 Columbus Road, Granville, OH 43023-1200

Ersan Demiralp, Tahir Çagin, and William A. Goddard III

Materials and Process Simulation Center, 400 South Wilson, Beckman Institute (139-74),

California Institute of Technology, Pasadena, CA 91125

Abstract

Molecular dynamics (MD) simulations can be used to gain insights into the atomic level structure of glasses not easily accessible to experiment. However, to reliably obtain accurate results it is essential to choose the proper force fields (FF), the proper length of the simulation cell, and the proper cooling cycle to generate the 300K structure from the melt. Herein we establish guidelines for these choices. We find that the MS-Q FF and the MSI glass FF both lead to good agreement with the radial distribution function (RDF) from SANS experiments.

We find that the simulation cell should contain about 3000 atoms to obtain a density within 1% and accurate RDF, but a cell of 648 atoms leads to a good RDF and a density within 4%. We find that a good compromise between accuracy and reproducibility of results and simulation time is to start with NVT dynamics at 8000K followed by cooling to room temperature at the rate of 100K/2ps.

PACS : 61.43.Fs, 64.70.Pf, 61.20.Ja

keywords : silica glass, molecular dynamics, force fields, structure, neutron scattering

1.0 Introduction

Over the past 15 years, the use of Molecular Dynamics (MD) techniques to simulate glass structures has become a valuable tool for gaining insight into the structure of glasses at the atomistic level [1]. However, the manner in which the MD simulation is carried out can affect the structure observed for the glass. Such simulations involve a series of MD simulations using a 3-dimensional periodic supercell containing 500 to 5000 atoms. Generally the system is randomized, for example by melting at very high temperature and then annealed at a sufficiently slow rate that the system can adopt the same amorphous structure as that of a real glass. For sufficiently long times and for sufficiently large periodic cells, one would expect to obtain an atomistic structure corresponding to the real system, assuming that the Force Field (FF) used to calculate the forces is accurate. However, for very large cells and very slow annealing, the calculational costs can become prohibitive. Consequently, it is of interest to understand just how small the cell can be and how fast the annealing can be and yet obtain accurate results. In addition, it is necessary to establish whether the FF leads to results in agreement with experimental observables. We address these issues of FF, cell length, and cooling rate in this paper, paper, for silica glass (SiO_2). Section 2 discusses the various aspects of the calculations, including the type of dynamics, the FF, the cell length, the cooling protocols, and the properties to be evaluated. Section 3 presents the results, while Section 4 discusses these results. The conclusions are given in section 5.

2.0 Elements of the Simulations

2.1 Dynamics

There are three flavors of MD in common use:

- NVE indicates that during the dynamics the Number of particles, Volume, and Energy are kept constant. This corresponds to classical Newtonian Dynamics of an isolated system. We did not use NVE in this paper.
- NVT differs from standard Newtonian dynamics (NVE) in that the energy of the system is allowed to fluctuate as if the system were in thermodynamic equilibrium with a bath at fixed temperature (a Nose-Hoover thermostat) [2]. We use NVT dynamics to anneal the system at high temperature, removing biases from the initial structure. Here we used a volume corresponding to a silica density of 2.17454 g/cc.
- NPT differs from NVT dynamics in that the volume of the systems is allowed to change in the same way as it would for a system in thermodynamic equilibrium with a pressure bath at fixed pressure (1 atmosphere). In order to allow the system to adopt the density demanded by the FF, we always anneal the system using NPT dynamics at $T = 300\text{K}$.

The software used for these MD calculations is release 3.0 and 3.5 of Cerius² by Molecular Simulations Incorporated [3]. All simulations used a time step of one femtosecond (0.001 picosecond).

2.2. Lengths

For the structure to be truly amorphous, we should use an infinite cell length. However, (small angle xray scattering) data [4] indicates significant variations (~1%) in the density of silica glass over distances of about 30 Å. This suggests that one should use cell lengths of over 30Å to obtain the least biased results.

We considered three cell lengths:

- Small: 648 atoms (216 Si and 432 O atoms) in a cubic cell ~ 21.5 Å on a side. Most tests were made on this system
- Medium: 1536 atoms (512 Si and 1024 O atoms) in a cubic cell ~ 28.6 Å on a side. Only a few calculations were made on this system.
- Large: 3000 atoms (1000 Si and 2000 O atoms) in a cubic cell ~ 35.8 Å on a side. We concluded that this is needed to obtain an accurate structure for silica.

