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Study of the Self-Assembly Process of Microporous Materials Using Molecular Modeling

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STUDY OF THE SELF-ASSEMBLY PROCESS OF MICROPOROUS MATERIALS USING MOLECULAR MODELING

A Dissertation Presented

by

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DEDICATION

To all my dear friends and family who have supported and encouraged me during my toughest of times.
ACKNOWLEDGMENTS

Firstly, I would like to express my sincere gratitude to my advisers Prof. Peter A. Monson and Prof. Scott M. Auerbach for their continuous support of my Ph.D study and related research; for their patience, motivation, and confidence in me. They have helped me immensely in improving my presentation and writing skills. I could not have imagined having better mentors for my Ph.D. study.

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ABSTRACT

STUDY OF THE SELF-ASSEMBLY PROCESS OF MICROPOROUS MATERIALS USING MOLECULAR MODELING

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Zeolites are an important class of materials in modern technology with applications in catalysis, separations, biosensing and microelectronics. There are over 200 different zeolite frameworks reported in literature, but only a handful have been used commercially. Understanding their self-assembly process would assist in the fabrication of new zeolites through the control of their pore size/shape, and surface area for advanced applications. With our research we aim to elucidate aspects of zeolite formation using molecular simulations.

We have extended the lattice model of silica tetrahedra developed by Jin et al. [L. Jin, S. M. Auerbach and P. A. Monson J. Chem. Phys. 134(13), 2011: 134703] to study silica polymerization under various pH values and silica concentrations. We have investigated the transition from gels, at the iso-electric point of silica, to nanoparticles in the initial stages of the formation of silicalite-1. We focus on two systems: one with low silica con-
centration with composition comparable to the clear solution silicalite-1 zeolite synthesis, and a high silica concentration system that leads to gel states. In the dilute system, clusters have a core-shell structure with the core predominantly comprised of silica with some SDA\textsuperscript{+} cations, surrounded by a shell of only SDA\textsuperscript{+} cations. In the concentrated system there are larger number of smaller nanoparticles than those in dilute system. Next, we focused our attention to study the effects of two different type of structure directing agent (SDA) molecules – quasi-spherical SDA and tetramethylammonium (TMA) – on crystalline tetrahedral frameworks in the synthesis of microporous materials. We have implemented parallel tempering Monte Carlo algorithm to simulate the formation of ordered crystalline materials, and we have demonstrated that the presence of SDAs result in the formation of previously unobserved crystalline frameworks. In the case of quasi-spherical SDAs we have observed three-dimensional fully-connected materials as well as two-dimensional layered materials in our simulations, and observed that the interaction between SDAs and silica plays a significant role in directing the final micropore structure. For TMA we have developed two types of models based on silica-TMA interaction – silica-nitrogen interaction vs silica-methyl interaction. In both of these models we have observed that the TMA molecule forms predominantly three dimensional materials, which suggests that the molecular structure directs the preferential formation of three dimensional frameworks as opposed to two dimensional layered materials. We have also studied the kinetics for formation of crystals using forward-flux sampling method. We have estimated the rate constant of transition from amorphous silica phase to crystalline silica phase. We have also predicted and characterized the transition state for this process. This is the first time when an enhanced sampling method is applied to understand the self-assembly process of microporous crystals.

This research has been crucial in understanding the nature of silica polymerization and elucidating the role of structure directing agents in zeolite synthesis; it has taken us
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C.7 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 100

C.8 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 100

C.9 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 001 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 011 \rangle$.............................. 101

C.10 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 101

C.11 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 001 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 001 \rangle$.............................. 101

C.12 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 102

C.13 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 102

C.14 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, 
$\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_4-T(OH)_4}$.
(a) plane $\langle 001 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 101 \rangle$.............................. 102

C.15 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, 
$\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_4-T(OH)_4}$.
(a) plane $\langle 010 \rangle$; (b) plane $\langle 0\bar{1}1 \rangle$; (c) plane $\langle 011 \rangle$.............................. 103

C.16 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, 
$\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_4-T(OH)_4}$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle \bar{1}0 \rangle$; (c) plane $\langle 110 \rangle$.............................. 103
CHAPTER 1
INTRODUCTION

Microporous materials have remained a topic of research due to their commercial applications. They have been extensively used in the process of catalysis where, for instance, they have been applied to convert methanol to hydrocarbons. Microporous materials have also been fabricated into membranes with high selectivity; one such example is ion-selective electrodes. Moreover, they play an important role in gas separation processes due to their unique property of selectively adsorbing one or more components. Molecular sieves, such as zeolites, have ordered arrangement of pores and channels resulting in novel electrical and photonic applications. Zeolites also have the ability of absorbing water which has led to their use as a blood-clotting agent. It is quiet evident that porous materials have tremendous importance in industrial applications, and although advancements have been made in synthesis techniques, such experiments are limited by trial and error methods. Therefore, a fundamental understanding of the synthesis process of these materials is imperative, to tailor design these materials by controlling pore structure, size and shape as well as chemistry of the constituents, which can open new avenues for advance technological applications. In a complex formation process where phenomena such as condensation reactions, electrical interactions, dispersion forces, acid-base equilibrium play a vital role, molecular modeling is an essential tool to understand their self-assembly process.

In this dissertation we aim to study the self-assembly of porous materials using molecular modeling. We have focused our attention on microporous materials, particularly zeolites, which are synthesized using silica and aluminum sources in the presence of
structure directing agents. A central component of zeolite synthesis is the polymerization of silicic acid which produces both sols (nanoparticles), at low silica concentrations, and gels (percolating networks), at high silica concentrations. However, a complete understanding of silica polymerization under various conditions of pH and silica concentration is still lacking. Moreover, there exists strong evidence that structure directing agent (SDA) molecules play a vital role in the synthesis of zeolites by promoting the formation of channels and cages. But the role of SDAs in promoting zeolite crystallization remains poorly understood, and the shape size of critical nucleus of zeolites remains a mystery till date. We seek to apply tools of statistical mechanics along with a powerful lattice model of silica polymerization to address the following questions:

(i) What is the nature of transition from gel phase to nanoparticle phase observed in the precursor mixture in the synthesis of silicalite-1?

(ii) What are the effects of SDA size, SDA structure, SDA concentration, and composition of synthesis mixture on microporous structures?

(iii) What are the structures and sizes of critical nuclei, and nucleation energy barrier of ordered microporous structures?

In the following sections we give a review of experimental synthesis of microporous materials, sol-gel chemistry of silica, and molecular modeling approaches to understand the fundamental process of zeolite formation.

1.1 Sol-Gel Chemistry of Silica

Sol-gel processing is an important technology used in the production of thin films, fibers, preforms, and nanoporous materials such as zeolites. Zeolites are nanoporous, crystalline, aluminosilicates with extensive applications as adsorbents, catalysts, and ion exchangers. All-silica zeolite frameworks such as silicalite-1 can be synthesized by sol-gel processing in aqueous media using a silica source and structure directing agents.
A fundamental understanding of the synthesis process of such materials would enable the prediction of various properties such as pore size, framework type, and surface structure. A central component of zeolite synthesis is the polymerization of silica that produces both sols (nanoparticles) and gels (percolating networks). A polymerization reaction between two silica species is shown below

\[ -\text{Si(OH)} + (\text{HO})\text{Si}^- \rightleftharpoons -\text{Si} - \text{O} - \text{Si}^- + \text{H}_2\text{O} \]

In contrast to the high pH behavior which results in sols (nanoparticles), at low pH near the iso-electric point of silica (pH~2-3), an aqueous silica solution evolves into a disordered state of condensed silica networks. Carman proposed that the formation mechanism of such networks is a two-stage process. In the first, initially formed Si(OH)$_4$ condenses to form colloidal particles. In dilute solution, particle aggregation may occur but does not lead to percolating networks, characteristic of gels. However, at higher concentration of silica, these networks link into a continuous, relatively rigid material that ultimately percolates the system leading to gelation. Devreux et al. studied the evolution of such aqueous silica networks using $^{29}$Si NMR. They observed the evolution of the $Q_n$ (the fraction of silicon atoms connected to $n$ bridging oxygen atoms) distribution both with time and with degree of condensation. Their results provide an excellent test for models of silica polymerization. Capturing the nature of the transition between nanoparticle and gel states of silica provides an important target for molecular modeling.

1.2 Synthesis of Microporous Crystalline Materials

At present, over 200 zeolite framework types have been identified; however only a handful have been utilized commercially. The design of zeolites for novel applications through the control of micropore size/shape and crystal size/shape has been a topic of great interest with emphasis on elucidating the roles of SDA species in the self-
assembly process\textsuperscript{36}. However, experimental characterization methods are not yet able to generate atomic-level resolution of silica-SDA structures on length scales characteristic of zeolite critical nuclei (5-10 nm)\textsuperscript{37}. Molecular modeling methods\textsuperscript{21,22} are thus well poised to complement experimental characterization by providing atomic-level information on the roles of SDA species during zeolite crystallization.

Zeolites are typically synthesized in the presence of organic structure directing agent molecules (OSDAs)\textsuperscript{23–25}. These organic molecules promote the formation of zeolites and play the role of structure directing agents, rather than as templates\textsuperscript{24} – molecules around which silica polymerizes. Understanding what different properties of these organic molecules play a role in structure direction would enable researchers to apply rational design to zeolite synthesis. Organic structure directing agents have been used in zeolite synthesis since 1960s. Kerr \textit{et al.}\textsuperscript{38,39} and Barrer \textit{et al.}\textsuperscript{40} used tetramethylammonium (TMA) to synthesize zeolite A with a higher Si/Al ratio. Tetraethylammonium (TEA) was used to synthesize zeolite Beta with a high silica content\textsuperscript{41}. Flanigen \textit{et al.}\textsuperscript{27} used tetpropylammonium (TPA) to synthesize ZSM-5 having an MFI framework which is a very important catalyst in oil refining\textsuperscript{42}. Advances in synthetic organic chemistry have enabled researchers to design OSDAs for different zeolites.\textsuperscript{24}

The synthesis of silicalite-1, relatively well studied zeolite, involves sols, i.e., suspended nanoparticles at short times that evolve with time and/or heat into zeolites.\textsuperscript{37} This pure silica form of the MFI zeolite framework contains parallel straight channels in one direction and zig-zag channels perpendicular to the straight channels. It was first synthesized by Flanigen \textit{et al.}\textsuperscript{27} by hydrothermal crystallization of a reactive form of silica in the presence of TPA as SDA at a temperature range of 100-200°C and pH near 10. Eventually, the SDA cations occupy the channel intersections and are removed by calcination in the presence of air at 500-600°C, to yield microporous silicalite-1 crystals. Studies of the formation mechanism of silicalite-1 crystals\textsuperscript{1,37,43–50} have shown that the process involves an intermediate nanoparticle phase that is believed to play an impor-
tant role in the nucleation process of these crystals. Scattering techniques, such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) suggest that these silica-SDA nanoparticles possess a core-shell type structure. The core of the nanoparticles is hypothesized to comprise primarily of silica, enveloped by a shell of cations. These particles, after being aged for a long period (~200 days), aggregate to give rise to a population of larger particles that contain the X-ray diffraction signature of silicalite-1 crystals. Yang et al. studied this system with the same components but at higher density and showed using SAXS that nanoparticle size decreases with increase in concentration of SDA cations. However, the structure and morphology of these nanoparticles remain poorly known. Nucleation is then hypothesized to occur inside these nanoparticles via a layer-by-layer growth mechanism where the critical nucleus of the crystals are thought to lie in the 5-10 nm range.

Several studies have been reported to elucidate the role of SDAs in the process of synthesizing zeolites and other pure-silica ordered materials. Important control parameters in the synthesis process include composition of the initial mixture, Si/Al ratio, pH, temperature and type and concentration of SDA. Gies and Marler argued that it is not straightforward to separately study the influences of pH and cationic SDAs on zeolite formation, because the cations are accompanied by a charge balancing species, commonly OH\(^{-}\), which also changes the initial solution pH. To disentangle these effects, Gies and Marler studied silica crystallization in the presence of various neutral SDAs in aqueous solutions, varying the size, shape, and chemical character of the SDAs. They observed that changing the chemical character of the SDA, from nonpolar to polar to hydrogen-bonding, does not bring significant change in the resulting cage structure, suggesting that silica micropore self-assembly is principally governed by silica-SDA van der Waals interactions. They also observed that increasing SDA size results in crystals with larger cages, with SDAs present in each cage. Lobo et al. summarized the final microporous silica structures obtained from a wide variety of SDAs observing that in-
creasing the sizes of linear and branched SDAs produce larger pores in both 1-D and 3-D zeolites, respectively. However, a more complete understanding of the effects of SDAs during the crystallization process is still lacking because characterization methods do not as yet provide atomic-level information on the dynamics of the process. In such cases, molecular modeling methods may provide valuable insights into the synthesis process.\textsuperscript{21,22}

1.3 Molecular Modeling

In this section we review molecular modeling methods – like quantum mechanical calculations, molecular dynamics, and Monte Carlo simulations etc., implemented to study silica polymerization, study role of SDA molecules in zeolite synthesis, and study of zeolite nucleation.\textsuperscript{22}

1.3.1 Modeling Silica Condensation

The polymerization of silica exhibits a complex interplay of several phenomena such as condensation/hydrolysis chemistry, acid-base equilibrium, metastability, and phase separation\textsuperscript{58–60}. Furthermore, SDA\textsuperscript{+} cations present in the system can influence the process via electrostatic interactions. Molecular modeling can potentially provide useful insights into the thermodynamic behavior of such systems especially considering that silica networks often fall into the nanoscale blindspot between NMR (< 1 nm) and X-ray (> 50 nm). Researchers have employed simulation techniques such as molecular dynamics (MD) and Monte Carlo (MC) simulations to investigate the phenomena of silica polymerization under various conditions. Garofalini and co-workers\textsuperscript{61,62} studied kinetics of silica polymerization using MD simulations and predicted that chains form at early stage followed by ring formation. Rao et al.\textsuperscript{63} performed large-scale MD simulations to find that initial stages of polymerization are dominated by Ostwald ripening\textsuperscript{59} followed by cluster aggregation at longer times. The computational limitations of the
models and MD, however, restricted such studies to relatively small system sizes, short times, and high temperatures to allow chemical bond breaking and reforming.

To simulate silica polymerization under ambient conditions, Wu and Deem\textsuperscript{64} used MC simulations to model silicate cluster formation. Using novel MC moves, they estimated the nucleation barrier for silica crystallization to be of order $10^2 \ k_B T$, and the critical nucleus size to be $\sim 50$ silicon atoms. Malani et al.\textsuperscript{31,32} developed a model of silica sampled with specialized MC simulations under ambient conditions at the iso-electric point, reproducing the measured $Q_n$ evolution using specialized MC moves allowing oligomerization, ring formation, and cluster aggregation. Despite this progress, off-lattice simulations have yet to describe crystallization of silica.

Recently we have deployed lattice models to study silica polymerization at the iso-electric point ($\text{pH} \sim 2$)\textsuperscript{33}, and also spontaneous formation of nanoparticles at high pH ($\text{pH} \sim 10$) in clear solution synthesis of silicalite-1\textsuperscript{65}. These models have also been applied to simulate the spontaneous formation of MCM-41 mesoporous silica materials\textsuperscript{66}, and the crystallization of microporous zeolite analogs.\textsuperscript{67} Here, we extend these studies across the pH range and study the distinction between the nanoparticles formed at low and high silica concentrations. We have used an atomic representation of corner-sharing silica tetrahedra on a body-centered cubic (BCC) lattice.\textsuperscript{33} The condensation reaction was modeled by simultaneous occupancy of hydroxyl groups from different tetrahedra on the same lattice site. Jin \textit{et al.}\textsuperscript{33} used this representation to predict network formation at the iso-electric point. Their results for the evolution of the $Q_n$ distribution agree well with data from $^{29}\text{Si}$ NMR experiments\textsuperscript{30}. However, the phenomena of silica polymerization for various pH values and silica concentrations remains yet to be explored. In particular, it is unclear whether the gel transforms smoothly or abruptly to nanoparticles as the pH is increased, and whether the nanoparticles are similar in size for systems with low and high silica concentrations.
1.3.2 Role of SDA Molecules in Zeolite Self-Assembly

Simulating zeolite formation is a daunting task because no single model has yet to include effects such as solvation, charge balancing, and hydrophobic effects, along with chemical interactions (e.g. silica polymerization), acid-base equilibria, and heteroatom energetics. In 1996, Lewis et al. reported a simulation study of a library of SDAs optimized in known zeolite frameworks to predict new SDAs for making target zeolites based on host-guest stabilities. This seminal study established the approach of optimizing host-guest interactions of putative SDAs in known zeolite frameworks, which can suggest new SDAs but says little about how zeolites actually form. More recently, Burton et al. reported energy optimization of various quaternary organic amines in known high-silica zeolites to elucidate thermodynamic factors that control the eventual zeolite phases found in synthesis experiments. They found that piperidine derivatives have a better fit with the pear shaped cage of AEI, whereas polycyclic quaternary ammonium compounds fit better inside the cylindrical shaped cage of CHA framework. Although such studies provide valuable atomic level details of the process, they do not give information on pathways leading to the formation of zeolite crystals.

