

Probing the Mechanism of Silica Polymerization at Ambient Temperatures using Monte Carlo Simulations

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ABSTRACT We have developed a model for silica polymerization at ambient temperatures and low densities and have studied this using reactive Monte Carlo simulations. The model focuses on SiO₄ coordination with the energetics of hydrolysis and condensation reactions treated via the reaction ensemble. The simplicity of the model makes large system sizes accessible on a modest computation budget, although it is necessary to make additional assumptions in order to use the reactive Monte Carlo method as a simulation of the system dynamics. Excellent agreement for the evolution of the Q_n distribution is obtained upon comparing the simulation results to experimental observations. The analysis of simulation trajectories provides mechanistic insight into the polymerization process, showing the following three regimes: oligomerization (0–1 h), ring formation (1–2.6 h), and cluster aggregation (2.6–5.6 h).



U nderstanding the mechanism of aqueous silica polymerization is an important problem at the core of many sol-gel processes, as well as the synthesis of porous silica materials such as all-silica zeolites¹ and mesoporous silica materials.² Optimizing the materials produced in these processes can greatly benefit from progress in understanding the underlying polymerization and assembly mechanisms. For example, for porous silica materials we anticipate improved control over pore structures, crystallite shapes and crystallite surface properties. These attributes play a crucial role in tailoring materials for applications such as adsorption, separations and catalysis.¹

In this paper we investigate the mechanism of silica polymerization using Monte Carlo (MC) simulations of an efficient model that blends atomistic and coarse-grained perspectives. We focus especially on the evolution of the Q_n distribution, describing the distribution of silica tetrahedra with different numbers of bridging oxygens (BOs). Experimentally, this distribution is accessible from NMR measurements. 3,4 The evolution of the Q_n distribution can be modeled successfully by solving material balances for the system, incorporating rate expressions for the formation and decomposition of various species.^{5,6} However, in order to describe the spatial structure of the system during the formation of porous silica materials, an atomistic modeling approach is required. Developing an efficient detailed force-field, managing the system size, and accessing large time-scales are the major challenges for modeling such a system using atomistic simulations. Despite these challenges, there has been encouraging efforts of studying silica polymerization using atomistic models that mimic the tetrahedral coordination in silica. $^{7-10}$ A difficulty in these studies has been the inability to



sample the configurations of the models at ambient temperatures within accessible time scales, limiting them to high temperature and densities, where configurations are not representative of those encountered in experiments at ambient conditions. The evolution of the Q_n distributions from these previous simulations does not follow that seen experimentally, indicating that the underlying polymerization mechanism is not preserved.

The present study is based on a different philosophy derived from a model of crystalline silica solids developed by Astala et al.¹¹ We seek the minimal complexity that can still yield realistic results for mechanism of silica polymerization. We assume that essentially tetrahedral SiO_4 coordination is everywhere maintained in the polymerization process; as such, we do not explicitly sample Si-O bond breaking. The energetics of polymerization is handled not through the model Hamiltonian, but instead via the reaction ensemble MC (REMC) method.^{12,13} This methodology does not require detailed reactive force-fields, enabling the study of the system within reasonable computational times. We seek not only to determine the equilibrium structure of the polymerizing system but also to develop insights into the mechanism by which it forms. Thus we contrive to make our MC simulations provide at least a qualitative picture of the dynamics in the system, and this is reflected in our reaction ensemble simulation protocol. In order to do this, it is necessary to introduce some approximations into the methodology, and we discuss the significance of these.