The initial arrangement of atoms in the cells is that of crystalline cristobalite, which has a density (2.176 g/cc) similar to that of silica glass (2.19 to 2.20 g/cc).

2.3. Force Fields

We considered three FF:

- MSI GFF: This is the glass force field 2.01 supplied with the Cerius² software [3]. Most calculations aimed at determining the effect of cooling cycle and cell length were carried out with this FF. In addition to two-body Morse bond interactions and fixed charges, the MSI GFF uses a 3-body term similar to that employed by Garofalini and coworkers [5]. In addition, it uses exponential-6 nonbond interactions plus Coulomb.
- TATM FF: This force field (FF) developed by Tsuneyuki et al. [6] uses two-body exponential-6 interactions between all atoms plus Coulomb terms with fixed charges.
- MS-Q FF: This FF developed by Demiralp et al [7] differs from previous FF's for SiO₂ in that it **allows the charges to adjust self consistently to the instantaneous configuration of atoms**. Otherwise, it uses a two body Morse stretch term but does not include 3-body terms. The concept behind MS-Q is that for ionic or polar materials, electrostatics plays an essential role in determining the structure and properties of the materials. However, the charges responsible for the electrostatic effects may depend on the atomic configuration. To predict the charges for MS-Q we use the charge equilibration procedure (QEq) [8]. QEq includes the short range shielding of charges so that there are no nonbond exclusions. In MS-Q, the 2-body terms were derived to fit the structural properties of cristobalite, stishovite, quartz, etc. Table I includes the Morse parameters for the MS-Q FF used in this paper.

2.4 Cooling Cycles

A typical MD simulation for silica glass begins with a NVT anneal at some high temperature (typically 6000 K or higher) for tens of picoseconds. This is done to remove any “memory” of the starting arrangement of the atoms. The temperature of the system is then reduced in steps of 100K to 2000 K, NVT annealing for some time at each step (typically tens of picoseconds), until the ambient temperatures are reached. The structures generated with these MD simulations are sensitive to the temperatures and times used in the multi-step procedure

We considered two types of cooling cycles.

- Big steps (type 1): Here the cooling cycles involve abrupt decreases in the temperature by decrements of 1000 K to 6000 K followed by a relaxation period. Table II specifies the details for the specific cooling cycles used here. For example, cooling cycle 1-I consists of 20 ps of NVT dynamics at 8000 K followed by 20 ps of NVT at 4000 K, 2000 K, and 1000 K. This is followed by 10 ps of NVT dynamics at 300 K and then 30 ps of NPT dynamics at 300 K and 1 atmosphere pressure. Figure 1 shows graphically the case of 1-VIII.
- Small steps (type 2): Here the temperature decrements are only 100 K during most of the cooling cycle. At each temperature step, a brief annealing is allowed. Table III specifies the details for the specific cooling cycles used here. For cycles 2-I through 2-V, the 100K decrements go from 3900K to 400K. For cycles 2-VI through 2-VIII, the 100K decrements go from 7900K to 400K. For example, in Cycle 2-I, 20ps of NVT dynamics are performed at 8000K followed by 60 ps at 4000K. NVT dynamics are then run at 3900 K for 4 ps, at 3800 K for 4 ps, at 3700 K for 4 ps, etc. through 400 K. Finally, at 300K we do 10 ps of NVT dynamics followed by 30 ps of NPT dynamics. Figure 1 shows graphically the case of 2-VIII.

2.5 Properties

In order to validate the accuracy of the force field and the efficacy of the MD procedure in predicting correctly the amorphous structure of silica glass, we want to compare with experimental structures. Unfortunately, the detail in the experimental data is limited by the amorphous nature of the systems.