Lewis et al. extended their study to forcefield-based optimizations of silica fragments likely to play a role in zeolite formation, testing the stabilities of open-framework silica fragments in the absence and presence of hydration and SDAs. They found that both charged and neutral SDAs are essential for stabilizing hydrated, open-framework silica fragments, hence corroborating the findings of Gies and Marler that silica-SDA van der Waals interactions are central to the formation of micropores. More recently, Van Santen and co-workers performed classical molecular dynamics and ab initio molecular dynamics to study the stabilities of silica-tetraalkylammonium cation clusters, finding that the cavities in silica oligomers are stabilized by the alkyl chains in tetra-alkylammonium SDAs, again pointing to the importance of silica-SDA van der Waals interactions. Despite this important progress in our understanding of silica-SDA clus-
ters, the computational costs of these methods restrict the systems to relatively small sizes and short simulations times, and hence do not provide pathways that proceed all the way to microporous crystal structures.

The development of efficient models and sampling of silica polymerization has been crucial for enhanced understanding of silica material synthesis. Several groups have reported simulation approaches for predicting libraries of hypothetical zeolites furnishing millions of new target structures for synthetic zeolite chemists. However, these simulations usually follow topological rules, hence deviating from actual molecular pathways of zeolite formation. More recently, Pophale et al. developed a novel simulation method for predicting the synthesis of SDAs from a given set of reagents and reactions, which may be useful making a target zeolite. SDA selection was performed following the method of Lewis et al., based on host-guest stability simulations between putative SDAs and the target zeolite. This method was experimentally verified by Schmidt et al. where they developed an SDA for synthesizing the STW zeolite framework. Although this approach is computationally efficient in generating SDAs for a given framework, it remains unclear how changing properties of the SDA would result in a different micropore structure.

Lattice models provide computational efficiency by discretizing continuous space into countable configurations, thereby allowing the sampling of longer lengths and times. Such discrete models have been successful in predicting the structures of micellar solutions and surfactant-silica systems. Recently our group reported a bcc lattice model – which can be viewed as two interpenetrating diamond sublattices for SiO$_2$ – of silicic acid to study silica polymerization to amorphous nanoparticles and gels at the iso-electric point of silica (pH $\sim$ 2), and across pH values and silica concentrations. This bcc lattice model is inspired by periodic DFT calculations on various dense all-silica polymorphs, showing that the cohesive energy per unit SiO$_2$ is remarkably uniform across this class of systems, varying only by about 10 kJ/mol SiO$_2$. While the lattice
model approach makes the study of these systems more computationally accessible, the lattice constrains allowed structures that can form during the simulations. For instance, the T-O-T bond angles accessible in the lattice model are more restricted than those seen in nature. Nevertheless, the studies described above demonstrate the power of lattice models to elucidate the properties of disordered systems, raising the question whether such lattice models may shed light on crystal structures as well.

Our group has also applied parallel tempering Monte Carlo (PTMC) simulations – statistical mechanical approach to bypass thermodynamic energy barriers – to identify crystalline states of the lattice model. PTMC accomplishes this by simulating several system replicas at various temperatures and attempting swaps of configurations between replicas in accord with detailed balance, thereby simulating heating/cooling cycles that efficiently move simulations between amorphous and ordered states. Jin et al. recently applied PTMC to study the bcc lattice model of silica, to examine the feasibility of using PTMC to identify dense and microporous crystalline phases of this model. Jin et al. initiated all PTMC simulations from disordered states, and demonstrated that PTMC can be used to generate a rich array of crystalline structures such as zeolite analogs, chalcogenides, and two-dimensional layered materials with this simple bcc lattice model. Although these PTMC simulations do not necessarily follow kinetically-relevant pathways as discussed above, they provide a way forward towards future studies of zeolite nucleation. In particular, these PTMC calculations were performed in the absence of SDAs, raising the question of how the presence and properties of SDAs may influence the microporous structures that emerge in these simulations.

1.3.3 Simulating Nucleation of Microporous Crystals

One of the difficulties in investigating zeolite formation is that the relevant length scales lies in the blindspot of NMR and diffraction techniques. Although several mechanisms have been proposed for zeolite formation, such as monomer addition to the
growing crystals and aggregation of nanoparticles on the growing crystal have been proposed, the molecular picture of zeolite self-assembly is still not complete. With the onset of computationally efficient machines and clusters, molecular simulations methods are well poised to shed light on the mechanisms of zeolite formation.

Although the formation pathways of zeolites are not completely understood, researchers agree that zeolite synthesis is an activated process where a reactive energy barrier separates the reactants and the crystalline product. Traditional molecular simulations such MD and MC cannot sample such events due to their unlikelihood. Therefore, specialized molecular simulation methods are required to surmount free-energy barriers separating amorphous and ordered phases of a given material. Such methods break up into the following two classes: kinetic approaches such as transition-path sampling and forward-flux sampling, which build up accurate pictures of free-energy barriers and dividing surfaces separating amorphous and ordered phases by sampling kinetically-relevant pathways; and thermodynamic methods such as parallel tempering Monte Carlo (PTMC), which may bypass free-energy barriers to efficiently sample free-energy minima associated with amorphous and ordered phases.

So far, according to our current literature knowledge, no one has applied a rare event sampling method to study zeolite formation. We hypothesize that a major challenge in such a study is to build a computationally efficient model of silica with built-in physical and chemical inter-species interactions. Jin et al. took a “big-leap” in this direction when they came up with a lattice model of silica polymerization, and they demonstrated that this model can capture long time dynamics of amorphous silica. We extended this model to incorporate quasi-spherical SDAs to study the effects of SDA concentration and silica-SDA interaction on resulting crystals. However, we have not yet probed the kinetically-relevant pathways, and the energy barrier which separates amorphous silica from its crystalline phases. We discuss our approach to study the self-assembly of silica using forward-flux sampling technique. We estimate the energy barriers between
amorphous silica and idealized-\( \beta \) cristobalite\(^{67} \), the transition state. This part of our research is going to build a platform of statistical mechanical tools, by which we aim to tackle the big question in zeolite science – “what is the role of SDAs in the self-assembly process of porous materials?”

### 1.4 Thesis Outline

The remainder of this dissertation is divided into 5 chapters. In chapter 2 we first discuss silica polymerization across pH spectrum and silica concentrations. In chapter 3 we study the effects of quasi-spherical SDAs on crystalline frameworks. In chapter 4 we incorporate molecular SDAs to study the effects of TMA-type molecules on 3D crystals. In chapter 5 we investigate the self-assembly process of crystalline structures observed from PTMC simulations. We conclude in chapter 6 by discussing the impact of our research and also elaborating directions for future research.
CHAPTER 2

STUDY OF SILICA POLYMERIZATION

In this chapter, we present Monte Carlo simulations of a lattice model describing silica polymerization with an emphasis on the transition between gel states and nanoparticle states as the pH and silica concentration are varied. The pH in the system is controlled by the addition of a structure directing agent (SDA) of the type SDA$^+$ (OH$^-$). The silica units are represented by corner sharing tetrahedra on a body-centered cubic lattice, and the SDA$^+$ species by single sites with near-neighbor repulsions. We focus on two systems: one with low silica concentration with composition comparable to the clear solution silicalite-1 zeolite synthesis, and a high silica concentration system that leads to gel states. In the dilute system, clusters have a core-shell structure with the core predominantly comprised of silica with some SDA$^+$ cations, surrounded by a shell of only SDA$^+$ cations. Moreover, the average cluster size gradually decreases from 2 nm to 1.6 nm with increasing pH. The concentrated system forms a gel that remains stable to increasing pH up to about 9.2. At pH values in the range 9.2-10, the gel transforms to nanoparticles of size around 1.0 nm, surprisingly smaller than those in the dilute system. We also study the evolution of the $Q_n$ distribution (a measure of silica network structure) for both systems and obtain good agreement with $^{29}$Si NMR data available for the concentrated system.

2.1 Background

Recently we have deployed lattice models to study silica polymerization at the isoelectric point (pH~2)$^{33}$, and also spontaneous formation of nanoparticles at high pH
(pH~10) in clear solution synthesis of silicalite-1. Here, we extend these studies across the pH range and study the distinction between the nanoparticles formed at low and high silica concentrations. We have used an atomic representation of corner-sharing silica tetrahedra on a body-centered cubic (bcc) lattice. The condensation reaction was modeled by simultaneous occupancy of hydroxyl groups from different tetrahedra on the same lattice site. Jin et al. used this representation to predict network formation at the iso-electric point. However, the phenomena of silica polymerization for various pH values and silica concentrations remains yet to be explored. In particular, it is unclear whether the gel transforms smoothly or abruptly to nanoparticles as the pH is increased, and whether the nanoparticles are similar in size for systems with low and high silica concentrations. We address this issue by introducing a salt of type SDA⁺(OH⁻) in our system to change the pH. The cation, SDA⁺ was represented as a single site on the lattice with near neighbor repulsions accounting for its size. We impose an orientation dependent interaction of SDA⁺ with the anionic portion of Si(OH)₃O⁻ to mimic electrostatic charge balancing. In this work we study low and high silica concentration systems and find the surprising result that the nanoparticles for the dilute silica system are larger than those in the concentrated system.

The outline of this chapter is as follows. In section 2.2 we discuss the model; in section 2.3, we describe the simulation techniques used; section 2.4 presents our results, first for a low silica concentration system and then for a high silica concentration system; in section 2.5 we compare our findings with experiments. Finally, in section 2.6 we present a summary of our results and conclusions.

2.2 Model

We follow closely the earlier work of Jin et al. The silica source is chosen to be tetraethyl orthosilicate [Si(OC₂H₅)₄ or TEOS] and we assume that it hydrolyzes completely into a molecule of silicic acid and four molecules of ethanol. For simplicity, we
do not distinguish between water and ethanol molecules, but rather we treat them as “solvent”. The pH of the system is controlled by adding a structure directing agent of type $\text{SDA}^+ (\text{OH}^-)$. We assume complete dissociation of $\text{SDA}^+ (\text{OH}^-)$ into $\text{SDA}^+$ and $\text{OH}^-$. Under such conditions, $\text{OH}^-$ deprotonates the neutral silica monomer $[\text{Si(OH)}_4]$ to produce an ionic silicate monomer $[\text{Si(OH)}_3\text{O}^-]$. We assume that any remaining $\text{OH}^-$ in the system goes to determine the pH. The cationic species ($\text{SDA}^+$) can vary from a sodium cation ($\text{Na}^+$) to a tetrapropylammonium cation ($\text{[N(C}_3\text{H}_7)_4]^+$ or $\text{TPA}^+$) which is used in the synthesis of silicalite-1.

![Figure 2.1. Representation of various species on the lattice. (a) Neutral Silica ($\equiv\text{Si-OH}$); (b) Ionic Silica ($\equiv\text{SiO}^-$); (c) Cation ($\text{SDA}^+$).](image)

We chose the body-centered cubic (bcc) lattice, which can be viewed as two interpenetrating diamond sublattices, as a model for silica. We adopt an atomic representation of silica on a BCC unit cell. The silicon atom, treated as a single site, is located at the center of the unit cell, whereas the hydroxyl groups, also treated as single sites, occupy either of the diamond sub-lattices. The neutral silica monomers ($\equiv\text{Si-OH}$ also denoted as “SN”) and the ionic silica monomers ($\equiv\text{Si-O}^-$ denoted as “SI”) are both represented by the BCC unit cell, as shown in Figs. 2.1(a) and 2.1(b).

To keep the model as simple as possible, we adopt a coarse-grained picture of the cation by representing it as a single site with near neighbor repulsions, accounting for
the size of the cation as shown in Fig. 2.1(c). We represent water and ethanol molecules as vacant sites on the lattice.

2.2.1 Neutral Polymerization

The iso-electric point for silica, i.e., the pH at which the charge on silica vanishes, has been observed to be in the range 2-3\(^{28}\). Under such conditions and at room temperature, the kinetics of condensation are slow and changes in silica network structure of the system can be observed spectroscopically (e.g., with\(^{29}\)Si NMR)\(^{30}\).

We adopt a simplified view of the reactions occurring in such a system; we define the neutral polymerization reaction as:

\[
\equiv Si - OH + OH - Si \equiv \leftrightarrow \equiv Si - O - Si \equiv + H_2O \tag{2.1}
\]

Here a silica cluster (\(\equiv Si-OH\)) reacts with another silica cluster resulting in the formation of a bridging oxygen and liberation of a water molecule, treated as a lattice vacancy. We model this reaction in our system allowing two tetrahedral vertices to share the same site with an accompanying lowering of the energy. This energy lowering represents the exothermicity of the condensation reaction, and has been calculated using density functional theory coupled with continuous dielectric model\(^{98}\). The resulting configuration is shown in Fig. 2.2.

*Figure 2.2.* Result of neutral polymerization producing a bridging oxygen between two SN molecules.
2.2.2 Alkaline Polymerization

As mentioned earlier, the pH of the system can be controlled by introducing a base of the type SDA⁺(OH⁻). In the presence of SDA⁺(OH⁻), the hydroxide ion (OH⁻) can deprotonate an SN, resulting in a singly deprotonated silicate species [Si(OH)O⁻ or “SI”]. To further simplify our model we consider only singly ionized monomers. Although doubly ionized silica [=Si-(O⁻)]; has been shown to exist at sufficiently high pH, it has been hypothesized to remain inert in polymerization process.

\[ \equiv Si - OH + OH - Si(O^-) = \quad \equiv Si - O - Si(O^-) = +H_2O \]  \hspace{1cm} (2.2)

Therefore, in the presence of SDA⁺(OH⁻) we need to consider two additional types of polymerization reactions: (i) SN reacting with SI forming a bridging oxygen as illustrated in Fig. 2.3, and (ii) condensation between two SI molecules to yield \( \equiv Si(O^-)-O-Si(O^-) \equiv \). We assume that the electrostatic repulsion between two SI molecules is strong enough to prohibit their condensation from taking place.

Figure 2.3. Alkaline polymerization forming bridging oxygen between SN and SI molecules.

Moreover, O⁻ is prohibited from forming a bridge with a hydroxyl group of another silica species. Such a reaction would result in the liberation of a hydroxide ion (OH⁻) instead of a water molecule, which is thermodynamically unfavorable.
2.2.3 Interaction of Cations

As a base case model, the cation (SDA\(^+\)) in our model is treated as a single site with excluded volume. We will consider more complex SDA\(^+\) models in a forthcoming publication. The excluded volume is accounted by imposing near-neighbor repulsions (between the cation site and its first nearest neighbors). Such a model may mimic a sodium cation or a tetralkylammonium cation depending upon the range of repulsions.

![Figure 2.4. Interaction of the SDA\(^+\) with O\(^-\) of an SI monomer](image)

2.2.4 Parameters

With four distinct species in our system, SN, SI, SDA\(^+\) and H\(_2\)O, there would be ten interaction energies in the system: SI-SN, SI-SI, SN-SN, SI-SDA\(^+\), SN-SDA\(^+\), SN-H\(_2\)O, SI-H\(_2\)O, SDA\(^+\)-H\(_2\)O, SDA\(^+\)-SDA\(^+\) and H\(_2\)O-H\(_2\)O. The Hamiltonian of the system is given by

\[
H = \sum_{i=1}^{m} \sum_{j \geq i}^{m} C_{ij} \epsilon_{ij}
\]

where \(m\) is the number of components in the system. \(C_{ij}\) is the total number of interaction contacts between components \(i\) and \(j\), and \(\epsilon_{ij}\) is the corresponding interaction energy. Jorge et al.\(^{65}\) defined the reduced temperature of such system as \(T^* = k_B T/|\epsilon_{SNSN}|\). Jin\(^{33}\) studied the change in solubility of an all-silica system with temperature and obtained \(\epsilon_{SNSN} = -3.4\) kcal/mol, which gives the value of room temperature as \(T^* = 0.15\). We use this value of \(T^*\) in the present work.

We now focus on specifying the remaining interaction energies in the system. The nature of SI-SN interaction should be attractive, as exothermic condensation takes place.
between SN and SI. Consistent with our previous work\textsuperscript{65}, we have assigned $\epsilon_{SISN} = 0.8\epsilon_{SNSN}$. As stated above, we assume that SI-SI condensation reaction does not contribute significantly to the polymerization process; hence we assign $\epsilon_{SISI} = 0$ which neither precludes nor favors this process.