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The silicic acid and silica units are modeled as flexible tetrahedra, each with four point particles at the corners, and by a hard sphere in the center to create excluded volume. The general formula for the tetrahedron is $Si(OH)_{4-n}O_n$, where n = 0 corresponds to silicic acid represented as a free tetrahedron (Q₀), while n = 4 corresponds to a silica unit with four BO atoms (Q_4) . Within a given tetrahedron, flexibility is introduced by employing six harmonic springs of the form $U_1 = k_{\rm S}(r_{ij} - r_0)^2/2$ between the four corner point particles, where $k_{\rm S}$ is the spring constant, r_{ij} is the distance between two corner particles in a tetrahedron, and r_0 is the equilibrium distance between two such particles. For corner-sharing tetrahedra, Si-O-Si angle fluctuations are modeled using harmonic springs of the form $U_2 = k_{\rm A} (\cos \theta - \cos \theta_0)^2 / 2$, where $k_{\rm A}$ is an angular spring constant, θ is the Si–O–Si angle, and θ_0 is the reference angle. The parameters ($k_{\rm S}$ = 851 kJ mol⁻¹ Å⁻², $r_0 = 2.61$ Å, $k_A = 226.74$ kJ mol⁻¹, and $\theta_0 = 155$) are taken from the work of Astala et al.,¹¹ who developed this model to reproduce the mechanical properties of several silica polymorphs. The hard sphere diameter for the excluded volume Si–Si interaction is set at $\sigma = 2$ Å; there are no other nonbonded interactions in the model. The solvent is not explicitly treated but it does play a role in the reaction equilibrium and in diffusivities of the silica monomers and clusters. We do not account for charged silicate species, making the present version of the model appropriate for studying polymerization under pH conditions near the isoelectric point of silicic acid.³ Our model is simpler than others; our focus has been on minimal complexity that can still yield realistic results for the mechanism of silica polymerization.

The MC moves used (with attempt probabilities) are translation and rotation of Si(OH)_{4-n}O_n tetrahedra (0.34 and 0.34), distortion of such tetrahedra through displacement of O/OH vertices (0.2), cluster displacement (0.1) and reaction moves (condensation and hydrolysis: 0.01 and 0.01). The MC moves were accepted or rejected using standard Metropolis criteria. Due to polymerization and the resulting silica gel, we found it impossible to implement cluster-rotation moves, because such moves either break or stretch Si–O bonds between periodically repeated atoms. This creates a highenergy penalty, which causes acceptance probabilities for such moves to essentially vanish. As a result, such moves are not included in our simulations.

In order that the translation moves for clusters in some way model diffusion in a real system, we have to make the probability of translation moves depend upon the cluster size. This models the effect of solvent drag on cluster diffusion. The Stokes-Einstein equation suggests that $D_{i,cl} \propto r_{i,cl}^{-1} \propto N_{i,cl}^{-\alpha}$, where $D_{i,cl}$, $r_{i,cl}$ and $N_{i,cl}$ are the diffusivity, radius, and size (number of tetrahedra) of the cluster *i*. The relative probability of cluster moves with respect to that of monomer moves is then given by $N_{i,cl}^{-\alpha}$. The values of the exponent α vary with geometry of the cluster, e.g., $\alpha = 1/3$ for a sphere, and $\alpha = 1$ for a linear rod-like cluster. In the simulations, the geometry of the clusters are continually changing, and for simplicity we have used $\alpha = 1$ in all cases.

A general silicic acid polymerization step can be expressed as

$$\equiv Si - OH + HO - Si \equiv \rightleftharpoons \equiv Si - O - Si \equiv + HOH$$
(1)

where the forward/backward reaction is condensation/hydrolysis. We modeled these using REMC, a general method for sampling reactive events with known equilibrium constants.^{12,13} A recent REMC study modeled quartz dissolution¹⁴ (the opposite of silica polymerization), establishing the validity of using REMC for reaction equilibria of network solids. Although Nangia et al.¹⁴ found that dissolution of Q_i tetrahedra is best understood through stepwise processes ($Q_i \leftarrow Q_{i-1}$), we still lack a detail atomistic picture of how silica structure builds from monomers and oligomers to solids.