Detailed information about the structure of silica glass may be obtained from neutron diffraction experiments. Here, the fundamental quantity to be compared is the total correlation function

$$T(r) = 4\pi r \rho \langle r(r) \rangle$$

where $\rho(r)$ is the density function. Thus, we compare the silica structures resulting from different force fields to an experimental total correlation function [9], which can be written as

$$T(r) = 4\pi r \rho_o N_{uc} \left\{ \sum_{i,j} f_i f_j b_i b_j G_{ij}(r) \right\}$$

where b_x is the neutron scattering length, f_x is the fraction of x-type atoms, ρ_o is the average density, N_{uc} is the number of atoms per unit composition, and $G_{ij}(r)$ is the radial distribution function. Figure 1 makes

such comparisons for the final structures from the NPT dynamics. Here we average over the final 15 ps of the 30 ps NPT dynamics using the structure every 0.1 ps.

Useful but much simpler characterizations are given by:

- the average coordination number of Si atoms (should be 4 for > 99%)
- the average coordination number of O atoms (should be 2 for > 98%)
- the distributions of Si-O bond distances (should be ~ 1.62 Å)
- the distributions of O-Si-O bond angles (should be $\sim 109.5^\circ$)
- the distributions of Si-O-Si bond angles (should be $\sim 150^\circ$)

The bond angles and coordination numbers are calculated based upon an algorithm by Garofalini [10]. A more global but very important parameter is the density of the glass, which we calculate every time step during NPT dynamics.

3.0 Results

The results are shown in Tables IV, V, and VI. In Tables IV and V, we used only the MSI gff. Table IV uses a cell containing 648 atoms while Table V uses a cell containing 3000 atoms. Table VI shows results for a variety of force fields.

The first column in Tables IV and V shows which cooling cycle from Tables II and III is used. Note that there are at least two (completely independent) runs for each of the cooling cycles.

The columns labeled O-Si-O and Si-O-Si characterizes the distribution in the bond angles in terms of:

- the location of the peak (in degrees) and
- the width of the peak at one-half the maximum peak height (fwhm) (the number after the “/”)

The location of the peak and width are calculated using one degree increments for the angle “bins” in the bond angles histogram. The Si-O-Si angle distribution peak is very broad: consequently, differences of 1° or 2° in the peak position are not considered significant.

The next column shows the percentage of Si atoms that are 4-fold coordinated. The balance of the Si atoms are either 3 or 5 coordinated. Two atoms are considered coordinated if they are within 1.1 times the sum of the bond radii of the two atoms.

The next column shows the percentage of O atoms that are 2-fold coordinated. The balance of the O atoms are 1 or 3 coordinated.

The next column, labeled Density Range, shows the range in the densities averaged over 200 femtosecond steps during the last 15 ps of the NPT simulations. The number after the “ / ” represents the range of the averaged densities. Typically, the density averaged over 200 fs oscillates with a period of 0.5 to 1 ps. (This frequency is determined by the Nose-Hoover thermostat, where the relaxation time constant is taken as 0.25 ps.)

The column labeled Average Density is the average density of the structure during the last 15 ps of the NPT simulations. For those cooling cycles with 40 ps of NPT dynamics, the densities are from the last 20 ps of the simulation.

In Table VI, data for different force fields are presented. The particular force field and the number of atoms in the cell are presented. Unless otherwise noted, the cooling cycle used in this table is 2-I. When alternate cooling cycles are used, it is also indicated in the first column of Table VI. The remaining columns in Table VI contain the same data as found in Tables IV and V.

4.0 Discussion

4.1 Radial Distribution Function

Figure 1 compares with experiment [9] the $T(r)$ for 648 and 3000 atom cells using the MSI and MS-Q Force Fields. Here we see quite similar results for the two lengths and quite good agreement with experiment for both the MS-Q FF and the MSI FF. In particular, the 3rd peak describes the Si-Si distance that determines the experimental Si-O-Si bond angle.

4.2 Cell length

Comparing the results in Tables IV and V, we see that Table V (with 3000 atoms) has considerably less variation in the density range than Table IV with 648 atoms. For example, considering simulations with identical cooling cycles run with both 648 and 3000 atom cells (1-IV, 1-VII, 1-VIII, 1-IX, 2-I, 2-VI), in Table IV, the density range for the 648 atom system is 0.025 g/cc while the density range for the 3000 atoms system is 0.011 g/cc. For identical cycles, the largest difference in average density for 648 atoms systems is 0.094 g/cc (more than a 4% variation) while the largest difference for 3000 atom systems is 0.021 g/cc (a 1% variation). We consider that 1% deviations should be acceptable for many purposes. However, we consider that 4% is not acceptable. **Thus, we consider that it is essential to use about 3000 atoms in order to obtain reliable structure for silica glass.** Apparently, there are significant random variations (~4%) in the density of the glass over regions of ~15 to 20Å.