In the present work, the SDA$^+$ cation occupies a single site, and has first neighbor repulsion to every species. This makes the size of the cation comparable to the size of the silica monomer, i.e., approximately 3.2 Å in diameter, or that of a TMA molecule\textsuperscript{101}. The interaction between cations is dominated by electrostatic repulsion; thus, we assume an infinite repulsion between cations extending to the first neighboring sites. The cation-cation repulsion is assumed to be short ranged in our model because of Debye-Hückel screening\textsuperscript{58}. The interactions between SI and SDA$^+$ are attractive because of electrostatic attraction. The interaction depends upon the orientation of SI and was calculated to be higher than the condensation energy of silica\textsuperscript{102}. Therefore, consistent with our previous work, we have assigned $\epsilon_{SISD A} = 2.0\epsilon_{SNSN}$. To maintain local charge balancing, we impose the condition that a molecule of SI interacts with only one molecule of SDA$^+$ and vice versa, as shown in Fig. 2.4. The interactions between SDA$^+$ and SN are set to zero for simplicity. Moreover, we assume for simplicity that the interaction of water (i.e., vacancies) with all the species is zero.

Using all the above simplifications the Hamiltonian now takes the form

$$H = \sum_{i=1}^{3} \sum_{j \neq i}^{3} C_{ij}\epsilon_{ij}$$

where the indices corresponding to 1, 2, 3 represent SI, SN and SDA respectively. The interaction strengths are given in table 2.1 and table 2.2.

\section*{2.3 Simulation Technique}

We use canonical ensemble Monte Carlo simulations to study the behavior of the system. We implement periodic boundaries conditions on the boundaries of the lattice
Table 2.1. Interaction energies for first neighbors.

<table>
<thead>
<tr>
<th></th>
<th>SI</th>
<th>SN</th>
<th>SDA⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI</td>
<td>0.0</td>
<td>-0.8</td>
<td>∞</td>
</tr>
<tr>
<td>SN</td>
<td>-0.8</td>
<td>-1.0</td>
<td>∞</td>
</tr>
<tr>
<td>SDA⁺</td>
<td>∞</td>
<td>∞</td>
<td>∞</td>
</tr>
</tbody>
</table>

Table 2.2. Interaction energies for second neighbors.

<table>
<thead>
<tr>
<th></th>
<th>SI</th>
<th>SN</th>
<th>SDA⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI</td>
<td>0.0</td>
<td>0.0</td>
<td>-2.0</td>
</tr>
<tr>
<td>SN</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>SDA⁺</td>
<td>-2.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

and start the simulation by placing molecules at random locations on the lattice. Next, we attempt three kind of moves to efficiently sample the different states of the system. The first move is translation where we select a molecule at random and another site at random on the lattice. If the selected site is vacant, we attempt to move the molecule to the new site. The second move is a swap between two molecules, where we attempt to exchange two molecules selected randomly. The third kind of move is the rotation of a silica tetrahedron. In case of SN we attempt to rotate the tetrahedron by randomly assigning it to the other diamond sublattice of the unit cell. Whereas, for SI, we move O⁻ randomly on one of the eight first nearest neighbors and the hydroxyl groups accordingly. All moves are accepted or rejected based on the Metropolis condition. An MC step consists of $N$ trial moves, where $N$ is the number of molecules in the system. A trial move comprises of an attempted translation, an attempted swap, and an attempted rotation. We study cluster size statistics using the Hoshen-Kopelman algorithm, where we consider two silica monomers to be part of the same cluster if they are connected by a bridging oxygen atom. In determining cluster statistics we (somewhat arbitrarily) define aggregates that have greater than fifteen silica units as a cluster.

We have studied both dilute and concentrated systems with respect to silica concentration. The dilute system has composition 40 TEOS : $x$ SDAOH : 9500 H₂O, whereas the concentrated system has composition 25 TEOS : $x$ SDAOH : 400 H₂O. Here, $x$ is the mole
proportion of SDA$^+(\text{OH}^-)$. The lattice size in both the systems is $100 \times 100 \times 100$, which has been found of sufficient size in previous work$^{33,65}$. Length scales in the system are controlled by the Si-O bond length which is approximately 1.6 Å. This makes the lattice dimension to be 18.5 nm in all the directions. Both the systems were studied for $10 \times 10^6$ MC steps, with the equilibrium found to be attained after $5 \times 10^6$ MC steps for low silica concentration system, and $7 \times 10^6$ MC steps for high silica concentration system.

The topology of silica networks changes significantly with pH. We study these changes by computing the variation in average cluster size with change in cation content. The diameter of a cluster can be calculated using the diameter of gyration:

$$D = 2 \sqrt{\frac{1}{2N^2} \sum_{j=1}^{N} \sum_{i=1}^{N} |\mathbf{r}_i - \mathbf{r}_j|^2},$$

where $N$ is the number of silica units in the cluster, and $|\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the $i^{th}$ and $j^{th}$ silicon atoms belonging to the same overall cluster. We implement the minimum image convention to calculate distances between silicon atoms. Next, we calculate the mass average and mole average size for every cluster in the system according to:

$$\langle \text{cluster size} \rangle_{\text{mole average}} = \frac{\sum_{k=1}^{M} D_k}{M},$$

$$\langle \text{cluster size} \rangle_{\text{mass average}} = \frac{\sum_{k=1}^{M} D_k N_k}{\sum_{l=1}^{M} N_l},$$

where $M$ is the total number of clusters, $N_l$ is the total silica units in cluster $l$, and $D_k$ is the diameter of the $k^{th}$ cluster. It should be noted that we only consider silica molecules, and not SDA$^+$ species, while calculating the average cluster size. The ratio of the mass to mole average cluster size gives the polydispersity ratio,$^{105}$ which is a measure of the heterogeneity in the cluster size distribution, with mono-disperse distributions showing a polydispersity ratio of unity, and poly-disperse systems exceeding unity.
We also compute the pair distance distribution function (PDDF) by plotting a histogram of distances between silicon atoms in a cluster, for comparison with distributions extracted from small angle X-ray scattering and small angle neutron scattering data. The structural properties of networks can be obtained by computing the $Q_n$ distribution, which gives the fraction of Si atoms bonded to $n$ bridging oxygens. Harris and co-workers$^{106,107}$ measured $^{29}$Si NMR chemical shifts in aqueous silicate solutions. Their findings indicate that $^{29}$Si chemical shifts are very different for neutral and anionic silica species,$^{59}$ suggesting that the chemical shifts that determine the $Q_n$ distributions for our system are dominated by connectivities around SN. Therefore, while calculating $Q_n$ distributions we only consider connectivities of silicon atoms around SN species in our simulations, and ignore connectivities of silicon atoms around SI in our simulations. The normalization of the $Q_n$ distribution is computed on the basis of the total SN present in the system.

2.4 Results and Discussion

2.4.1 Dilute System

Fedeyko et al.$^{52}$ characterized the intermediate nanoparticle phase observed during the synthesis of silicalite-1 using small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) on a system dilute with respect to silica with the following composition: 40TEOS : xSDAOH : 9500H$_2$O. They hypothesized that the difference between the pair distance distribution functions obtained by SAXS and SANS may be evidence of the existence of a diffuse double layer around the silica clusters including SDA$^+$ cations and compensating anions. They also proposed that the nanoparticles have a core-shell structure with silica in the core and SDA$^+$ cations in the shell. We have modeled this composition to investigate whether a core-shell structure emerges in our simulations.
2.4.1.1 Snapshots

A series of system snapshots at various $\text{SDA}^+$ mole fractions is shown in Fig. 2.5, generated using Visual Molecular Dynamics package\textsuperscript{108}. The qualitative behavior of the simulations is similar to our earlier work on silica polymerization\textsuperscript{33}. In each case, starting from a random initial configuration, the clusters grow with the phenomenon of Ostwald ripening\textsuperscript{59}, involving smaller clusters dissolving rapidly, adding their silica tetrahedra to larger clusters. In the absence of $\text{SDA}^+$ cations, a nanoparticle phase is observed containing clusters of silica as seen in Fig. 2.5(a). As the $\text{SDA}^+ (\text{OH}^-)$ concentration is increased more neutral silica molecules are deprotonated to ionic silica. There exists a competition between the electrostatic attraction of $\text{SI-SDA}^+$, and the condensation energy between silica that leads to the formation of nanoparticles possessing core-shell structures. The cores of these nanoparticles have silica surrounded by a shell of cations as shown in Fig. 2.5(b). When the mole proportion of $\text{SDA}^+ (\text{OH}^-)$ reaches a value close to that of TEOS, virtually all silica is in the form of SI and hence no clusters are observed in the system.

![Figure 2.5. Snapshots of system after $10 \times 10^6$ Monte Carlo steps with composition 40TEOS:$x\text{SDAOH}:9500\text{H}_2\text{O}$. (a) $x = 0.0$; (b) $x = 9.0$; (c) $x = 38.0$. Yellow spheres: SN, red spheres: SI, blue spheres: SDA. Note that the snapshots show only clusters having 15 or more SN and SI tetrahedra.](image)

We find under these dilute conditions that the concentration of silica is not high enough to produce percolating networks in our simulations. This suggests that we need
to consider higher silica concentrations to observe the transition from nanoparticles to gels.

2.4.1.2 Cluster statistics

Figure 2.6 shows the effect of SDA$^+$ (OH$^-$) mole fraction on mass and mole average cluster size and also on the total number of clusters. Greater weights are assigned to larger clusters in the mass average cluster size calculation, making it greater than the mole average cluster size for which equal weights are assigned to each cluster. We observe that both the average cluster sizes gradually decrease with increase in SDA$^+$ (OH$^-$) mole fraction. As the amount of SDA$^+$ increases, the amount of SI also increases because SDA$^+$ carries the strong base which deprotonates SN to yield SI. The mass average cluster size obtained in our simulations (1.6-2.0 nm) is comparable to results from experiments performed at the composition: 40TEOS : 9SDAOH : 9500H$_2$O$^{52}$.

Size distributions may be further understood by analyzing pair distance distribution functions (PDDF) shown in Fig. 2.7, which reveals that as the mole fraction of SDA$^+$ (OH$^-$) increases, the PDDF peak shifts to the left indicating a gentle trend towards smaller clusters. Increasing the concentration of SI yields smaller clusters for two reasons: in contrast with SN, which is a tetravalent network-forming species, SI is only a trivalent network former; and SI-SI condensation is not driven by a favorable interaction because of electrostatic repulsion. The polydispersity, given by the ratio of the mass to mole average cluster sizes, falls in the range 1.1-1.2 from these simulations, indicating reasonably monodisperse cluster size distributions. The tails of the PDDF curves are associated with the maximum cluster size in the simulations. The total number of clusters present in the system first increases weakly and then systematically decreases with $x$. However, the decrease after $x \sim 26$ is due to our definition of a cluster as an aggregate with silica units greater than fifteen. We note that the case of $x = 0$ (pH $\sim 2$-$3$) is treated separately when it comes to the pH calculation.
Figure 2.6. Effect of SDA mole fraction on cluster sizes and number of cluster in the system, giving relatively monodisperse cluster size distribution with a polydispersity of 1.1-1.2.
Fedeyko et al. measured the PDDF using small angle X-ray scattering (SAXS) and small angle neutron (SANS) scattering experiments. Because X-rays are scattered mostly by silica (higher electron density) whereas neutrons are scattered both by silica and SDA$^+$ species, we model the SAXS data by computing the PDDF including only silica, and the SANS data by computing the PDDF including both silica and associated SDA$^+$ within each cluster. To compare our findings with these scattering experiment results, we have calculated the PDDF for silica, SDA$^+$, and silica + SDA$^+$ as shown in Fig. 2.8. The PDDF curves for silica and SDA$^+$ indicate a core of silica surrounded by a shell of SDA$^+$ cations. However, the PDDF for SDA$^+$ species also contains smaller pair distances than the average cluster size, suggesting that the SDA$^+$ cations are present inside the clusters as well. The difference between the PDDF of silica and the PDDF of silica + SDA$^+$ at
higher pair distances is indicative of the presence of SDA$^+$ surrounding the cluster as predicted by Fedeyko et al.$^{52}$. Overall, Fig. 2.8 shows that SDA$^+$ species in our model are in both core and shell of these core-shell nanoparticles.

![Figure 2.8](image)

**Figure 2.8.** Pair distance distribution functions for silica, SDA$^+$, and silica + SDA$^+$ at 40TEOS:9SDAOH:9500H$_2$O.

### 2.4.1.3 $Q_n$ distribution

The $Q_n$ distribution provides another structural descriptor of the connectivity around silicon atoms, and is measured by $^{29}$Si NMR.$^{58}$ Figure 2.9 shows the evolution of the $Q_n$ distribution with MC steps. We observe that $Q_0$, the fraction of monomers in the system, monotonically decays as monomers combine to form higher order polymerized units. $Q_1$, which is indicative of oligomers, peaks at approximately 100 steps. $Q_2$, which accounts for rings and chains, peaks at 1,000 steps. $Q_3$ is representative of silica units in small clusters, and peaks around 100,000 steps. $Q_4$, which accounts for
condensed clusters, monotonically increases. The degree of condensation, defined as 
\[ c = \frac{1}{4} \sum_{n=0}^{4} nQ_n \], is a monotonically increasing function of MC steps. The qualitative behavior of the curves in Fig. 2.9 is similar to the ones observed in our previous work.\[33\].

\[\begin{align*}
Q_0 & \quad Q_1 \\
Q_2 & \quad Q_3 \\
Q_4 & \quad c \\
\end{align*}\]

**Figure 2.9.** Evolution of \(Q_n\) distribution with MC steps at 40TEOS:9SDAOH:9500H\(_2\)O.

### 2.4.2 Concentrated System

Having established the existence of nanoparticles in the low silica concentration system, we now focus our attention on the high silica concentration system with composition 25TEOS : xSDAOH : 400H\(_2\)O, which has been used in previous experimental studies.\[109\].

#### 2.4.2.1 Snapshots

A series of snapshots of the higher silica concentration system at various mole proportion of the cation is shown in Fig. 2.10. At such a high silica concentration, the system...
would have a large number of molecules which would be a hindrance in viewing the networks. To overcome this difficulty, we omit aggregates of size 15 tetrahedra or smaller in Fig. 2.10.

Figure 2.10. Snapshots after $10 \times 10^6$ MC steps with composition 25TEOS:xSDAOH:400H$_2$O. (a) $x = 0.0$; (b) $x = 16.0$; (c) $x = 22.0$. Only clusters of size 15 or bigger are shown here.

In the absence of cations ($x = 0$), we observe a large network that percolates the simulation cell as shown in Fig. 2.10(a). The spatial extent of this network is limited by the size of the system we study. The existence of such a network has been associated with gelation\cite{59}. As cation content is increased, more SN is converted to SI. Moreover, since there is no attraction present between SI molecules, the amount of silicate anions present in the solution increases. This behavior is similar to the low silica concentration system we studied. The presence of the percolating network persists to high values of $x$ ($x = 16.0$) as shown in Fig. 2.10(b). At even higher values of $x$ ($x = 22.0$), we observe the nanoparticle regime. These nanoparticles are different from our predictions in the low silica concentration system: they are more numerous but smaller in size than those obtained at low silica concentrations. This is surprising as we may expect nanoparticle size at higher silica concentration to exceed that at lower silica concentration.
2.4.2.2 Cluster Statistics

We now study cluster statistics as a function of SDA\(^+\) mole fraction. Similar to Fig. 2.6, we have computed the mass and mole average cluster sizes, shown in Fig. 2.11. In contrast to Fig. 2.6, we see in Fig. 2.11 that the mass average cluster sizes are significantly greater than the mole average values. This indicates high polydispersity of the clusters in this system. We observe two plateaus in the mole average cluster size with an increase in \(x\). These plateaus may be misinterpreted as a gel regime for \(0 \leq x \leq 15\) and a nanoparticle regime for \(16 \leq x \leq 24\); however, the mass average cluster size suggests a different picture. It predicts a percolating network for compositions in the range \(0 \leq x \leq 21\), where the average cluster size is close to half the simulation cell size (~ 9.25 nm). Due to the high silica concentration, we do not observe independent clusters as in Fig. 2.5, but rather we see clusters that are connected to each other by links of condensed silica. For \(x \geq 22\), the mass average cluster size drops precipitously to a low value, suggesting the transition to the nanoparticle regime, where the size of the nanoparticles is ~1.0 nm. No clusters are observed for SDA\(^+\)(OH\(^-\))/TEOS \(\geq 1\) (\(x \sim 25\)). The polydispersity drops to nearly unity for \(22 < x < 25\), indicating a rather monodisperse collection of relatively small silica nanoparticles.