In general, silica polymerization can be viewed as a multicomponent system with many reactions, sampled efficiently with REMC¹⁵ using the following reaction probability:

$$P_{\rm rxn} = e^{-\Delta U/k_{\rm B}T} \prod_{i=1}^{n_{\rm c}} \frac{N_i!}{(N_i + \nu_i)!} \prod_{i=1}^{n_{\rm c}} q_i^{\nu_i}$$
(2)

where ΔU is the change in potential energy, $k_{\rm B}$ is Boltzmann's constant, T is absolute temperature, n_c is the total number of components, and N_i , ν_i , and q_i are the number of molecules, stoichiometric coefficient, and molecular partition function of reactant *i*, respectively. The molecular partition functions are related to the standard Gibbs free energy and equilibrium constant as $\prod_{i=1}^{n_c} q_i^{\nu i} = \exp(-\Delta G_{rxn,0}/RT) = K_{eq}$. Since the REMC method is an equilibrium simulation, the reaction probability does not depend on any activation energy. It depends on the molecular configuration and the standard free energy of reaction. The partition function q_i of cluster *i* is a function of size $(N_{i,cl})$, number of bridging oxygens (N_{BO}) , and molecular configuration. Calculating q_i (and hence K_{eq}) for each and every different cluster configuration represents a combinatorial explosion of computational expense. However, ab initio calculations of condensation/hydrolysis energies for various Q_i species show that these energies are remarkably uniform, roughly independent of the precise nature of reacting species.^{16,17} We thus approximate the above generalized reaction (eq 1) as two hydroxyl groups reacting to form a BO and a water molecule, reducing the set of K_{eq} to a single value. We have used $K_{eq} = 500$ in this work, which gives a condensation free energy of 3.7 kcal mol^{-1} comparing reasonably well with the condensation energy of 3.2 kcal mol^{-1} obtained from density functional theory for dimerization in water.18

We bring about condensation reactions in two ways. When the two selected OH groups are part of different monomers or clusters, then the two clusters are moved toward each other such that the two selected OH groups coincide. The two OH groups are then replaced with a BO atom. By bringing two large clusters together in one MC move, we have increased the reaction rate since the diffusion steps bringing the groups together have been bypassed. This bias can be removed by dividing the reaction probability by the number of MC moves that would be required to bring these two clusters within the reaction cutoff. This latter quantity is directly proportional to the intercluster distance squared (assuming diffusive motion) and inversely related to the diffusivity. Hence the reaction move is accepted with a corrected reaction probability $P_{\rm rxn,corr} = P_{\rm rxn}/N_{\rm MC,ij}$, where $N_{\rm MC,ij}$ is the number of diffusive MC moves required to displace two clusters *i* and *j* such that

two hydroxyl groups (vertices) overlap, and is given by

$$N_{\rm MC, \, ij} \propto \frac{|\mathbf{r}_{\rm OH, \, i} - \mathbf{r}_{\rm OH, \, j}|^2}{D_{i, \, \rm cl} + D_{j, \, \rm cl}} = k \frac{|\mathbf{r}_{\rm OH, \, i} - \mathbf{r}_{\rm OH, \, j}|^2}{1/N_{i, \, \rm cl} + 1/N_{j, \, \rm cl}}$$
(3)

where $r_{OH,i}$ are the coordinates of a hydroxyl group mounted on cluster *i* of size $N_{i,cl}$, and *k* is the proportionality constant. The value of k is computed based on the nonreacting silicic acid system. We assume that in a system of volume V containing N(monomer) silicic acid molecules, the average distance that can be traversed by a molecule without collision is $(V/N)^{1/3}$. This assumption is based on choosing an initially ordered arrangement of monomeric system. Hence the value of k is obtained from eq 3, assuming that two monomers (*i* and *j*, $N_{i,cl} = N_{j,cl} = 1$) are displaced by this distance $(|r_{OH,i} - r_{OH,i}| = (V/N)^{1/3})$ without overlapping each other in one MC move ($N_{MC,ij} = 1$), which gives $k = 2(N/V)^{2/3}$. We emphasize that eq 3 will underestimate $N_{\text{MC},ij}$ because it assumes that two clusters diffuse on the line joining two hydroxyls (OH_i and OH_i), instead of treating the full three-dimensional stochastic motion. To our knowledge, there are currently no models present that can calculate the exact value of $N_{MC,ij}$ based on the initial positions of cluster for a distribution of clusters in three-dimensional space. In the absence of such a model, we used the above one-dimensional directed motion estimates as an initial guide to perform the simulations. As a consequence of underestimating N_{MC,ij} in onedimensional directed motion, this approximation may lead to faster aggregation in the simulations as compared to experiment. Estimating better three-dimensional contact times (or $N_{MC,ii}$) is an important area for future improvement of our modeling approach.