These variations probably arise at high temperatures. As the temperature decreases, the mobility of the various atoms decreases and the random variations are “frozen in” to the room temperature structure. We do not find the density variation to be correlated with either the calculated bond angle peaks or the coordination numbers.

To further characterize density variations, we analyzed a number of 3000 atom simulations by partitioning the cell into 5 slabs of equal volume (each with ~ 600 atoms). The difference between the actual number of atoms in the slab with the least and the most atoms was typically 5 to 7%. However for one simulation, we observed a density variation of over 11%. These results suggests that regions of ~600 atoms may exhibit variations in apparent density by 6%.

From stereoscopic visual examination of the final structure, we find “voids” of 6 to 8 Å in diameter contained in the glass network. However, we observe no evidence of crystalline ordered regions separated by “defects.” This suggests that the variations in density are **not** associated with a “crystallite” type of structure but rather the random variations of atomic density dictated by the various lengths of the SiO₂ rings in the glass structure.

Experimental SAXS data on amorphous silica suggests significant density fluctuations in regions about 30 Å in diameter. This corresponds to a region containing about 2000 atoms. This suggests that to validate the accuracy of MD simulations in representing the glass structure by comparison to experimental data, **one should use simulations with cell volumes of at least 40 nm³ (a cube about 34 Å on a side).**

4.3 Cooling Cycle

Focusing now on the impact of cooling cycles upon the structural parameters, the most prominent item in Table IV is the very narrow peak distributions and coordination number distributions for cooling cycle 1-V. In this particular cooling cycle, 40ps of dynamics at 6000° K apparently did not significantly distort the atoms from their crystalline lattice positions. As a result, the subsequent lower temperature dynamics simulations allowed the atoms to reorganize into a very nearly crystalline lattice arrangement. Note, however, that the density is quite low for the cristobalite-like structure that was generated. (The MSI force field was not parameterized to fit cristobalite). From the results using other cooling cycles (e.g. cooling cycles 1-I and 2-I) it appears that **a minimum of 20 ps of NVT dynamics at 8000 K is required** to displace the atoms from their original location sufficiently to remove all “memory” of the initial structure from the final room temperature structure.

Cooling cycles 1-II, 1-VI, 1-VII and 1-X suggest that some relaxation at temperatures between 2000 and 4000 K is essential to obtain well-equilibrated glass structures. For example, cooling cycles 1-II, 1-VI and 1-VII (with no intermediate temperature MD) lead to structures with 95% or less of the oxygen atoms being 2-fold coordinated. Cooling cycle 1-X has 40 ps of relaxation at 2000 K but even here, the percentage of 2-fold coordinated oxygen atoms is still only 97%. Indeed cycle 2-V [which omits the 4000K simulation but has gradual (100K/ps) anneal from 4000K] produces structures with less than less than 97% 2-fold coordinated O atoms. With annealing times at 4000 K of 20 to 60 ps before the gradual anneal, the structures contain more than 98% two coordinated oxygen atoms. In addition to the relatively low numbers of 2-fold coordinated oxygen atoms, the Si-O-Si bond angle distribution is relatively broad for these cooling cycles that quench too rapidly. We find that **cooling cycle 2-VIII is close to an optimum** trade off between fairly well relaxed structures and the time required for the cooling cycle.

4.4 Dependence of density on Force Fields

Table VI shows results for three different force fields. The first item to notice in this table is the difference in final density with the three force fields. Thus using cooling cycle 2-I with the 648 atom cell, the density varies from an average of 2.17 g/cc (range 0.08g/cc) for the MSI FF to 2.24 g/cc (range 0.06 g/cc) for the MS-Q FF to 2.31 g/cc (range 0.02 g/cc) for the TATM FF. For 3000 atoms the MSI FF lead to 2.141 (cooling cycle 2-I), 2.147 (cycle I-VIII), and 2.169 (cycle 1-IX) whereas MS-Q leads to 2.23 g/cc (cycle 1-VIII) and 2.236 (cycle 1-X). Thus, it appears that the MSI FF leads to densities 0.07 to 0.09 g/cc lower than MS-Q while the TATM FF gives densities about 0.07 g/cc higher than the MS-Q FF. It is also interesting to note that the density spread and the density for the MS-Q force field appears to be less sensitive to the amount of low temperature annealing than is the MSI force field (e.g. cooling cycle 1-VIII vs. 1-X for the 3000 atom simulations).