Similar conclusions can be derived from Fig. 2.12, which shows the pair distance distribution function. At \(x = 0.0\) and \(x = 16.0\), the tails of the distribution functions are greater than half the system dimension, indicative of percolation. At \(x = 22.0\), the function resembles that of Fig. 2.7, with the peak at a lower distance suggesting that the cluster sizes are smaller than those of the low silica concentration system.
Figure 2.11. Average cluster sizes and number of clusters as a function of SDA\(^+\) mole fraction at 25TEOS:xSDAOH:400H\(_2\)O.

Figure 2.12. Pair distance distribution function for gel (\(x = 0\)), transition (\(x = 16.0\)) and nanoparticle (\(x = 22.0\)) states.
2.4.2.3 $Q_n$ Distribution

The evolution of the $Q_n$ distribution with MC steps for the concentrated system is shown in Fig. 2.13. We observe that $Q_0$ monotonically decays as the monomers combine to form higher order polymerized units. $Q_1$ (oligomers) peaks at approximately 10 steps; $Q_2$ peaks after 100 steps; and $Q_3$ peaks around 7,000 steps. These results are qualitatively similar to those described above for the low silica concentration system. This finding suggests that the $Q_n$ distribution is relatively insensitive to differences in silica polymerization arising from different silica concentrations.

![Figure 2.13](image)

**Figure 2.13.** Evolution of $Q_n$ distribution with MC steps at 25TEOS:22SDAOH:400H$_2$O

2.5 Comparison with experiments

We now present a comparison of our calculated $Q_n$ distributions with experiments of dilution studies (increase in the water content instead of decrease in SDA$^+$(OH$^-$) mole fraction) by Follens *et al.*$^{109}$ in Fig. 2.14. They measured $Q_1$, $Q_2$, $Q_3$ and $Q_4$ values using $^{29}$Si NMR during the clear solution synthesis of silicalite-1 under various conditions. The vertical line represents the degree of condensation at which the $Q_n$ measurements
were made, and the color of points on the line corresponds to the respective $Q_n$ values. It should be noted that the experimental values of $Q_2$ and $Q_3$ are the same ($\sim 0.171$) in Fig. 2.14(a). We observe that our simulations reproduce the $Q_n$ values reasonably well, suggesting that our model captures aspects of the silica polymerization mechanism in the high water content systems (Fig. 2.14(b), Fig. 2.14(c), and Fig. 2.14(d)) to a good extent. However, in the low water content system (Fig. 2.14(a)), the model gives only a qualitative agreement with the $Q_n$ values. We believe this may be due to the assumptions made about the various interactions with water being set to zero.

Figure 2.14. $Q_n$ distribution compared with experiments. (a) 25TEOS : 9SDAOH : 400H$_2$O; (b) 25TEOS : 9SDAOH : 900H$_2$O (c) 25TEOS : 9SDAOH : 1900H$_2$O; (d) 25TEOS : 9SDAOH : 4000H$_2$O. Color of points on the vertical line corresponds to the respective color of the $Q_n$ curves.
2.6 Summary and Conclusions

Building on previous work, we have further developed and applied a lattice model for silica polymerization over a broad pH range and for different silica concentrations. We represent silica monomers as rigid tetrahedra on a unit cell of a body centered cubic (BCC) lattice, where a silicon atom occupies the body center of the unit cell and hydroxyl groups are at the vertices. The pH in the system is controlled by the amount of structure directing agents (SDA) carrying strong base in the form of SDA⁺(OH⁻). The SDA cations, SDA⁺, are represented as single sites on the lattice with first neighbor repulsions to every species. We have modeled the condensation reaction via double occupancy of hydroxyl groups at a single lattice site, hence representing corner sharing tetrahedra. We also considered short ranged attractions between O⁻ of SI and SDA⁺. As with our previous work with this model, we have imposed energy penalties on three and four membered rings, and have prohibited the formation of two membered rings. With appropriate interaction energies between components, this model has been found to elucidate the silica polymerization process over a broad pH range.

We have applied this model to two systems: at low and high silica concentrations. In the case of low silica concentration, we observed that mass and mole average cluster sizes are quite similar indicating a relatively mono-disperse cluster distribution. These cluster sizes were found to decrease very gradually with increase in the SDA⁺(OH⁻) mole fraction. We also studied the pair distance distribution function (PDDF) of clusters under these conditions. The peak and the spread of the PDDF for silica was found to shift to lower distances as the SDA⁺(OH⁻) concentration increases, consistent with computed average cluster sizes. The difference between the PDDF of silica, and the PDDF of silica + SDA⁺ suggests that SDA⁺ cations not just surround the cluster, but are also contained to some extent within the cluster. To further investigate the formation mechanism of the nanoparticles we studied the evolution of the Qₙ distribution. Our results suggest a
common form for the $Q_n$ distribution that may be expected under many different conditions of silica polymerization.

We have also studied networks in a high silica concentration system with density comparable to that in sol-gel processing. We observed a gel regime at low and intermediate SDA$^+(\text{OH}^-)$ mole fractions. This regime is marked by the presence of percolating networks in our simulations. The MC sampling is slow in this region, indicating that the dense network imposes long relaxation times. The mass average and mole average cluster sizes differ significantly indicating polydispersity of clusters under these conditions. As the SDA$^+(\text{OH}^-)$ mole proportion reaches close to that of the initial tetraethyl orthosilicate, we observe a nanoparticle regime that is marked by a sudden drop in the mass average cluster size. The resulting nanoparticles are smaller than those obtained under more dilute conditions of silica, a surprising result considering that higher silica concentration might be expected to produce larger nanoparticles. The formation mechanism of these clusters, studied using the $Q_n$ distribution, is similar to that in the low silica concentration system. The PDDF reflects percolating networks at low and intermediate SDA$^+(\text{OH}^-)$ mole fractions, whereas at sufficiently high SDA$^+(\text{OH}^-)$ concentrations, the PDDF shows a mono-disperse nanoparticle phase.

This simple model provides significant insights into silica polymerization across a range of pH values and silica concentrations. In the next chapter we focus our attention on crystalline silica materials, where we investigate the effects of quasi-spherical structure directing agents on microporous structures which emerge from the model.
CHAPTER 3
FORMATION OF ZEOLITE ANALOGUES USING PARALLEL TEMPERING MONTE CARLO SIMULATIONS: EFFECTS OF QUASI-SPHERICAL STRUCTURE DIRECTING AGENTS

We have used parallel tempering Monte Carlo simulations to search for crystalline states of a lattice model of silica polymerization in the presence of structure directing agents (SDAs). Following previous work where we have discretized continuous space into a body-centered cubic (bcc) lattice, we have modeled tetrahedral molecules (T(OH)$_4$) as corner–sharing tetrahedra on a bcc unit cell. The SDAs were represented as quasi-spherical species with diameters of 6.4 Å and 10.4 Å, to study the effect of SDA size on the resulting crystal structures. Our parallel tempering Monte Carlo simulations produce fully-connected crystalline structures finding the emergence of 3D microporous materials with SDAs occupying the pore spaces, and 2D layered materials with SDAs occupying the gallery space in between layers. We have found that the strength of SDA-oxygen attraction plays a significant role in directing final micropore structures. For relatively strong attractions (> 1.2 kcal/mol SDA-oxygen contacts) we have found only 2D layered materials; for attractions below this cut-off we observed 3D microporous crystals; and for no attraction – modeling the SDA as a quasi hard sphere – we again found only 2D layered materials. In the space of 3D microporous crystals, we have also found that using larger SDAs or a lower concentration of a given SDA generate crystals with larger rings.
3.1 Introduction

Specialized molecular simulation methods are required to surmount free-energy barriers separating amorphous and ordered phases of a given material. Such methods break up into the following two classes: kinetic approaches such as transition-path sampling\cite{91,92} and forward-flux sampling,\cite{93,94} which build up accurate pictures of free-energy barriers and dividing surfaces separating amorphous and ordered phases by sampling kinetically-relevant pathways\cite{95}; and thermodynamic methods such as parallel tempering Monte Carlo (PTMC),\cite{96,97} which may bypass free-energy barriers to efficiently sample free-energy minima associated with amorphous and ordered phases. PTMC accomplishes this by simulating several system replicas at various temperatures and attempting swaps of configurations between replicas in accord with detailed balance, thereby simulating heating/cooling cycles that efficiently move simulations between amorphous and ordered states. Jin et al. recently applied PTMC to study the bcc lattice model of silica, to examine the feasibility of using PTMC to identify dense and microporous crystalline phases of this model. Jin et al. initiated all PTMC simulations from disordered states, and demonstrated that PTMC can be used to generate a rich array of crystalline structures such as zeolite analogs, chalcogenides, and two-dimensional layered materials with this simple bcc lattice model.\cite{67} Although these PTMC simulations do not necessarily follow kinetically-relevant pathways as discussed above, they provide a way forward towards future studies of zeolite nucleation. In particular, these PTMC calculations were performed in the absence of SDAs, raising the question of how the presence and properties of SDAs may influence the microporous structures that emerge in these simulations. In this chapter, we extend the PTMC simulations of this bcc lattice model of silica by incorporating SDAs to study their effects on final microporous crystal structures. Our particular focus is on SDA size, concentration, and interaction with silica species. The SDA is modeled below as a quasi-spherical species with excluded volume and van der Waals-like, near-neighbor attractions to silica oxygens. We find that silica polymer-
ization in the presence of bigger SDAs results in zeolites with larger rings, and higher concentrations of SDAs lead to zeolites with smaller rings. We also find a relatively narrow range of silica-SDA attraction values that lead to 3D microporous materials.

The remainder of this paper is organized as follows: in Sec. 3.2 we discuss the model and its parameters; in Sec. 3.3 we describe the Monte Carlo simulation technique; Sec. 3.4 presents our results on the effects of SDA concentration, size, and attraction strength on crystal structure; and finally in Sec. 3.5, we present a summary of our results and concluding remarks on future research implied by the findings in this article.

3.2 Model

Our model extends the work of Jin et al.\textsuperscript{33}, where three-dimensional continuous space is discretized onto a body-centered cubic (bcc) lattice. A tetrahedral molecule (T(OH)\textsubscript{4}) is represented in a bcc unit cell with the tetrahedral (T) atom located at the body-center of the unit cell and the hydroxyl groups (-OH) located at four of the eight vertices, as shown in Figure 5.1a. This model has been applied to study silica polymerization\textsuperscript{33} at the iso-electric point of silica (pH $\sim$ 2)\textsuperscript{59}, and the self-assembly zeolite analogs.\textsuperscript{67} The SDAs are modeled below as quasi-spheres by imposing far-neighbor repulsions from a single lattice site, as shown in Figure 5.1b. We consider two SDA sizes as summarized in Table 4.1: a medium SDA with a diameter of 6.4 Å which excludes 59 bcc sites, and a large SDA with a diameter of 10.4 Å, excluding 181 bcc sites. We have recently applied this silica-SDA lattice model to study silica polymerization to amorphous nanoparticles and gels for various pH values and silica concentrations\textsuperscript{87}. In general, we make the approximation of treating the solvent as vacancies on the lattice, as we have consistently done in our earlier work\textsuperscript{65}. 

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Figure 3.1. Representation of different species on the bcc lattice. (a) T(OH)$_4$ molecules with T atom at the center of the unit cell and oxygen atoms located on the vertices; (b) an SDA molecule as a single site with far neighbor repulsions, here SDA diameter is 3.2Å. Red tetrahedra represents excluded sites and green cubes represent attraction contact points.

With three species in our model — SDA, T(OH)$_4$, and solvent — there can be a total of six interactions energies. As in our earlier work$^{65}$, we have set the reference energy scale to be the condensation energy between adjacent tetrahedral molecules, $\varepsilon_{T(OH)_{4}-T(OH)_{4}}$. In a condensation reaction, the hydroxyl groups from two tetrahedra come together (via allowed double occupancy by hydroxyl groups) to create a bridging oxygen which liberates a water molecule, represented as a new vacancy on the lattice created by the allowed double occupancy$^{33}$ (see Figure 3.2a). Each condensation reaction is assumed to change the total system energy by $\varepsilon_{T(OH)_{4}-T(OH)_{4}} = -4$ kcal/mol,$^{33,98}$ representing the exothermicity of silica condensation, one of the driving forces for silica network formation. We prohibit the formation of two-membered rings as those would have a high angular strain$^{110}$. As such, all fully-connected silica networks that can form in our bcc lattice model exhibit the same energy per T(OH)$_4$, broadly consistent with periodic DFT results for dense and zeolitic silica polymorphs$^{88}$. This also indicates that silica-SDA in-
teractions will determine the eventual crystalline ground states of this silica-SDA lattice model.

We model attractions between SDAs and T(OH)$_4$ tetrahedra according to the spirit of van der Waals interactions, following the work of Gies and Marler$^{57}$, Lewis et al.$^{70}$, and van Santen and coworkers$^{71,72}$. In particular, for each SDA size, we allow attractions to bridging oxygens at sites just beyond the region of excluded volume (see Figure 3.2b). We do not allow SDA–T(OH)$_4$ attractions to terminal OH groups because we focus on van der Waals-type and not highly polar, attraction types in this work. For each medium/large SDA there are 6/48 possible SDA-O attraction sites (see Table 4.1). For each attraction site we posit an attraction strength of $\varepsilon_{O-SDA} \leq 0$; we vary $\varepsilon_{O-SDA}$ over 11 values $f \times \varepsilon_{T(OH)4-T(OH)4}$ where $f$ takes the values (0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0), to determine how the strength of SDA-T(OH)$_4$ interactions influences final crystal structures. Below we show specific results for the cases $f = 0.2$ and 1.0; the remaining results are given in appendix. Table 4.1 summarizes all systems studied.

To complete the specification of our model, we note that SDA-SDA interactions are assumed to be hard-sphere in nature. In addition, all interactions with solvent (vacancies) are neglected for computational simplicity, consistent with our previous development of this lattice model$^{33,65}$. 
3.3 Simulation Methodology

We have applied parallel tempering Monte Carlo simulations\textsuperscript{96,97} (PTMC) to study crystalline states of silica in the presence of SDA species. The scaled temperature of the lattice model $T^* = k_B T / \epsilon_{T(OH)_4 - T(OH)_4}$ corresponding to ambient conditions has been estimated to be 0.15 using a previous silica solubility analysis\textsuperscript{33}. PTMC simulates multiple copies of the system, each with a different temperature, and attempts configurational swaps between (typically adjacent) replicas with probabilities that obey detailed balance within the canonical ensemble. We have used room temperature ($T^* = 0.15$) as the lowest temperature in our PTMC temperature grid, which contained 50 temperatures for all PTMC simulations reported below. We have chosen the highest PTMC temperature to produce a largely dissolved state wherein the majority of $T(OH)_4$ units are unpolymerized; our previous study indicates that $T^* = 0.30$ is suitable for the PTMC.
maximum temperature. Temperature grid spacing was determined such that the acceptance probability of exchange between adjacent replicas is close to 20%. This was achieved by running short Monte Carlo simulations of 5000 steps and refining the temperature grid to the point where the average acceptance probability is around 20%. We performed PTMC simulations in a parallel implementation using the message passing interface (MPI) protocol.

We have implemented the following three kinds of canonical ensemble Monte Carlo moves (along with replica exchange moves): translations, rotations, and swaps. A translation move is made where any molecule, among SDAs and T(OH)$_4$ tetrahedra, is selected at random and is attempted to be moved to any vacant site on the lattice. A rotational move is where a random T(OH)$_4$ molecule is selected and is attempted to be rotated to the other four vertices in the corresponding bcc unit cell. The third kind of move is a swap where a T(OH)$_4$ tetrahedron and an SDA are selected at random, and an exchange is attempted between their positions. The acceptance probabilities for these moves are based on the Metropolis criterion. One Monte Carlo “step” comprises $N$ translations, $N$ rotations, and $N$ swaps, where $N$ is the total number of molecules in the system. Exchanges between configurations are attempted every 5000 MC steps. Ninety percent of such exchanges are attempted between adjacent temperature configurations, and 10% of the exchanges are attempted by randomly selecting temperatures that lie within a quarter length of the temperature grid. The acceptance probability of exchanging configurations at temperatures $T_1$ and $T_2$ with energies $E_1$ and $E_2$, respectively, is given by:

$$\min \left[ 1, \exp \left\{ \frac{1}{k_B T_1} - \frac{1}{k_B T_2} \right\} (E_1 - E_2) \right]$$

We have simulated a cubic lattice of size $8 \times 8 \times 8$ unit cells with periodic boundary conditions for $10 \times 10^6$ MC steps. The system length scale is defined by the Si-O bond
length of 1.6 Å, which sets the length of the simulation box to be 14.8 Å. Table 4.1 shows the T(OH)₄ concentration that has been studied in this work. For comparison, the dense silica polymorph β-cristobalite contains 64 T(OH)₄ tetrahedra in this simulation box.