When two selected OH groups are part of the same cluster, then one can represent the condensation reaction by replacing them with a BO positioned at their center of mass. However, by a simple calculation using eq 2, one can estimate that if $|\mathbf{r}_{OH,i} - \mathbf{r}_{OH,i}| > 0.25$ Å, the reaction probability of such a move would be less than 0.01, and most displacements greatly exceed 0.25 Å. If such a reaction were to occur, then the configuration of atoms around the condensing OH groups would change substantially.⁷ To our knowledge, there is no technique available that can sample this process efficiently while maintaining detailed balance. We have found that we can improve the likelihood of this reaction move by relaxing the system in the direction dictated by the forces on the cluster. To achieve this, we replace two hydroxyl groups by a BO at the center of mass of these two hydroxyl groups, and execute a sequence of 500 MC steps where a step consist of displacement of all vertices of the cluster in the direction of force. The choice of 500 steps is somewhat arbitrary; it corresponds roughly to 50 ps of physical time assuming that standard thermal fluctuations of tetrahedral vertices lead to a diffusivity of 10^{-5} cm²/s. After 500 MC steps, the acceptance probability is calculated using eq 2, where ΔU is the change in cluster energy due to cluster relaxation. This is the only move where cluster relaxation is incorporated. If the move is rejected by the Metropolis acceptance criterion, then the entire reaction move including cluster relaxation is rejected, and the old configuration with hydroxyl groups before cluster relaxation is retained. The directed motion during cluster relaxation (as opposed to random motion) imposes a bias into the system. This bias cannot be removed completely, but can be mitigated by employing few such force-bias condensation moves; we attempt such moves for 10 % of all intracluster condensation moves. We have found that acceptance probabilities of such force-bias moves are extremely small: only around 5% of the total attempted force-bias intracluster condensation moves are accepted. We might expect increase in bias due to force-bias moves with system size; however, we observed that results for different system sizes are essentially the same. This lends confidence that bias from force-bias moves is small, and does not appreciably affect the final system equilibrium from what it would have been were we able to correct for the bias.

The hydrolysis reaction is performed by replacing a randomly selected BO with two hydroxyl groups on the same location of deleted BO. The change in potential energy (mainly due to removal of Si-O-Si angle potential) is calculated, and the move is accepted with the reaction probability (eq 2).

The simulation is started with random initial configuration of 1000 monomers $(Si(OH)_4)$ in a cubic box of dimension 104 Å at 300 K. The concentration of the system represents the experimental conditions of Devreux et al.³ For this system, the cluster diffusion factor is k = 0.018. The monomers are equilibrated for 0.1 million MC steps, where a step consists of 1000 attempted MC moves, during which reactions are not attempted. After the equilibration period, reactions are started, and the simulation is performed for another 0.1 million MC steps. During the simulations, the Q_n , number averaged cluster size, ¹⁹ and ring-size²⁰ distributions are monitored to probe the mechanism of polymerization.