4.5 Deviation of Si and O coordination of force field.

Considering 648 atoms and cycle 2-I we see that the TATM FF has almost all (> 99%) Si in 4-fold coordination sites and O in 2-fold coordination sites. Although both the MSI and MS-Q FF also give structures having > 99% of the Si atoms 4-fold coordinated sites, the number of 2-fold coordinated O atoms is ~ 98% for the MSI FF and ~ 96% for the MS-Q FF. It is interesting that the distribution of Si-O-Si angles is larger for the TATM FF than it is for the MSI or MS-Q FF in spite of the TATM FF

giving a larger number of 2-fold coordinated O atoms. The peak position of the Si-O-Si angle distribution is about 152° for the MSI FF, about 145° for the TATM FF and 142° for the MS-Q FF.

The bulk modulus of the materials is another property that can be used to judge how well the calculated models simulate the actual material. The experimental bulk modulus of amorphous silica is 36.54 GPa. For the MSI FF, the calculated value is 100.58 GPa while for the MS-Q FF, it is 39.31 GPa and for the TATM FF it is 38.67 GPa. Thus both the MS-Q and TATM FF's appear to fairly well represent the “stiffness” of the bonds in the model while the MSI FF tends to make the structure more rigid than it actually is.

5.0 Conclusions

All three FF give reasonably accurate descriptions of vitreous silica. Based on the comparisons to SANS, we find that MS-Q and MSI do well at representing the first coordination sphere of the atoms. Comparing to the annealed density, it appears that the TATM FF gives densities about 5% too large, the MS-Q is about 1% too large while MSI is about 2% too low. Simulations employing various cooling cycles suggest that a box of 3000 atoms is necessary to get accurate and precise results and that the cooling cycle should require at least 20ps at 8000K and significant (150 ps) relaxation time between 8000K and 1000K. There is some indication that the MS-Q FF is less sensitive to the cooling cycle employed than is the MSI FF.

6.0 Acknowledgment

This research was funded by Owens Corning Corporation. The facilities of the MSC are supported by grants from DOE ASCI, NSF (ASC 92-17368 and CHE 91-12279), ARO (MURI and DURIP), and Beckman Institute.

7.0 References

- 1) T. F. Soules, J. Non-Cryst. Solids, **123**, 48 (1990) and references therein.
- 2) T. Çagin, W. A. Goddard, III and M.L. Ary, Comput. Polym. Sci. **1**, 241 (1991).; T. Çagin, N. Karasawa, S. Dasgupta and W. A. Goddard, III, in *Computational Methods in Materials Science*, pp. 61-6, eds. J.E. Mark, M.E. Glicksman, S.P. Marsh; 1992.
- 3) Cerius², Molecular Simulations Incorporated, San Diego, CA.
- 4) G.N. Greaves. W. Smith, E. Giulotto, E. Pantos, J. Non-Cryst. Solids **222**, 13 (1997).
- 5) B. P. Feuston, S. H. Garofalini, J. Chem. Phys. **89**, (1988), 5818. The MSI 2.01 Glass Force Field in Cerius2 Version 3.0 includes a combination of two-body and three-body non-bond potentials and associated parameters presented in the several publications by T.F.Soules and coworkers, S.H.Garofalini and coworkers
- 6) S. Tsuneyuki, H. Aoki, M. Tsukada., Y. Matsui, Phys. Rev. Lett. **61** (1990).
- 7) E. Demiralp, T. Çagin, N. T. Huff, W. A. Goddard, Proceedings of the XVIII International Congress on Glass, San Francisco, CA, 5-10 July, 1998, Paper ICG-468-D8-002; T. Çagin, E. Demiralp, W. A. Goddard, III, Pressure Induced Phase Transformations in Silica, in *Microscopic Simulation of Interfacial Phenomena in Solids and Liquids*, Vol. 492, 287-292 (1998), Eds. S. Phillpot, P. Bristowe, D. Stroud, J. Smith; E. Demiralp, T. Çagin, W. A. Goddard, III, Phys. Rev. Lett., submitted.
- 8) A. K. Rappe and W. A. Goddard, III, J. Phys. Chem. **95**, 3358 (1991)
- 9) A. C. Wright, J. Non-Cryst. Solids **179**, 84 (1994).
- 10) H. Garofalini, private communication.