**Table 3.1.** Simulation parameters studied in this work

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO₄ concentration (T(OH)₄/box)</td>
<td>tetrahedral units in simulation</td>
<td>32, 40, 48, 56</td>
</tr>
<tr>
<td>SDA concentration (SDAs/box)</td>
<td>low</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>high</td>
<td>4</td>
</tr>
<tr>
<td>SDA diameter (Å)</td>
<td>medium</td>
<td>6.4</td>
</tr>
<tr>
<td></td>
<td>large</td>
<td>10.4</td>
</tr>
<tr>
<td>SDA-T(OH)₄ attraction</td>
<td>ε₀–SDA = f ε_T(OH)₄–T(OH)₄</td>
<td>f = 0.1n, n = 1, 2, 3...10</td>
</tr>
</tbody>
</table>

We have studied SDAs with two sizes as listed in Table 4.1 – the diameter of the medium size SDA is 6.4 Å with 59 excluded sites and 6 SDA-O interaction contacts. Whereas the diameter of the larger SDA is 10.4 Å, slightly greater than the ionic diameter of tetra-propylammonium cation (9.0 Å), with 181 excluded sites and 48 SDA-O interaction contacts. We studied 11 values of the parameter ε₀–SDA, and we considered SDA concentrations of either 2 or 4 SDAs per simulation cell, giving a total number of 44 distinct systems studied (see Table 4.1 for a detailed summary), each simulated at 50 temperatures on the PTMC grid. These simulations produced 10 distinct crystalline microporous structures with three-dimensional connectivity, and another roughly 10 two-dimensional layered materials. The layered materials that form in our simulations are all comprised of fully-connected (i.e., all Q₄) silica, in contrast to many synthesized layered materials that are stabilized by terminal silanols. Due to the stochastic nature of these simulations, a consistent final structure is not always observed at each of the temperature values on the PTMC grid. However, to study the effects of SDA size, and SDA concentration on the final structure, the most frequently occurring structures on the PTMC grid were selected. All the structures discovered through this materials discov-
ery platform are shown in the appendix, including the conditions found in our PTMC simulations that produced each material.

We have characterized the materials resulting from our simulations based on their ring size distributions (RSD), where the ring size is defined as the total number of T-atoms present in a given ring. We have used the R.I.N.G.S. package\textsuperscript{112} to compute the total number of primitive rings\textsuperscript{113} in each crystal structure.

### 3.4 Results and Discussion

Here we show the results of several PTMC simulations of silica polymerization around SDAs with various SDA concentrations, sizes, and interaction strengths, to determine how SDA properties influence final silica crystalline structures. In particular, we have studied the influence of SDA concentration by considering 2 and 4 SDAs per simulation cell for both medium (M) and large (L) SDAs, giving the following four systems: 2M, 2L, 4M, and 4L. We found in our PTMC simulations that the 4L system produces exclusively partially condensed two-dimensional layered structures, while we are predominantly interested in studying three-dimensional microporous networks characterized by their distribution of rings (ring-size distribution or RSD). As such, we show below 2M and 4M systems (with $\varepsilon_{O-SDA} = 0.2 \times \varepsilon_{T(OH)4-T(OH)4}$) to study the effect of SDA concentration on RSDs; we then show the comparison between 2M and 2L systems (same $\varepsilon_{O-SDA}$ value) to study the effect of SDA size on RSDs. Finally, we show PTMC results for the 2M system with $\varepsilon_{O-SDA}/\varepsilon_{T(OH)4-T(OH)4} = 1.0$ to investigate the effect of SDA interaction strength. The crystalline frameworks obtained for all other systems are given in the appendix.
We begin by illustrating various configurations from a PTMC simulation at $T^* = 0.15$ with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), and $\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_4-T(OH)_4}$. (see Figure 3.3). The simulation began by placing all species at random locations on the lattice, as shown in Figure 3.3a. Figure 3.3b shows the emergence of a two-dimensional layered material, observed after $2 \times 10^6$ MC steps. In such a configuration, all tetrahedra are fully condensed and the SDAs occupy the space between the layers. The maximum SDA-O interaction contacts per SDA is 1 for this 2D material. Figure 3.3c provides a system snapshot after $10 \times 10^6$ MC steps, where we observe a three-dimensional microporous crystal. In this configuration the maximum number of SDA-O interaction contact per SDA is 4, which is lower in energy than the 2D structure, making it the thermodynamically favorable configuration. A $2 \times 2 \times 2$ periodic extension of this material is shown in Figure 3.4 from three perspectives, revealing that the SDAs are present inside the micropores. This particular framework was not observed in the absence of SDA molecules, which suggests that the presence of these SDAs has directed the formation of this framework.
Figure 3.4. 2×2×2 periodic extension of Figure 3.3c showing SDAs in the micropores. (a) Plane $\langle 001 \rangle$; (b) Plane $\langle 110 \rangle$; (c) Plane $\langle 110 \rangle$.

3.4.1 Effect of SDA Concentration

We have observed that decreasing the $\text{T(OH)}_4$ concentration keeping SDA concentration fixed has the same effect on RSD as that of increasing the SDA concentration keeping $\text{T(OH)}_4$ units fixed. Therefore, in this work we only discuss the effect of change in SDA concentration. Here we compare 2 and 4 medium SDA systems ($\varepsilon_{O-SDA} = 0.2 \times \varepsilon_{T(OH)_4-T(OH)_4}$) to study the effects of SDA concentration on RSDs. Figures 3.5 and 3.6 show the microporous frameworks that arise from PTMC simulations with 2 and 4 medium SDAs, respectively. In Figure 3.7 we show the ring size distributions for both structures. Figure 3.7 shows that silica polymerization around 2 medium SDAs produces rather large rings containing in excess of 18 T-atoms; these are likely artifacts of the bcc lattice model. Figure 3.7 also shows that increasing the SDA concentration to 4 medium SDAs produces a microporous framework with smaller rings, all with 12 or fewer T-atoms. We rationalize this trend in terms of the assembly of frameworks that optimize SDA-O contacts, considering that all fully-connected silica networks exhibit the same silica energy in our model. Having more SDAs in the simulation cell provides the opportunity for lowering the system energy by building microporous frameworks with more such SDA-O contacts. Indeed, the average SDA-O interaction contacts increase from 4 to 16 for 2 and 4 medium SDAs respectively. This increase in average contacts
result in the formation of a more compact microporous framework in Figure 3.6 with smaller rings than those in Figure 3.5.

**Figure 3.5.** Microporous crystalline material observed with 48 T(OH)$_4$ and 2 medium SDAs ($D_{SDA} = 6.4$ Å), shown as $2 \times 2 \times 2$ periodic extension of the simulation box. (a) plane $\langle 011 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 100 \rangle$.

**Figure 3.6.** Microporous crystalline material observed with 48 T(OH)$_4$ and 4 medium SDAs ($D_{SDA} = 6.4$ Å), shown as $2 \times 2 \times 2$ periodic extension of the simulation box. (a) plane $\langle \overline{1}10 \rangle$; (b) plane $\langle 100 \rangle$; (c) plane $\langle 110 \rangle$. 

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Figure 3.7. Ring size distributions for micropore structures shown in Figs. 3.5 (2 medium SDAs) and 3.6 (4 medium SDAs), showing that increasing SDA concentration produces frameworks with smaller rings to optimize SDA-T(OH)$_4$ attractions.

3.4.2 Effect of SDA Size

Here we show the comparison of microporous frameworks that arise from PTMC with 2 medium SDAs (6.4 Å) and 2 large SDAs (10.4 Å), respectively, as shown in Figs. 3.5 and 3.8. The ring size distributions for these two frameworks are shown in Figure 3.9, which once again shows rather larger rings in both structures. Figure 3.9 shows qualitatively that using the larger SDA pushes the ring size distribution to deplete smaller rings in favor of larger ones. While this finding – that bigger SDAs produce more large rings – makes intuitive sense from the standpoint of templating and molecular fit, we can analyze these results from an energetic standpoint as well. In particular, we find that the average SDA-O interaction contact is 4 for micropore structure for with medium SDA (Figure 3.5), and is 24 for the structure formed around the large SDA (Figure 3.8). Such a change in SDA-O interaction contacts is consistent with that seen above when changing
SDA concentration. However, while increasing SDA concentration and size both lead to increased SDA-O contacts, such enhanced attractions lead to opposite trends in ring size: smaller rings for higher SDA concentration and larger rings for larger SDA size. These model predictions are qualitatively consistent with the experimental findings of Gies and Marler,\textsuperscript{57} who found in the synthesis of pure-silica caged materials that using larger SDAs produces materials with larger rings and cages. It will be interesting to see if this general trend holds in our future studies with structured SDAs.

Figure 3.8. Microporous crystalline material observed with 48 T(OH)$_4$ and 2 large SDAs ($D_{SDA} = 10.4$ Å), shown as 2×2×2 periodic extension of the simulation box. (a) plane ⟨101⟩; (b) plane ⟨100⟩; (c) plane ⟨101⟩.
Figure 3.9. Ring size distributions for micropore structures shown in Figs. 3.5 (2 medium SDAs) and 3.8 (2 large SDAs), showing that increasing SDA size produces a framework with fewer smaller rings and more large rings, driven by the combination of molecular fit and optimizing SDA-O attractions.

3.4.3 Effect of Silica-SDA Attraction Strength

Here we discuss PTMC simulation results from varying silica-SDA attraction strength through the parameter $\varepsilon_{O-SDA}$, which was varied over 11 values of $f \times \varepsilon_{T(OH)_{4} - T(OH)_{4}}$ ($f = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, \text{ and } 1.0$). Below we show results with 2 medium SDAs from the extreme case of $f = 1$; the remaining results are shown in Supplemental Information. Figure 3.10 shows that PTMC with very strong silica-SDA attractions ($\varepsilon_{O-SDA} = \varepsilon_{T(OH)_{4} - T(OH)_{4}}$, i.e., $f = 1$) produces a two-dimensional layered material with SDAs positioned in the galleries between silica layers, in analogy with the structures of pillared clays. In general, we have observed that three-dimensionally connected microporous materials arise in our PTMC simulations only in a relatively narrow range of
silica-SDA attractions, characterized by $0 < |\varepsilon_{O-SDA}| \leq 0.3|\varepsilon_{T(OH)_{4}-T(OH)_{4}}|$; for stronger attractions such as those in Figure 3.10 we observe only layered materials. Although the average SDA-O interaction contact per SDA is 5, the SDA is strongly attracted to oxygens, making the 2D materials in Figure 3.10 the thermodynamic stable state. This transition from 3D to 2D architectures with increasing $|\varepsilon_{O-SDA}|$ is driven by the optimization of silica-SDA attractions via flattened pore structures. We note that in the particularly interesting case of $\varepsilon_{O-SDA} = 0$, in which the SDA species act simply as hard quasi-spheres, PTMC produces only layered materials implying that silica-SDA attractions are essential for the formation of fully-connected microporous frameworks. We find it remarkable that there is such a relatively narrow range of such attractions – a “Goldilocks” scenario – that produces 3D microporous materials.

Figure 3.10. Perspectives of ordered, layered material arising from PTMC with strong silica-SDA attractions ($\varepsilon_{O-SDA} = \varepsilon_{T(OH)_{4}-T(OH)_{4}}$) with 2 medium SDAs (6.4 Å) and 48 T(OH)$_4$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 110 \rangle$.

3.5 Summary and Conclusions

In this work we have applied PTMC simulations to search for crystalline states of a lattice model of silica polymerization in the presence of structure directing agents (SDAs). Consistent with our previous work, we have modeled silica monomers [Si(OH)$_4$] as corner-sharing tetrahedra in the bcc unit cell, with each Si atom at the body center and OH groups on one of two possible sets of tetrahedral vertices. SDAs were modeled
as quasi-spheres with diameters of 6.4 Å and 10.4 Å. To mimic silica-SDA van der Waals interactions, silica-SDA attractions are allowed in lattice sites just outside the region of SDA excluded volume. Silica polymerization is represented through condensation processes, modeled through the double occupancy by terminal OH groups producing a new bridging oxygen. We have implemented parallel tempering Monte Carlo with a grid of 50 temperatures, allowing these simulations to pass efficiently from disordered initial silica-SDA conditions to crystalline silica materials with structures driven in part by the properties of the SDAs. We have varied SDA concentration, size, and attraction strength to silica, to determine how these SDA properties affect the final crystalline silica structures.

These PTMC simulations have produced 3D microporous materials and 2D layered materials with SDAs occupying the pore and gallery spaces, respectively. We observed 3D microporous materials that were not found in the absence of SDAs, suggesting a structure-directing affect in our simulations. We have observed more 2D structures than 3D structures over the temperature range studied, which may suggest that there could be more pathways leading to 2D structures than those leading to 3D in our model. We have discovered a remarkably narrow range of silica-SDA attraction values (≤ 1.2 kcal/mol SDA-oxygen contacts) that produces 3D microporous materials. Otherwise, for either no silica-SDA attraction or too strong an attraction, 2D layered materials were obtained from PTMC. When considering only 3D microporous materials, we have found that decreasing SDA concentration and increasing SDA size both lead to materials with smaller rings shifted to larger rings in the ring size distributions, driven in our simulations by optimization of silica-SDA attractions.

This simulation study raises many intriguing avenues for future work. We plan to compare our present results from quasi-spherical SDAs to those for structured SDAs such as tetra-alkyl-ammonium species, whose tetrahedral structures are easily accommodated on the bcc lattice. Through such comparisons we may discover the effects
of SDA structure on micropore structure. We also plan to compare our PTMC results — which may not follow kinetically-relevant pathways — to those from methods such as forward-flux sampling\textsuperscript{93,94} to determine the nature of kinetically-relevant pathways, and if such pathways may produce different micropore crystalline structures. Such a comparison will begin to suggest whether all-silica zeolite formation is principally controlled by thermodynamics or kinetics. Although the present study does not yet answer the question “how do all-silica zeolites crystallize?” our present results do provide an important direction forward for answering such an important question. Such studies will represent a significant step forward in understanding the synthesis of crystalline microporous materials such as all-silica zeolites.
CHAPTER 4

FORMATION OF ZEOLITE ANALOGUES USING PARALLEL TEMPERING MONTE CARLO SIMULATIONS: EFFECTS OF MOLECULAR STRUCTURE DIRECTING AGENTS

4.1 Background

So far we have discussed the quasi-spherical model of the SDA molecules, where we represented the SDA as a single site with near neighbor repulsions. The extent of the repulsions is a measure of the SDA diameter. Using this model of SDA along with Jin’s model of silica tetrahedra on bcc lattice, we have observed transitions from gel to nanoparticle in sol-gel synthesis of silica. We have also demonstrated that silica-SDA interaction plays a crucial role in self assembly process of tetrahedral units. We now consider a more complex model of the SDA, where we are particularly interested in tetramethylammonium cation (TMA), used in the synthesis of zeolite A. This model of SDA would give further insights into the nature of structure direction of molecules. Moreover, this would provide an opportunity to study the effect of molecular size and structure on the self assembly process of T(OH) units. We aim to elucidate the crystalline structures observed in the presence of TMAs, and the effect of molecular structure of TMA on resulting microporous frameworks. To compare the effects of molecular SDAs with those from quasi-spherical SDAs on microporous structures, molecular SDAs were modeled to have comparable excluded sites with those of quasi-spherical SDAs. We have studied the effects of of SDA size, SDA concentration, and SDA flexibility on ring size distribution of 3D micropores.

The remainder of this chapter is organized as follows: in Sec. 4.2 we discuss our lattice model; in Sec. 4.3 we describe the Monte Carlo simulation technique and parame-
ters; Sec. 4.4 presents our results on the effects of T(OH)$_4$ concentration, TMA concentration and silica-TMA attraction strength on crystal structure; and finally in Sec. 4.5, we present a summary of our results and concluding remarks on future research implied by the findings.

4.2 Model

We follow closely with our previous work$^{115}$ – effects of quasi-spherical SDAs on microporous frameworks resulting from PTMC simulations – and incorporate TMA-type molecules in our simulations. We treat the system as a body centered cubic lattice (bcc) which can be viewed as two interpenetrating diamond sub-lattices. The silica source is chosen to be tetraethylorthosilicate with water as solvent. We assume that tetraethylorthosilicate reacts completely with four molecules of water to yield four molecules of ethanol, and silicic acid according to the reaction below

$$Si(OC_2H_5)_4 + 4H_2O \rightleftharpoons Si(OH)_4 + 4C_2H_5OH$$

We treat water and ethanol as part of the solvent – in accordance with our previous research$^{65}$ – and are modeled as vacant sites on the bcc lattice. The silica monomers are represented as unit cells on the bcc lattice where the silicon atom occupies the center of the unit cell and the hydroxyl groups are located at its vertices. Two such silica monomers are shown in figure 5.1(a). The TMA molecule is represented as a multi-site species on the lattice. The central site of the nitrogen atom (blue bead in figure 5.1(b)) has first neighbor hard sphere repulsions to every other species and second neighbor attractive sites. The central site of the alkyl groups (cyan beads in figure 5.1(b)) are located at fifth nearest neighbor to the central site of the nitrogen atom. The methyl groups have first and second neighbor hard sphere repulsions and third neighbor attractions from its central site. The TMA molecule thus excludes a total of 65 sites on the lattice, which is comparable in volume to the 59 sites for the medium SDA we studied in our previous
The pink color cubes in figure 5.1 are the interaction contact points between TMA – both for nitrogen bead and methyl beads – and silica. This model of TMA is useful in understanding the effects of molecular structure of SDA – spherical vs tetrahedral – on crystalline frameworks.