Strictly speaking, understanding the underlying mechanism of polymerization requires monitoring the concentrations of all intermediate species. However, due to the enormous number of intermediate products, monitoring each individual species is not possible. In the experiments,² the number of BOs in each tetrahedron (Q_n) is monitored. We compare the Q_n distribution obtained from the simulations with the NMR experimental data in Figure 1. Also shown is the evolution of the degree of condensation, which is a measure of the extent of polymerization, defined as $c = \sum_{i=1}^{4} iQ_i/4$. A mapping between MC steps and time is required to make a direct comparison of Q_n distribution obtained from simulations with the experimental data. We establish the relationship between the time scales by defining a common reference between the two evolutions of Q_n . In the experimental results, the first data point is reported at 0.1 h at which the Q_0 and Q_1 profiles cross each other around $Q_0 = Q_1 \simeq 0.45$. The corresponding point in the MC simulation is observed at 148 MC steps, and we use this point as the reference to compare the simulation with the experimental data as shown in Figure 1.

We observe that the simulation accurately captures the initial evolution of the Q_n distribution. Significant differences between the simulation results and experimental data emerge primarily at later times. The mole fractions of Q_3 and Q_4 increase more rapidly in the simulations when compared with experiments. This discrepancy may be due to underestimation of diffusive length (i.e., $N_{MC,ij}$) in our simulations leading to faster cluster aggregation. This is evident in the Q_3 distribution



Figure 1. (a) Evolution of Q_n distribution during polymerization obtained from simulations. (b) Q_n distribution obtained from NMR experiments³ (drawn by extracting data from Figure 3 of that reference).

where a rapid increase is observed in the range of 3000-7000 MC steps during which the average cluster size increases from 70 to 1000. Despite this variation, the simulations capture the time dependence of Q_n concentrations, the locations of maxima in the Q_n distribution, and the relative concentrations of different species (e.g., Q_n concentration at maxima of Q_1) very well. We also note that the degree of condensation, *c*, increases monotonically in both simulation and experiments. This suggests that the degree of condensation can be used as an alternative to time to compare the evolution of the Q_n distributions between simulation and experiment. Moreover, using the degree of condensation as the parameter with which to track the Q_n distributions does not require defining a reference time.

The Q_n distributions versus degree of condensation from experiment and simulation are compared in Figure 2. The comparison (Figure 2) indicates excellent quantitative agreement between the simulation results with the experimental observations, by capturing all the crossing points accurately. This indicates that the simulations are able to capture the underlying mechanism. Indeed, a change in mechanism would change the evolution of Q_n distributions as a function of the degree of condensation.³ For example, if the reaction mechanism were to favor the formation of linear chains, then the reaction would stop at c = 0.5, and the system would form one or more linear chains consisting mostly of Q₂ silicons. Despite the lack of an MC simulation clock (as exists in typical kinetic MC of reaction system) and the simplicity of the model, the simulation results for the evolution of the Q_n distribution are in remarkable agreement with experiment. This agreement suggests that silica polymerization kinetics are not limited by individual reaction events and their barriers, but



Figure 2. (a) Variation of Q_n distribution as a function of the degree of condensation obtained from simulations. (b) Q_n distribution obtained from NMR experiments³ (drawn by extracting data from Figure 3 of that reference).

rather are limited by network structural constraints, which are treated in our model as described by ΔU . Nevertheless, there is clearly much more to be done to understand why this is the case.

We can learn about the mechanism of polymerization by analyzing the Q_n distribution while tracking cluster and ring sizes. We have found that in the simulations the initial phase corresponds to oligomerization during which small size units are formed. The oligomerization process is marked by the rapid decrease in the monomer concentration, Q_0 fraction, as soon as reactions are started in the simulations. These observations are consistent with experiment where monomer concentration decreases to 0.45 mol fraction in 6 min.³ The fast oligomerization is due to high concentration of OH groups unhindered by network connectivity constraints. Figure 3 shows that the initial oligomerization occurs in the range of 0-900 MC steps during which the degree of condensation changes from 0 to 0.43. The corresponding change in degree of condensation during experiments illustrates that oligomerization regime corresponds to initial 1 h in experiments. During this regime, small oligomers of size 1-40 monomers are formed with an average cluster size of 8 monomers.