Table 1. Morse Potential Parameters.

$$E(R) = D_0 \{ \exp[\mathbf{g}(1 - \mathbf{r})] - 2 \exp[\frac{1}{2}\mathbf{g}(1 - \mathbf{r})] \}, \text{ where } \mathbf{r} = R / R_0$$

Interaction	Ro (Å)	Do (kcal/mol)	γ
O-O	3.7910	0.5363	10.4112
Si-Si	3.7598	0.17733	15.3744
Si-O	1.6280	45.9970	8.6342

Table II: Big Step Cooling Cycles (Type 1)

Cycle	8000 K NVT	6000 K NVT	4000 K NVT	2000 K NVT	1000 K NVT	300 K NVT	300 K NPT	Total time
1-I	20 ps	0	20 ps	20 ps	20 ps	10 ps	30 ps	120 ps
1-II	40 ps	0	0	0	0	10 ps	30 ps	80 ps
1-III	40 ps	0	40 ps	20 ps	0	10 ps	30 ps	140 ps
1-IV	40 ps	0	40 ps	40 ps	0	10 ps	30 ps	160 ps
1-V	0	40 ps	0	0	20 ps	10 ps	30 ps	100 ps
1-VI	40 ps	0	0	0	20 ps	10 ps	30 ps	100 ps
1-VII	60 ps	0	0	0	20 ps	10 ps	30 ps	120 ps
1-VIII	50 ps	50 ps	50 ps	50 ps	50 ps	20 ps	40 ps	310 ps
1-IX	100 ps	50 ps	50 ps	50 ps	50 ps	20 ps	40 ps	360 ps
1-X	40 ps	0	0	40 ps	0	10 ps	30 ps	120 ps
1-XI	40 ps	0	40 ps	40 ps	40 ps	10 ps	30 ps	200 ps
1-XII	100 ps	0	40 ps	40 ps	0	10 ps	30 ps	220 ps
1-XIII	100 ps	30 ps	30 ps	30 ps	30 ps	10 ps	30 ps	260 ps

Table III: Small Step Cooling Cycles (Type 2)

Cycle	8000 K NVT	4000K NVT	Gradual Range K	Time per 100 K Step	300 K NVT	300 K NPT	Total time
2-I	20 ps	60 ps	3900-400	4 ps	10 ps	30 ps	264 ps
2-II	20 ps	60 ps	3900-400	1 ps	10 ps	30 ps	156 ps
2-III	20 ps	20 ps	3900-400	1 ps	10 ps	30 ps	116 ps
2-IV	40 ps	20 ps	3900-400	1 ps	10 ps	30 ps	136 ps
2-V	40 ps	0	3900-400	1 ps	10 ps	30 ps	116 ps
2-VI	100 ps		7900-400	1 ps	10 ps	30 ps	216 ps
2-VII	20 ps		7900-400	1 ps	10 ps	30 ps	136 ps
2-VIII	20 ps		7900-400	2 ps	10 ps	30 ps	212 ps

Table IV: Structural Parameters for 648 Atom Cells Using the MSI Glass Force Field 2.01