Silica polymerization is modeled as the overlap of bridging oxygen atoms from two different monomers on the same site, which results in the formation of a bridging oxygen atom, as shown in figure 4.2. The vacancy created due to this overlap is assumed to be occupied by the water molecule which is liberated from the reaction. Similar to our previous studies,\textsuperscript{33} we treat the energy scale to be the condensation energy between two silica monomers, $\varepsilon_{TO_4-TO_4}$. Jin et al.\textsuperscript{33} estimated the value of $\varepsilon_{TO_4-TO_4}$ to be -4 kcal/mol based on solubility of silica. This reduction in energy with every overlap is the driving force for silica network formation. We prohibit the formation of two-membered rings in our simulations as these would have a high angular strain\textsuperscript{110}. The scaled temperature of the system is given by $T^* = k_B T / \varepsilon_{TO_4-TO_4}$. Because the condensation energy is same for
every silica species reacting with each other, the thermodynamics of ordered crystalline states is controlled by the silica-TMA interactions.

**Figure 4.2.** Representation of different species on the bcc lattice. (a) T(OH)$_4$ molecules with T atom at the center of the unit cell and oxygen atoms located on the vertices; (b) an SDA molecule as a single site with far neighbor repulsions, here SDA diameter is 3.2Å. Red tetrahedra represents excluded sites and green cubes represent attraction contact points.

Following the work of Gies and Marler$^{57}$, Lewis *et al.*$^{70}$, and van Santen and coworkers$^{71,72}$, we model attractions between TMAs and T(OH)$_4$ tetrahedra according to the spirit of van der Waals interactions. We incorporate near neighbor attractions between TMA and the oxygen atoms, and we do not incorporate attractions between TMA and terminal -OH group because we focus our attention on non-highly polar attractions. We model the nitrogen bead of the TMA, as having six second neighbor attraction sites, and the methyl beads as having 12 third neighbor attraction sites each. The nitrogen beads and methyl beads are modeled as having distinct attraction strength with the oxygen atoms. This distinction results in two different models of TMA; the ON-model where only the nitrogen bead interacts with the oxygen atom with strength $\epsilon_{ON}$, and the OR model where only the methyl groups interact with the oxygen atom with strength $\epsilon_{OR}$. These models of TMA provide us molecular level information of the TMA interaction with the crystalline frameworks. We will compare their results with experiments to determine which, if either, is closer to the reality.
We incorporate hard-sphere repulsions between TMA molecules and every other species – both for nitrogen beads and methyl beads. We do not incorporate interaction of solvent with any species for computational simplicity, in accordance with our previous studies\textsuperscript{65}.

### 4.3 Simulation Methodology

Jin \textit{et al.} suggested that there exists a network free-energy barrier between amorphous phases and crystalline phases in our lattice model of silica polymerization\textsuperscript{67}; such an energy barrier can be difficult to surmount via tradition Monte Carlo simulation methods. Using parallel tempering Monte Carlo (PTMC) method, Jin \textit{et al.} discovered ground states of our lattice model in the absence of SDAs. We extended their study to incorporate TMAs in our calculations to observe their effects on resulting microporous structures. In a PTMC calculation several copies of the system are simulated all having the same value of parameters but different temperature values. The lowest temperature in the ensemble is chosen to be room temperature, $T^* = 0.15\textsuperscript{33}$. Whereas, the highest temperature is chosen to be sufficiently high where silica molecules exist predominantly in monomeric state; for the purpose of this study this temperature value was chosen to be $T^* = 0.35$ which is slightly above the one used in our previous study. The grid spacing was determined such that the average exchange acceptance ratio is $\sim 20\%$; the appropriate grid size was chosen to be 50 temperature values. Message passing interface (MPI) protocol was used to implement PTMC algorithm.

We have used canonical ensemble Monte Carlo simulations to sample the equilibrium states of our system. Our Monte Carlo protocol involves two different kind moves; translation moves and rotation moves. In a translation move, we pick a molecule at random and a site at random. If the site is vacant, the molecule is attempted to be moved to that site. In a rotation move, both silica and TMA molecule are attempted to be rotated to the second corresponding diamond sublattice corresponding to their respective
unit cell. The acceptance probabilities of the moves are based on the Metropolis criterion. The acceptance probability of replica exchanges with temperatures $T_1$ and $T_2$ with energies $E_1$ and $E_2$ respectively is given by:

$$\min\left[1, \exp\left\{\left(\frac{1}{k_B T_1} - \frac{1}{k_B T_2}\right)(E_1 - E_2)\right\}\right]$$

We performed MC simulations on an $8 \times 8 \times 8$ simulation box with periodic boundary conditions. The system length scale is defined by the Si-O bond length of 1.6 Å, which sets the length of the simulation box to be 14.8 Å. The simulations are carried out for $10 \times 10^6$ Monte Carlo steps, where one Monte Carlo step is defined as $N$ rotations and $N$ translations ($N$ being the sum of TMAs and T(OH)$_4$ molecules). One exchange sweep is carried out every 5000 Monte Carlo step, where one exchange sweep is $M$ exchanges between replicas at adjacent temperatures ($M$ begin the total number of replicas). Table 4.1 shows the simulation parameters used in this study.

**Table 4.1.** Simulation parameters studied in this work

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO$_4$ concentration (T(OH)$_4$/box)</td>
<td>tetrahedral units in simulation</td>
<td>40, 48</td>
</tr>
<tr>
<td>TMA concentration (TMAs/box)</td>
<td>low, high</td>
<td>2, 4</td>
</tr>
<tr>
<td>ON model interactions</td>
<td>$\varepsilon_{OR} = 0$, $\varepsilon_{ON} = f \varepsilon_{T(OH)A-T(OH)4}$</td>
<td>$f = 0.1n, n = 1,2,...10$</td>
</tr>
<tr>
<td>OR model interactions</td>
<td>$\varepsilon_{ON} = 0$, $\varepsilon_{OR} = g \varepsilon_{T(OH)4-T(OH)4}$</td>
<td>$g = 0.1n, n = 1,2,...10$</td>
</tr>
</tbody>
</table>

We have studied 2 T(OH)$_4$ concentration, and 2 TMA concentration as stated in table 4.1. To understand the significance of molecular structure of an SDA on the resulting crystalline frameworks; one needs to have an an “apples-to-apples” comparison between the findings from the quasi-spherical SDA and the TMA. To accomplish this
task we have scaled the silica-TMA interaction values for the ON model and the OR model according to the equation below.

\[ \eta_{QSD-A-O} \times \varepsilon_{QSD-A-O} = \eta_{TMA-O} \times \varepsilon_{TMA-O} \]

where \( \eta_{QSD} \) and \( \eta_{TMA-O} \) are the maximum possible interaction sites between oxygen and quasi-spherical SDA (6 sites), and between oxygen and TMA respectively (6 sites for ON model and 48 sites for the OR model). The corresponding interaction strengths are given by \( \varepsilon_{QSD-A-O} \) and \( \varepsilon_{TMA-O} \). The scaled values for the interaction strengths are mentioned in table 4.1 for the ON model and the OR model. The energies of frameworks observed on the PTMC grid differ from each other based on the interaction between TMA and silica. To study the effects of \( T(OH)_{4} \) concentration, TMA concentration, TMA-silica interactions, and TMA molecular structure, we chose frameworks having minimum energy from the PTMC grid.

Materials were characterized based on their ring-size distributions, where the ring size is defined as the total number of T-atoms present in a given ring. We have used the R.I.N.G.S. package to compute the total number of primitive rings in each crystal structure.

### 4.4 Results

Here we present our results of our lattice model of silica polymerization and TMA molecule. We study the effects of \( T(OH)_{4} \) concentration, TMA concentration, silica-TMA interactions, and influence of molecular structure of TMA on crystalline frameworks emerging from PTMC simulations. In particular we consider two \( T(OH)_{4} \) concentrations; 40 (0.625 \( x_{\beta} \)) and 48 (0.75 \( x_{\beta} \)) molecules; where \( x_{\beta} \) is the number of \( T(OH)_{4} \) in an idealized \( \beta \)-cristobalite crystal, which is 64 for an \( 8 \times 8 \times 8 \) simulation box.\(^6\) We
have also studied two concentrations of TMA molecule; 2 TMAs/box and 4 TMAs/box. The simulation parameters for the silica-TMA interaction are mentioned in the table 4.1, however, unless otherwise mentioned we take \( \epsilon_{ON} = 0.2\epsilon_{T(OH)4-T(OH)4} \) for the ON model and hence \( \epsilon_{OR} = 0.025\epsilon_{T(OH)4-T(OH)4} \) for the OR model. These values allow us to compare structures from the TMA model to those observed from the quasi-spherical SDA model, under the same conditions. We first discuss the effects of T(OH)\(_4\) concentration for 2 TMA and 4 TMA, and for the ON model and the OR model. We observe that 40 T(OH)\(_4\) molecules give rise to only one type of microporous framework. In discussing the effects of TMA concentration on crystalline structures, we consider 2 TMA and 4 TMA in the presence of 48 T(OH)\(_4\), for both the ON model and the OR model. Finally we discuss the effects of molecular structure of the TMA molecules by comparing our findings with those from our previous research.\(^{115}\) Furthermore all the crystalline frameworks that are going to be discussed are shown as a 3 × 3 × 3 periodic extension of the simulation box.

### 4.4.1 Effect of TMA Concentration

We report the effects of TMA concentration on frameworks emerging from PTMC simulations, both for the ON model and the OR model. We have studied frameworks having 48 T(OH)\(_4\) with 2 TMA and 4 TMA. We have observed that decreasing the T(OH)\(_4\) concentration keeping TMA concentration fixed has the same effect on RSD as that of increasing the TMA concentration keeping T(OH)\(_4\) units fixed. Therefore, in this work we only discuss the effect of change in TMA concentration.

**ON Model**

Figures 4.3 and 4.4 show the frameworks observed with 48 T(OH)\(_4\) : 2 TMA and 48 T(OH)\(_4\) : 4 TMA respectively. The TMAs are present in micropores and the cages in both the frameworks. Figure 4.5 compares the RSD between structures in figure 4.3 and 4.4. We observe that for the ON model, as the TMA concentration is increased, frameworks
with larger rings are observed – structure with 2 TMA produces rings smaller than 12 T atoms whereas framework with 4 TMA produces framework with predominantly rings with 24 T atoms and 28 T atoms. As discussed in chapter 3, quasi-spherical SDAs were found to generate frameworks with smaller rings at higher SDA concentration; the opposite trend was found with the TMA ON model. The trend observed with the TMA ON model also agrees qualitatively with the experimental work of Testa et al. They observed that ZSM-48 was observed at higher TMA concentration where TMAs can favor six-membered rings of the framework, and at lower TMA concentration double five-membered rings of ZSM-5 were favored. Moreover, the total number of silica-TMA interaction contacts also increases from 4 for 2 TMAs to 16 for 4 TMAs leading to a more thermodynamically stable framework.

Figure 4.3. Snapshots during PTMC with $T^* = 0.15$, $48\, (\text{OH})_4$, 2 TMAs, and $\varepsilon_{O-N} = 0.2\varepsilon_{T(\text{OH})_4-T(\text{OH})_4}; \varepsilon_{O-R} = 0$. (a) Plane $\langle \bar{1}10 \rangle$; (b) plane $\langle 100 \rangle$; (c) plane $\langle 110 \rangle$.

Figure 4.4. Snapshots during PTMC with $T^* = 0.15$, $48\, (\text{OH})_4$, 4 TMAs, and $\varepsilon_{O-N} = 0.2\varepsilon_{T(\text{OH})_4-T(\text{OH})_4}; \varepsilon_{O-R} = 0$. (a) Plane $\langle \bar{1}01 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 100 \rangle$. 

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Figure 4.5. Ring size distributions for micropore structures shown in Figs. 4.3 (2 TMA) and 4.4 (4 TMA), showing that increasing TMA concentration produces frameworks with smaller rings.

**OR Model**

In this section we report the effects of the TMA concentration on crystalline structures for the OR model with the scaling procedure $\epsilon_{OR}$ mentioned in section 5.3. Figure 4.6 and 4.7 and shows framework with 2TMAs and 4TMAs respectively. Figure 4.8 shows RSDs for the two frameworks. We observe that with an increase in TMA concentration, frameworks with smaller rings are produced; 4 TMAs produce rings smaller then 12 T atoms whereas 2 TMAs generate structures with larger micropores. Framework with 4 TMAs is stabilized with greater number of silica-TMA contacts, 56 silica-TMA contacts, as opposed to framework with 2 TMAs, 48 silica-TMA contacts. This trend of smaller micropore formation at higher concentration of TMA molecules was also observed in the presence of quasi-spherical SDAs\textsuperscript{115}. But the effect of change in TMA concentration
for the OR model is opposite to the work of Testa et al.\textsuperscript{116}, which suggests that TMA ON model is closer to reality than the TMA OR model.

Figure 4.6. Snapshots during PTMC with $T^* = 0.15$, 48 T(OH)$_4$, 2 TMAs, and $\varepsilon_{O-N} = 0$; $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_{4}-T(OH)_{4}}$. (a) Plane $\langle \bar{1}01 \rangle$; (b) plane $\langle 010 \rangle$; (c) plane $\langle 100 \rangle$.

Figure 4.7. Snapshots during PTMC with $T^* = 0.15$, 48 T(OH)$_4$, 4 TMAs, and $\varepsilon_{O-N} = 0$; $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_{4}-T(OH)_{4}}$. (a) Plane $\langle \bar{1}01 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 001 \rangle$. 
Figure 4.8. Ring size distributions for micropore structures shown in Figs. 4.3 (2 TMA) and 4.4 (4 TMA), showing that increasing TMA concentration produces frameworks with smaller rings.

4.4.2 Effects of TMA-Silica Interaction

We now discuss the effects of TMA-silica interaction for the two different models – the ON model and the OR model. For the ON model we varied $\varepsilon_{ON}$ from 0 to $\varepsilon_{T(OH)_{4}-T(OH)_{4}}$ for both 40 T(OH)$_{4}$ and 48 T(OH)$_{4}$, and 2 TMA and 4 TMA. Under all conditions, we observed fully connected ordered crystalline frameworks, mentioned in the appendix. The same analysis was performed for the OR model with scaled values of $\varepsilon_{OR}$, such that $0 \leq \varepsilon_{OR} \leq 0.125\varepsilon_{T(OH)_{4}-T(OH)_{4}}$. We again observed that all the values of $\varepsilon_{OR}$ lead to the emergence of fully connected frameworks. These findings are contrary to our observations from quasi-spherical SDAs$^{115}$, where we observed that there exists “sweet-zone”, $0 < \varepsilon_{OSDA} \leq 0.3\varepsilon_{T(OH)_{4}-T(OH)_{4}}$, where fully connected connected structures were observed. However, for $\varepsilon_{OSDA} > 0.3\varepsilon_{T(OH)_{4}-T(OH)_{4}}$ and $\varepsilon_{OSDA} = 0$ two-dimensional layered structures were observed with quasi-spherical SDA model.
4.5 Summary and Conclusions

In this chapter we have applied PTMC simulations to study the effects of TMA molecules on the crystalline states of our lattice model of silica polymerization. We have modeled silica monomers \([\text{T(OH)}_4]\) as unit cells on the bcc lattice, with silicon atom occupying the center of the lattice and hydroxyl groups located on one of two possible sets of tetrahedral vertices. The TMAs was modeled as a multi-site species – having a central nitrogen bead and four methyl beads – occupying a total of 65 lattice sites. The total excluded sites of the TMA molecule is comparable to the medium size quasi-spherical SDA studied in our previous work. Silica polymerization is modeled as the overlap of bridging oxygen atoms from two different monomers on the same site, which results in the formation of a bridging oxygen atom. The vacancy created due to this overlap is assumed to be occupied by the water molecule, liberated from the reaction. To mimic silica-TMA van der Waals interactions, we have developed two models of TMA; the ON model where the nitrogen bead interacts with the oxygen atoms located just outside the bead, and the OR model where the methyl beads interact with the oxygen atoms located just outside the bead. We have varied, silica concentration, TMA concentration, ON attraction strength and OR attraction strength to determine how these properties affect the final crystalline silica structures.