The reaction can proceed further either by cluster aggregation or ring closing reactions within oligomers. If the reaction were to proceed via cluster aggregation, then the average cluster size would increase rapidly, but this is not observed in the simulations. On the contrary, the total number of primitive rings formed increases rapidly from 4 to 114 in the range of 900–3300 MC steps (corresponding to 1–2.6 h regime in experiments), indicating that polymerization proceeds with ring formation. The reason for ring formation is the overall decrease in free OH concentration and decrease in mobility due to oligomer formation. These two factors reduce the collision frequency between OH groups, which delays cluster

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Figure 3. Variation of cluster size (average and maximum) and total number of rings observed during the MC simulation. The three regions I, II, and III correspond to the three initial stages of polymerization: oligomerization, ring formation, and cluster aggregation, respectively.

aggregation. However the local concentration of OH groups in oligomers is much higher than the global concentration, which favors ring-closing reactions. Oligomers with small rings work as primary building units that subsequently aggregate to form the large network.

Further ring closing in small primary units is no longer favored due to the energy barriers to chain deformations, and hence the polymerization proceeds further by cluster aggregation. Such cluster aggregation occurs in the range of 3300-6300 MC steps where the average and maximum cluster sizes rapidly converge to 1000, which is the system size. However, the overall characteristics of the profile were observed for different system sizes as well. This cluster aggregation step corresponds to the regime between 2.6 and 5.6 h in experiments. At this point, the degree of condensation, c = 0.61, indicates that the polymerization reaction is still not complete, yet clusters have grown to maximum sizes. This suggests that further reactions occur via processes within clusters leading to an aging gel structure.

The randomness and absence of any crystal symmetry in the resulting silica gel is shown in Figure 4a,b. The network formed due to random short-range structure is characterized using the ring size distribution. The ring size distribution obtained from simulations compares well with previous studies (Figure 4c). Long-range structure is studied by computing the fractal dimension, which is the measure of porosity and self-similarity in the system. In the regular space-filling scenario, the system would have a fractal dimension close to 3. However, experiments on silica-gel obtained using sol-gel condensation under dilute concentrations (similar to the current studies) have reported values in the range of 2.0-2.3 using NMR and small-angle X-ray scattering.^{22,23} In the simulations the fractal dimension is defined as $d_f = d \ln N(r)/d \ln r$, where N(r) is the number of molecules (or atoms) surrounding a central atom up to a distance r.⁹ In the current study, a fractal dimension of 2.0 is observed (Figure 4d) for the resulting silica-gel, which compares well with experimental values reported in the literature.^{22,23}



Figure 4. (a) Snapshot of silica cluster containing 1000 monomeric units at the end of 0.1 million MC steps. Green: Si; red: O (bridging); and white: OH group. (b) Inset of panel "a" showing the complex network structure of silica gel. (c) Comparison of ring size distribution obtained from simulation with other studies. (d) Fractal dimension calculated from the slope of $N_{Si-Si}(r)$ versus $r \log$ -log plot.

In conclusion, we have presented both a new approach to, and fresh insights from studying silica polymerization using MC simulations of a simplified atomistic model. In comparison to previous work,^{7–9} our model enables study of polymerization reactions at both low density and ambient temperature. The agreement with experiment for the evolution of the Q_n distribution is remarkably good. This gives us confidence in the polymerization mechanism revealed by the simulations. Our results suggests that polymerization starts with initial oligomerization

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followed by ring formation in small oligomer units. These small oligomers with rings act as primary building units and aggregate to form larger clusters. Further reaction within the large clusters leads to gelation. Given the apparent utility of our new model in studying silica polymerization and the relative efficiency with which it can be implemented, we believe it offers new opportunities for studying silica polymerization in other circumstances such as the growth of zeolites or the formation of ordered mesoporous silica materials. At the same time, it has been necessary to make additional approximations in order to use the REMC method for simulations of the dynamics, especially in choosing the relative frequencies of the different kinds of moves. Developing more rigorous alternatives to these approximations should be a priority for future work.

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