Cooling Cycle	O-Si-O peak/fwhm degrees	Si-O-Si peak/fwhm degrees	% Four Coord Si	% Two Coord O	Density Range g/cc	Average Density g/cc
1-I	108/15	152/34	97.5	96.0	2.142-2.163/21	2.15005
1-I	107/15	161/35	98.4	97.0	2.141-2.167/26	2.15293
1-II	108/15	150/35	96.6	93.8	2.210-2.232/22	2.22012
1-II	108/17	156/38	96.8	94.6	2.210-2.238/28	2.22253
1-III	108/15	155/33	99.2	97.6	2.161-2.187/26	2.17403
1-III	107/14	156/33	98.9	97.8	2.104-2.128/24	2.11527
1-IV	108/17	154/37	98.8	95.8	2.167-2.192/25	2.17688
1-IV	108/15	153/36	98.5	94.5	2.131-2.163/32	2.14837
1-V	108/5	175/7	100	100	1.901-1.937/36	1.92057
1-V	108/5	175/8	100	100	1.911-1.937/26	1.92299
1-VI	108/18	150/43	96.9	93.1	2.164-2.186/22	2.18047
1-VI	107/17	158/44	97.8	95.1	2.188-2.209/21	2.19896
1-VII	108/17	157/41	96.9	95.0	2.112-2.137/25	2.12418
1-VII	107/17	154/40	97.5	94.7	2.227-2.250/23	2.23836
1-VII	107/16	156/38	97.1	95.8	2.145-2.163/18	2.15448
1-VIII	108/14	153/33	99.4	99.4	2.121-2.145/24	2.13327
1-VIII	108/14	157/32	99.5	97.9	2.166-2.192/26	2.17890
1-IX	108/14	153/30	99.3	98.0	2.190-2.214/24	2.20188
1-IX	108/14	157/31	99.9	99.1	2.183-2.211/28	2.19794
2-I	107/14	150/36	99.3	98.5	2.129-2.154/25	2.14216
2-I	107/15	153/34	99.3	98.6	2.210-2.238/28	2.22253
2-I	108/14	154/33	99.6	97.9	2.131-2.149/18	2.14026
2-II	107/15	150/34	99.6	98.3	2.153-2.176/23	2.16453
2-II	107/14	152/33	99.8	98.2	2.126-2.148/22	2.13646
2-III	107/14	155/32	98.8	97.9	2.122-2.150/28	2.13599
2-III	107/16	155/29	99.0	98.6	2.155-2.177/22	2.16600
2-IV	108/18	157/35	98.8	96.8	2.188-2.212/24	2.20108
2-IV	109/14	158/33	99.1	98.1	2.149-2.171/22	2.16089
2-V	107/16	155/34	98.4	96.1	2.167-2.189/22	2.17725
2-V	108/15	157/34	98.0	97.2	2.166-2.190/24	2.17742
2-V	109/16	154/32	98.7	95.5	2.153-2.180/27	2.16517
2-VI	107/14	157/27	99.3	98.0	2.153-2.180/27	2.16642
2-VI	108/16	159/35	99.7	98.3	2.138-2.160/22	2.14903

Table V: Structural Parameters for 3000 Atom Cells Using the MSI Glass Force Field 2.01

Cooling Cycle	O-Si-O peak/fwhm degrees	Si-O-Si peak/fwhm degrees	% Four Coord Si	% Two Coord O	Density Range (g/cc)	Average Density (g/cc)
1-IV	108/14	153/34	99.4	97.6	2.151-2.159/8	2.15529
1-IV	108/15	154/35	99.0	96.9	2.159-2.170/11	2.16520
1-VII	108/17	154/41	97.5	95.0	2.179-2.189/10	2.18373
1-VII	108/20	155/41	97.6	95.1	2.167-2.181/14	2.17417
1-VIII	107/14	158/33	99.3	98.1	2.154-2.171/17	2.16258
1-VIII	108/14	156/31	99.3	97.9	2.135-2.147/8	2.14118
1-VIII	108/14	157/33	99.2	98.3	2.139-2.148/9	2.14310
1-VIII	107/14	155/34	99.3	98.3	2.135-2.146/11	2.14132
1-IX	108/14	156/34	99.3	97.7	2.157-2.168/11	2.16263
1-IX	108/14	156/34	99.2	98.2	2.160-2.171/11	2.16774
1-IX	108/14	156/34	99.3	97.7	2.146-2.158/12	2.15173
1-X	107/16	154/38	98.3	96.2	2.157-2.166/9	2.16094
1-X	108/17	157/37	98.3	96.0	2.171-2.184/13	2.17705
1-XI	108/14	156/35	98.9	97.4	2.144-2.158/14	2.15130
1-XI	108/15	157/36	99.3	97.5	2.163-2.185/22	2.17447
1-XI	108/15	152/34	99.0	97.6	2.147-2.168/21	2.15798
1-XII	108/15	155/35	99.2	97.8	2.144-2.160/16	2.15233
1-XII	108/15	155/33	98.8	97.0	2.156-2.166/10	2.16127
1-XII	108/16	154/33	99.3	97.2	2.142-2.153/11	2.14751
1-XIII	108/14	157/33	99.3	98.1	2.151-2.163/12	2.15708
1-XIII	108/14	157/33	98.9	97.8	2.165-2.183/18	2.17378
2-I	108/14	156/33	99.2	97.9	2.140-2.147/7	2.14342
2-I	107/14	154/33	99.3	98.3	2.134-2.146/12	2.14003
2-VI	107/14	157/34	99.1	98.0	2.155-2.166/11	2.16022
2-VI	108/14	155/33	99.1	97.8	2.155-2.165/10	2.16028
2-VII	108/14	155/32	99.0	97.7	2.157-2.169/12	2.16289
2-VII	108/14	157/33	98.9	98.0	2.125-2.139/14	2.13192
2-VIII	107/14	156/33	99.2	98.1	2.142-2.154/12	2.14806
2-VIII	108/14	157/32	99.1	98.0	2.141-2.155/14	2.14825