The PTMC simulations have produced all 3D fully-connected crystalline states of silica with the TMA molecule located in the micropores, as opposed to our previous work on quasi-spherical SDAs where we observed both 3D microporous crystals and 2D layered materials from our simulations. We observed that with the TMA ON model at fixed \(\text{T(OH)}_4\) concentration, higher TMA concentration produced more larger rings larger pores, which is in qualitative agreement with the experimental findings. Whereas, with the OR model higher TMA concentration produced smaller pores. In both the models, the increase in TMA concentration produced frameworks with more silica-TMA contacts resulting in a lower energy of the system. Moreover, we observe that it is not just
silica-TMA interactions, but also TMA concentration and T(OH)$_4$ concentration which play an important role in the formation of frameworks in our simulations.

This work raises many intriguing avenues for future research. We plan to extend this study to tetraethylammonium molecules and tetrapropylammonium molecules to study the effects of the SDA size and SDA flexibility of structure directing agent molecules. Such studies will represent a significant step forward in understanding the synthesis of crystalline microporous materials such as all-silica zeolites.
CHAPTER 5
INVESTIGATION OF THE SELF-ASSEMBLY PROCESS OF CRYSTALLINE STRUCTURES

5.1 Background

So far we have discussed Monte Carlo simulations to study silica polymerization as well as the effects of structure directing agents on ordered microporous crystals. However, we did not comment on pathways that lead to the formation of crystalline states. In this chapter we focus on understanding the kinetics of the self-assembly of microporous frameworks using forward-flux sampling method.

Crystallization of zeolites is hypothesized to be an activated process, involving a free energy barrier between the reactants and the crystalline products\(^{22,117}\). Enhanced sampling methods such as transition interface sampling,\(^{118,119}\) transition path sampling,\(^{91,92,120,121}\) and forward-flux sampling (FFS)\(^{93,94}\) are required to probe time scales that are computationally inaccessible by molecular dynamics. Forward-flux sampling (FFS) is a computationally efficient method which can be used to study the crystallization process, and can generate pathways from reactants to products. FFS requires an order parameter that distinguishes the initial and final configurations of our system. Some common order parameters include number of particles in crystallization process, number of translocated monomers in polymer translocation, and the difference in reactants and products in a chemical reaction. Next, interfaces with increasing value of order parameter \((\lambda_i)\) are constructed between initial region (A) and final region (B). Trajectories are then launched from region A and ending up in region B, and rate constant of transition can be calculated using the method discussed in section 5.3. In this chapter we discuss the self-assembly process of ideal \(\beta\)-cristobalite\(^{67}\) from amorphous silica. The crystalline phase
has a higher degree of condensation than the amorphous phase, therefore we have considered the order parameter to be the total number of completely bonded silicon atoms. We have predicted the transition state for the self-assembly process, and also estimated the rate constant for the process.

The remainder of this paper is organized as follows: in Sec. 5.2 we discuss the model and its parameters; in Sec. 3.3 we describe the simulation methodology; Sec. 3.4 presents our results and determine the transition interface, predict structure of the transition state, and estimate the values of rate constant for transition at different temperature values.

5.2 Model

To study the transition between amorphous silica phase and idealized $\beta$-cristobalite, we again adopt Jin et al. lattice model of silica polymerization. The silica monomers $(\text{T(OH)}_4)$ are treated as unit cells on the bcc lattice; the tetrahedral T-atom is located in the center of the unit cell and the hydroxyl groups extend outwards to the vertices, as shown in figure 5.1. The polymerization reaction is said to occur when hydroxyl groups from different $\text{T(OH)}_4$ monomers overlap on a site resulting in the formation of a bridging oxygen atom. The water molecule created in this reaction is then said to “occupy” the vacancy created on the lattice. Following our previous research, we model the solvent as vacancies on the lattice.

The silica polymerization reaction is accompanied by a decrease in the total energy of the system by $\epsilon_{\text{T(OH)}_4-\text{T(OH)}_4}$, which is taken to be the energy scale of the system. Jin et al. calculated the value of $\epsilon_{\text{T(OH)}_4-\text{T(OH)}_4}$ using the solubility of silica; the value was computed to be -4 kcal/mol. Moreover, we assume the energy decreases by the same amount when a bridging oxygen atom is formed between any species of silica. The scaled temperature is given by $T^* = k_B T / \epsilon_{\text{T(OH)}_4-\text{T(OH)}_4}$. Jin et al. estimated the scaled room temperature as $T^* = 0.15$. We do not incorporate interaction of solvent with any species for computational simplicity, in accordance with our previous studies.
5.3 Simulation Methodology

We use the forward-flux sampling (FFS) method\textsuperscript{93,94} to study the transformation of amorphous silica phase to an ideal $\beta$-cristobalite\textsuperscript{67} crystal. FFS was initially developed to study transitions between any two states – the states do not need to be in equilibrium. Here, we have applied FFS technique to estimate the energy barrier, and the activated state in the self-assembly process of ideal $\beta$-cristobalite. In a FFS scheme, the state $x$ of the system is defined by an order parameter, $\lambda(x)$. In nucleation events, $\lambda$ can be the total number of molecules in the largest cluster, in a polymer diffusing through a pore $\lambda$ can be the number of diffused monomers\textsuperscript{94}. The rare event can be viewed as a spontaneous transition from two well defined regions in "phase-space" (positions and momenta of particles), region A and region B; region A defined by ($\lambda < \lambda_A$) and region B defined by ($\lambda > \lambda_B$). A series of interfaces, with monotonically increasing values of order parameters, $\lambda_0, \lambda_1, ..., \lambda_n$, are constructed between region A and region B. The rate constant of transition from region A to region B is given by\textsuperscript{93}.

$$k_{AB} = \frac{\Phi_{A,0}}{\hat{h}_A} P(\lambda_n|\lambda_0) = \frac{\Phi_{A,0}}{\hat{h}_A} \prod_{i=0}^{n-1} P(\lambda_{i+1}|\lambda_i)$$

This rate constant, $k_{AB}$, is a product of flux of trajectories from region A to the first interface, $\Phi_{A,0}$, and probability of transition from the first interface, $\lambda_0$ to the final interface,
\( \lambda_n \). Here, \( \tilde{h}_A \) is the population operator; it is unity when the system is in region A and zero when in region B. The term, \( P(\lambda_n | \lambda_0) \), can be written as a product of probabilities of transition of the system to adjacent interfaces. Identifying the underlying constitutive kinetic equation behind \( k_{AB} \) is going to be the focus of future research.

The estimation of \( k_{AB} \) is a two stage process: (1) The system is simulated in region A and configurations that reach the first interface, \( \lambda = \lambda_0 \) are tracked. This process is carried out until \( M_0 \) configurations are collected at the first interface. The flux, \( \Phi_{A,0} \), is defined by the ratio of \( M_0 \) and the total MC simulation steps. (2) For every interface, \( \lambda_i \), a saved configuration is selected at random and the simulation is continued until the configuration reaches \( \lambda_{i+1} \) or goes back to A. This procedure is continued until \( M_i \) configurations are collected at \( \lambda_{i+1} \). The probability, \( P(\lambda_{i+1} | \lambda_i) \), is the fraction of trajectories that reach the next interface. Step (2) is continued until region B is reached. The rate constant of transition from region A to region B is then calculated by the equation above, which has the units of transitions per MC step.

As mentioned earlier, the order parameter should be monotonically increasing when going from region A to region B, and should clearly distinguish region A from region B. To study crystallization processes in various systems, researchers have employed Steinhardt order parameters, which define the degree of crystallinity of molecular clusters. In the present work the basin A, is an amorphous silica phase with degree of condensation less than unity, and B is the region where there exists the idealized \( \beta \)-cristobalite crystal with a degree of condensation close to unity. The difference between region A and region B is that region B has a higher number of silicon atoms connected to oxygen atoms than the amorphous phase in region A. Therefore, we have defined our order parameter as follows:

\[
\lambda_{Q_4} = Q_4 \times N_{T(OH)_4}
\]
where, $Q_4$ is the fraction of silicon atoms connected with four bridging oxygen atoms and $N_{T(OH)_4}$ are the total number of silica molecules; basically, $\lambda Q_4$ is the total number of fully bonded silicon atoms. The definition of the two basins of attraction, A and B is further discussed in section 5.4.

Although Monte Carlo (MC) simulations do not correspond to “real-time”, Jin et al.\textsuperscript{33} demonstrated that the lattice model of silica can capture kinetics of silica polymerization to a great extent using Monte Carlo simulations. Therefore, we have used canonical ensemble MC simulations to study the transition from an amorphous silica phase to idealized $\beta$-cristobalite. We have implemented the following two kinds of canonical ensemble MC moves: translations and rotations. A translation move is made where any $T(OH)_4$ molecule is selected at random and is attempted to be moved to any vacant site on the lattice. A rotational move is where a random $T(OH)_4$ molecule is selected and is attempted to be rotated to the other four vertices in the corresponding bcc unit cell. The acceptance probabilities for these moves are based on the Metropolis criterion\textsuperscript{103}. We have simulated 64 $T(OH)_4$ molecules corresponding to the concentration of ideal $\beta$-cristobalite in an $8 \times 8 \times 8$ bcc lattice. Consistent with our previous research\textsuperscript{33}, we have imposed ring penalties on three-member rings and four-member rings, which are necessary to produce idealized $\beta$-cristobalite. We have prohibited the formation of two-member rings.
To determine the location of the two basins A and B in $\lambda_{Q_4}$ space, we have analyzed the distribution of $\lambda_{Q_4}$ for amorphous silica (basin A) and ideal $\beta$-cristobalite (basin B). Simulating a system containing pure silica monomers result in glassy-type metastable states of amorphous silica. To make the system ergodic, where transition are possible between the amorphous phase and crystalline phase, we have studied order parameters for $0.15 \leq T^* \leq 0.30$. Figure 5.2 shows the distribution of order parameter in region A, amorphous silica, and region B, ideal $\beta$-cristobalite for $T^* = 0.27$. The distributions are averaged at $\langle \lambda^A_{Q_4} \rangle = 24$ and $\langle \lambda^B_{Q_4} \rangle = 56$ which provides a good estimate of the two regions.

In our FFS calculations, we have defined region A as states with $\lambda_{Q_4} \leq \langle \lambda^A_{Q_4} \rangle$, and region B as $\lambda_{Q_4} \geq \langle \lambda^B_{Q_4} \rangle$. We have placed interfaces at equal intervals, and the distance between adjacent interfaces, $d_A$, as two units. In future we care going to consider the effects of
The crystal of ideal $\beta$-cristobalite is not stable at sufficiently high temperatures ($T^* > 0.30$); therefore we have calculated the rate constant for transition, $k_{AB}$ for $0.26 \leq T^* \leq 0.30$. In the first stage of FFS we have equilibrated the system for $10 \times 10^6$ MC moves. We have considered $M_I=500$ at every interface. We have characterized configurations using their ring size distributions (RSDs), where the ring size is defined as the total number of T-atoms present in a given ring. We have used the R.I.N.G.S. package\textsuperscript{112} to compute the total number of primitive rings\textsuperscript{113} crystal structure.

5.3.1 Method Verification

To verify our implementation of the FFS algorithm, we have applied FFS on a model system that has already been studied in literature. We have implemented FFS to study homogeneous nucleation in an Ising model, previously studied by Sear\textsuperscript{124} and Valeriani \textit{et al.}\textsuperscript{125} They calculated the rate constant for the transition – in a square lattice – from a spin down phase to a up phase – for different regions A and B. The studied involved the study of nucleation in an Ising magnet, given by equation below,

$$H = -J \sum_{ij} s_i s_j - h \sum_{k} s_k$$

where, $H$ is the total energy, $J$ is the coupling constant, $s = \pm 1$ is the spin on the lattice, and $h$ is an external field. The simulation parameters used by Sear and Valeriani \textit{et al.} are shown in table 5.1. One MC step in these calculations is one attempted spin flip, which gives the units of $k_{AB}$ as transitions per MC step per site. The order of the magnitude of $k_{AB}$ is a topic of future research.

We observe that with three statistically independent calculations, our simulations agree well with the work of Valeriani \textit{et al.} and Sear. With this successful reproduction of published research, we now have the necessary tools to apply FFS method to study the self-assembly process of ideal $\beta$-cristobalite.
Table 5.1. Simulation parameters used by Sear and Valeriani et al.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Sear</th>
<th>Valeriani et al.</th>
</tr>
</thead>
<tbody>
<tr>
<td>square lattice size</td>
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<td>$45 \times 45$</td>
</tr>
<tr>
<td>$\hbar/k_B T$</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>$J/k_B T$</td>
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<td>0.65</td>
</tr>
<tr>
<td>$\lambda_A$</td>
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<td>30</td>
</tr>
<tr>
<td>$\lambda_B$</td>
<td>550</td>
<td>$1000 &lt; \lambda_B &lt; 1050$</td>
</tr>
<tr>
<td>$k_{AB}$ (MC step$^{-1}$ spin$^{-1}$)</td>
<td>$3.3 \times 10^{-13} \pm 0.3 \times 10^{-13}$</td>
<td>$2.8 \times 10^{-13} \pm 0.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>our results of $k_{AB}$ (MC step$^{-1}$ spin$^{-1}$)</td>
<td>$3.1 \times 10^{-13} \pm 0.5 \times 10^{-13}$</td>
<td>$2.5 \times 10^{-13} \pm 0.4 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

5.4 Results

Forward-flux sampling (FFS) is a very useful method in studying rare events as it provides not only the rate of transition between the two basins of attraction, but also the transition pathways. In this section, we are first going to estimate the rate constant for transition from region A to region B, and then the determination of the “critical-interface”.

5.4.1 Identification of the Transition Interface

Figure 5.3 shows the transition probabilities at every interface as a function of $\lambda_{Q_4}$ for $T^* = 0.27$. We observe that the probabilities at first increases for $22 \leq \lambda_{Q_4} \leq 26$, as the polymerization reaction increases the degree of condensation, and hence $\lambda_{Q_4}$. Locally dense amorphous silica phases are observed in this region; one such state is shown in 5.4(a). For $26 < \lambda_{Q_4} < i \leq 36$ the transition probability decreases, as a collective rearrangement of molecules is required in order to increase the degree of condensation further. In chapter 3 and chapter 4 this arrangement was brought about by parallel tempering Monte Carlo simulations. We define the minimum of transition probabilities as the activated interface; unlikely to be reached by trajectories originating at the previous interface. As the simulation proceeds beyond the activated interface, transition probabilities start to increase again with an increase in $\lambda_{Q_4}$. A typical configuration at the interface closest to the activated interface, $\lambda_{Q_4} = 38$, is shown in figure 5.4(b). The tran-
sition probability eventually plateaus for $\lambda Q_i \geq 44$, which implies for each subsequent interface, all initiated trajectories end up at the next interface. A typical configuration of region B is shown in 5.4(c). We have calculated the values of $k_{AB}$ and $\Phi_{A,0}/\bar{h}_A$ for the transition of an amorphous silica phase into a crystalline phase at $T^* = 0.27$; $\Phi_{A,0}/\bar{h}_A = 6.73 \times 10^{-3}$ transition MC move$^{-1}$, and $k_{AB} = 2.37 \times 10^{-6}$ molecule$^{-1}$MC move$^{-1}$. We are currently working on understanding the underlying length scales and time scales behind these values.

![Figure 5.3](image.png)

**Figure 5.3.** Transition probabilities at every interface for $T^* = 0.27$.

Since, in FFS, the transition probabilities reach unity for interfaces closer to region B, it becomes difficult to estimate transition probabilities for the complete order parameter configuration space – ergo it is difficult to estimate the rate constant for the reverse process. In future we are going to perform a reverse-FFS where we will start with an ideal $\beta$-cristobalite crystal in region A and then estimate the rate constant for the transition to an amorphous phase of silica. Moreover, we are also going to study the influence of tem-
perature on $k_{AB}$ for this process. Such an analysis would help us draw parallels between the self-assembly process and transition state theory.

![Figure 5.4](image)

**Figure 5.4.** Configurations different interfaces $T^* = 0.27$. (a) Amorphous state, typical configuration at $i = 0$; (b) transition state, typical configuration at $i = 8$; (c) crystalline state, typical configuration at $i = 18$.