Table VI: Structural Parameters for Various Force Fields and Cooling Cycles

Force Field	Cooling Cycle	atoms	O-Si-O Peak /fwhm degrees	Si-O-Si peak /fwhm degrees	% Four Coord Si	% Two Coord O	Density Range (g/cc)	Average Density (g/cc)
MSI gff 2.01	2-I	648	107/14	150/36	99.3	98.5	2.129-2.154/25	2.14216
MSI gff 2.01	2-I	648	107/15	153/34	99.3	98.6	2.210-2.238/28	2.22253
MSI gff 2.01	2-I	648	108/14	154/33	99.6	97.9	2.131-2.149/28	2.14026
TATM	2-I	648	106/16	143/38	99.9	99.6	2.276-2.324/48	2.29877
TATM	2-I	648	107/15	146/40	99.6	99.7	2.291-2.336/45	2.31401
MS-Q	2-I	648	107/18	144/35	99.2	96.7	2.236-2.284/48	2.26411
MS-Q	2-I	648	107/15	140/33	99.6	96.1	2.242-2.276/34	2.25971
MS-Q	2-I	648	108/14	143/35	99.3	96.2	2.186-2.213/27	2.19946
MSI gff 2.01	2-I	1536	107/14	153/36	99.3	98.6	2.157-2.169/12	2.16278
MSI gff 2.01	2-I	1536	107/14	155/30	99.1	97.9	2.148-2.160/12	2.15476
MSI gff 2.01	2-I	3000	108/14	156/33	99.2	97.9	2.140-2.147/7	2.14342
MSI gff 2.01	2-I	3000	107/14	154/33	99.3	98.3	2.134-2.146/12	2.14003
MSI gff 2.01	1-VIII	3000	107/14	158/33	99.3	98.1	2.154-2.171/17	2.16258
MSI gff 2.01	1-VIII	3000	108/14	156/31	99.3	97.9	2.135-2.147/12	2.14118
MSI gff 2.01	1-VIII	3000	108/14	157/33	99.2	98.3	2.139-2.148/9	2.14310
MSI gff 2.01	1-VIII	3000	107/14	155/34	99.3	98.3	2.135-2.146/11	2.14132
MS-Q	1-VIII	3000	107/15	142/37	98.9	95.8	2.222-2.237/15	2.23000
MSI gff 2.01	1-X	3000	107/16	154/38	98.3	96.2	2.157-2.166/9	2.16094
MSI gff 2.01	1-X	3000	108/17	157/37	98.3	96.0	2.171-2.184/13	2.17705
MS-Q	1-X	3000	107/15	143/36	98.5	95.3	2.225-2.245/20	2.23557

Figure Captions

Figure 1. A schematic representation of cooling schemes using a time temperature diagram. We show two different cooling schemes mentioned in the text, 2-VIII and 1-VIII.

Figure 2. Comparison with experiment of the total correlation function, $T(r)$ for silica structures calculated using NPT molecular dynamics at 300 K. The scattering length for oxygen is $b_{\text{O}} = 5.805$ femtometer (fm) while the scattering length silicon is $b_{\text{Si}} = 4.1491$ fm.

a) MS-Q FF with 648 and 3000 atoms

b) MSI gff with 648 and 3000 atoms.

Cooling Cycles