### 5.4.2 Analysis of Configurations at the Transition Interface

We have characterized configuration in the amorphous phase, activated interface, and the crystalline phase using their ring size distribution (RSD) shown in figure 5.5. We observe that RSD for the amorphous phase is wider with ring sizes going from 3 rings to 10 rings. For the crystalline phase, the ring size is peaked at six rings. However, for a typical configuration at the activated interface larger rings are more likely, and the fraction of six-member ring – signature of ideal $\beta$-cristobalite crystal – is greater than in the amorphous phase. Hence, configurations at the activated interface are structurally closer to the crystalline phase. We are in the process of studying the influence of the placement of interfaces on the activated interface and the configurations observed there.
Figure 5.5. Ring size distribution for typical configurations in the amorphous silica phase, activated interface and crystalline phase.

5.5 Summary and Conclusions

We have studied aspects of the self-assembly of ideal $\beta$-cristobalite using forward-flux sampling method. Consistent with our previous work we represent silica monomers as rigid tetrahedra on a unit cell of a body centered cubic (BCC) lattice, where a silicon atom occupies the body center of the unit cell and hydroxyl groups are at the vertices. The polymerization reaction is modeled as overlap of hydroxyl groups on the same site resulting in the formation of a bridging oxygen atom. The water molecule created in this reaction is then said to occupy the vacancy created on the lattice. We have imposed energy penalties on three and four membered rings, and have prohibited the formation of two membered rings. We have applied forward flux sampling method (FFS) to study the self-assembly process of ideal $\beta$-cristobalite.

We have used the total number of fully bonded silicon atoms as the order parameter ($\lambda_{Q_4}$) to perform the FFS calculation. We have calculated the transition probabilities as
a function of the order parameter. We observe that the transition probabilities first in-
crease reaching a maxima at $\lambda_{Q_4} = 26$, and then decrease with a minima at $\lambda_{Q_4} = 38$. We
have taken $\lambda_{Q_4} = 38$ as the activated interface. As the FFS simulation proceeds beyond
the activated interface, the transition probabilities increase and eventually plateau at
$\lambda_{Q_4} = 44$. In this region, all the configuration starting at a particular interface, end up
at the next interface. We have also quantified typical configuration in the amorphous
silica region, activated interface, and the crystalline region using ring size distributions
(RSDs). We have observed that the RSD for amorphous silica has a wider distribution
with a large fraction of six-membered rings. The RSD for ideal $\beta$-cristobalite crystal is
peaked at six membered rings. The activated state has a higher fraction of 6-rings than
the amorphous silica – signature of the ideal $\beta$-cristobalite framework.

This study has opened new avenues of research in the study of the self-assembly
process of microporous crystals. The FFS method can provide us with rate constant of
transition for rare events as well as formation pathways. Using an appropriate order
parameter, this method can be used to probe the self-assembly process of the micropor-
ous crystals discussed in chapter 3 and chapter 4, and can be used to study the role
of structure directing agents. This would be a very important step in answering the vital
question – “How do silica zeolites form?”
CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE RESEARCH

We have demonstrated that our body-centered cubic (bcc) lattice model of silicic-acid can capture essential physics behind silica polymerization, and the self-assembly of silica under various conditions. We have extended Jin et al.\textsuperscript{33} lattice model of atomic silica to study silica polymerization under various pH values and silica concentrations.\textsuperscript{87}; we have gained valuable insights into the nature of transition from gel phase to nanoparticle phase. We also applied our SDA models of quasi-spherical SDAs and TMA molecules to investigate the self-assembly of ordered crystalline materials using parallel tempering Monte Carlo simulations. We observed that the presence of SDA molecules changes that distribution of crystalline states over the temperature range. We also quantified the effect of T(OH)\textsubscript{4} concentration, SDA concentration, and SDA size using ring size distributions. This research has shown us the importance of SDA molecules in directing final crystalline frameworks. In our study of the self-assembly process of ideal $\beta$-cristobalite using forward flux sampling method, we elucidated the rate of transition from amorphous silica phase to crystalline phase, and we also characterized the transition state for the process. With this study we have developed the necessary tools to study the kinetics of micropore formation, and will open fascinating avenues in the modeling zeolite self-assembly. In the remainder of this chapter, we discuss future research direction.

6.1 Self-Assembly Process of Microporous Structures

So far we have investigated the self-assembly process of ideal $\beta$-cristobalite using forward-flux sampling method, where we have predicted the rate of transition from an
amorphous silica phase to a crystalline phase. However, we did not comment on the formation process of other microporous frameworks discussed in chapters 3 and 4. It has been hypothesized that zeolite nucleation can be explained with the help of classical nucleation theory, where the formation of critical nuclei is succeeded by crystal growth. In this proposed future work we seek to answer:

1. What dynamical pathways lead to the formation of microporous structures?

2. What are the structures and sizes of critical nuclei, and nucleation energy barrier?

As discussed in chapter 5, forward-flux sampling requires an order parameter that distinguished the initial and final configuration of our system. Some common order parameters include number of particles in crystallization process, number of translocated monomer in polymer translocation, and the difference in reactants and products in a chemical reaction. In these calculations a targeted order parameter like the Hausdorff distance can be used to characterize the two basins of attractions. Moreover, one can then consider nucleating a cluster instead of a periodically connected crystal which we discussed in chapter 5.

6.2 Atomic Model of Structure Directing Agents

So far we have discussed the quasi-spherical model of the SDA, and the TMA model. We have studied the effects of SDA concentration, $T(OH)_4$ concentration on frameworks resulting from PTMC simulations. We have also demonstrated that silica-SDA interaction plays a crucial role in self assembly process of tetrahedral units.

We now aim to consider more complex model of the SDA, where we are particularly interested in models of tetraethylammonium cation (TEA), and tetrapropylammonium cation (TPA) as shown in figure 6.1. In a rigid model, the alkyl chains are fixed, whereas in a flexible model individual segments are free to move on the lattice maintaining their connectivity. Such models may give further insights into the nature of structure direc-
tion of molecules. Moreover, this would provide an opportunity to study the effect of molecular size and structure on the self assembly process of T(OH)$_4$ units. Using these models, we can answer the following questions:

1. What is the effect of the size of atomic SDA on crystalline frameworks?

2. How does the flexibility of SDA molecules influences the final microporous structures?

![Figure 6.1. Atomic SDA models.](image)

**Figure 6.1.** Atomic SDA models. (a) TMA molecule; (b) rigid TEA molecule; (c) rigid TPA molecule; (d) flexible TEA molecule; (e) flexible TPA molecule

To compare the effects of atomic SDA with quasi-spherical SDA on microporous structures, atomic SDAs should have comparable excluded sites with that of quasi-spherical SDAs. Then one can proceed to study the effects of SDA size, SDA concentration, and SDA flexibility on ring size distribution of 3D micropores.
6.3 Simulating Density Fluctuations Using Hyper Parallel Tempering Monte Carlo Algorithm

In chapters 3 and 4 we discussed the effects of SDAs on frameworks emerging from PTMC simulations. We observed new framework types in the presence of SDA molecules that were earlier inaccessible. Such simulations were done at constant number of molecules, and it remains unclear whether we have observed all the possible frameworks on the lattice, for a given system size. Some of the unanswered research question are:

1. What other frameworks are possible in the lattice model?

2. How does the transition takes place from layered materials to fully connected materials, and vice versa?

We believe that grand canonical Monte Carlo (GCMC) simulation can shed some light on this issue. To search for ordered states, we have used hyper-parallel tempering Monte Carlo algorithm\textsuperscript{127}. In the beginning we consider the system in the absence of T(OH)\textsubscript{4} molecules. Along with temperature, we now have an additional tempering variable, the chemical potential.

![Lattice filling and empting isotherm for a T(OH)\textsubscript{4} system with dimensions 8 \times 8 \times 8 at T^* = 0.15](image)

**Figure 6.2.** Lattice filling and empting isotherm for a T(OH)\textsubscript{4} system with dimensions 8 \times 8 \times 8 at $T^* = 0.15$
In PTMC simulations, it is straightforward to decide the range of operating temperature values, based upon the fact that at higher temperature values the system would be in unpolymerized state, in contrast to a system at low temperature where T(OH)$_4$ units are in condensed form. However, in an HPTMC choosing the relevant values for chemical potential is not so easy. Therefore, we have run GCMC simulations on a system comprising only T(OH)$_4$ molecules, and constructed lattice-filling and lattice-emptying isotherms. Figure 6.2 shown a plot of the average fraction of sites occupied by the T atom ($\langle x_T \rangle$) versus the chemical potential of T(OH)$_4$ units. At low chemical potential all of the lattice site are unoccupied; as the chemical potential is increased there is a step jump of $\langle x_T \rangle$ to a high value at chemical potential $-1.9$. The value of $\langle x_T \rangle$ keeps increasing and saturates at $\langle x_T \rangle \sim 0.23$. The density of T(OH)$_4$ molecules in these states is very high where the second diamond sub-lattice neighbours of the T atom are occupied by other T atoms. When the chemical potential is decreased, the lattice begins to gradually empty from $\mu_{TO_4} \sim 1.0$ till $\mu_{TO_4} \sim -1.4$, beyond which the lattice is completely empty. We also observe a narrow hysteresis region in the region $-1.6 < \mu_{TO_4} < -1.4$. The horizontal dotted line corresponds to the value of idealized $\beta$-cristobalite$^{67}$, below which we have observed all the fully connected frameworks from PTMC simulations. Although the operating range of chemical potential values is $-1.6 < \mu_{TO_4} < -1.4$, we expect this range to result in stable densities in HPTMC calculations involving high temperatures.

To search for ordered states, we aim to apply hyper-parallel tempering Monte Carlo algorithm.$^{127}$ To begin with we consider the system in the absence of SDA molecules. Along with temperature, we now have an additional tempering variable, the chemical potential. We have applied this method to study stable states of the model by tempering in $\mu_{TO_4}$ as well as $T$. 
Figure 6.3. Snapshots of an ordered fully connected framework at $T^* = 0.15$ and $\mu_{TO_4} = -1.82$. The density of the system is $0.875x_\beta$, where $x_\beta$ is the density of idealized $\beta$-cristobalite. (a) Plane $\langle 0\bar{1}1 \rangle$; (b) plane $\langle 010 \rangle$; (c) plane $\langle 011 \rangle$

We first consider $\mu_{TO_4}$ as the tempering variable. Figure 6.3 and 6.4 shows new frameworks by tempering in $\mu_{TO_4}$. The number of observable structures over range of $\mu_{TO_4}$ and $T$ are less compared to those observed in PTMC simulations, which is due to the narrow range of operating $\mu_{TO_4}$.

Figure 6.4. Snapshots of an ordered fully connected framework at $T^* = 0.15$ and $\mu_{TO_4} = -1.87$. The density of the system corresponds to that of idealized $\beta$-cristobalite. (a) Plane $\langle 100 \rangle$; (b) plane $\langle 110 \rangle$

Next, we studied our model using hyper-parallel tempering simulations. Figure 6.5 and figure 6.6 two framework types observed from our HPTMC calculations. Surprisingly, we have observed materials which were observed with PTMC simulations in the presence of SDA molecules. This finding indicates that the fluctuations in the density
and energy, in a pure T(OH)$_4$ system, in a HPTMC simulation are similar to energy fluctuations in a PTMC simulations of a system comprising of T(OH)$_4$ units and SDA molecules.

Figure 6.5. Snapshots of an ordered fully connected framework at $T^* = 0.16$ and $\mu_{T(OH)_4} = -1.90$. The density of the system is $0.875x_\beta$, where $x_\beta$ is the density of idealized $\beta$-cristobalite. (a) Plane $\overline{1}01$; (b) plane $1\overline{1}0$; (c) plane $001$

Figure 6.6. Snapshots of an ordered fully connected framework at $T^* = 0.32$ and $\mu_{T(OH)_4} = -1.90$. The density of the system is $0.625x_\beta$, where $x_\beta$ is the density of idealized $\beta$-cristobalite. (a) Plane $0\overline{1}1$; (b) plane $010$; (c) plane $011$

This study can be extended by incorporating temperature as a tempering variable, as well as SDA molecules in our system. One can consider the quasi-spherical model of SDA, as discussed in chapter 3 and TMA in chapter 4.
6.4 Associating Simulated Structures with Synthetic Materials

Our lattice model although efficient and capable of providing valuable qualitative information about the system, suffers from a narrow bond angle distribution. Specifically, due to the lattice we can observe just three bond angles in our calculations – $70^\circ$, $109^\circ$ and $180^\circ$. However, the bond angle in zeolites ranges from $130^\circ$ to $180^\circ$, which is responsible for over 200 different framework types. This fact raises a question – “Have we simulated any experimental structure?”. Jin et al.\textsuperscript{33} proposed the idealized version of $\beta$-cristobalite where all the bond angles are $180^\circ$ as opposed to $150^\circ$ in experimentally synthesized $\beta$-cristobalite, as shown in figure 6.7.

![Figure 6.7. Snapshots of idealized and experimental. (a) idealized $\beta$-cristobalite (b) experimental $\beta$-cristobalite](image)

X-ray diffraction patterns for the two structures are shown in figure 6.8. The relative position of the two prominent peaks are the same but their absolute positions are different, due to a difference in atomic positions between the two structures. Moreover, we do not observe minor peaks at high angle.
**Figure 6.8.** Comparison of x-ray diffraction patterns for idealized and experimental β-cristobalite.

Further investigations are required in this area to develop a scheme to compare the simulated structures with experimental ones. One such approach is as follows: First we compare ring size distributions of our structures with experimental observations. We hypothesize that if we have simulated a synthetic structure on lattice, it would still retain the connectivity with its off-lattice structure. This would result in same ring size distribution. This first step is a filtering algorithm for such large zeolite frameworks by comparing RSDs of our simulated structures with experimental materials. Secondly, once the candidate structures are finalized, we would perform isobaric-isothermal simulations – in presence of a T-O-T bond potential – which would relax the bond angles of the lattice structure.
APPENDIX A

ESTIMATION OF SYSTEM PH IN SILICA SOLUTION

The prediction of pH with change in composition is an important component in the study of such systems because of the complex chemistry involved. Here we solve the concentration of components and pH corresponding to the composition \( y \text{TEOS} : x \text{SDAOH} : z \text{H}_2\text{O} \). We assume that the \( \text{OH}^- \), released from the dissociation of \( \text{SDA}^+ (\text{OH}^-) \), deprotonates silicic acid to form a singly ionized ionic silicate monomer according to the reaction

\[
\text{Si(OH)}_4 + \text{OH}^- \rightleftharpoons \text{Si(OH)}_3^- + \text{H}_2\text{O}
\]

The initial mole fractions calculated for each component are given by:

\[
x_{SN}^0 = \frac{y}{2x + z + 5y}, \quad x_{SI}^0 = 0, \quad x_{OH}^0 = \frac{x}{2x + z + 5y}, \quad x_{H_2O}^0 = \frac{z + 4y}{2x + z + 5y}
\]

The numbers 2 and 5 in the denominators arise because we assumed that each TEOS molecule hydrolyzes into a molecule of silicic acid and four molecules of ethanol, and that a molecule of \( \text{SDA}^+ (\text{OH}^-) \) dissociates into a molecule each of \( \text{SDA}^+ \) and \( \text{OH}^- \). After the reaction \( A \) attains equilibrium, we assume that the activities of the individual species are the same as their concentrations. At equilibrium the concentrations are related to the dissociation constant of the reaction by

\[
K_D = \frac{x_{SI}x_{H_2O}}{x_{SN}x_{OH}^-}
\]

In this calculation, we have assumed that the system is dilute but we do account for the change in water moles. We also take the value of \( pK_a \) as 9.5 for the first deprotonation.
of silicic acid,\textsuperscript{99} and the value of pK\textsubscript{w} of water as 13.8. Furthermore, we have assumed that the concentration of water (H\textsubscript{2}O) remains constant at the value of 55.6 mol/L.

We then assign a change, \( \delta \), in the moles of each species from their initial concentration. Thus, the equilibrium compositions become

\[
\begin{align*}
x_{SN} &= \frac{y - \delta}{2x + z + 4y}; \\
x_{SI} &= \frac{\delta}{2x + z + 5y}; \\
x_{OH^-} &= \frac{\delta}{2x + z + 5y}; \\
x_{H_2O} &= \frac{z + 4y + \delta}{2x + z + 5y}
\end{align*}
\]

Substituting these in the previous equation of \( K_D \), we obtain a quadratic equation for \( \delta \). We then chose the value of \( \delta \) that gives us positive concentration for each species and next calculate the equilibrium composition of each species. The case of \( x = 0 \) can be treated by traditional acid-base equilibrium calculations, which results in pH \( \sim 2.30 \) at \( x = 0 \). The pH of the mixture, at non-zero \( x \), is then computed by:

\[
pH = pK_w + \log \left( \frac{x}{y - x} \right)
\]

As mentioned earlier, we then consider the remaining OH\textsuperscript{−} part of the solvent. Hence, the pH of the system remains fixed at the initial value.
Figure A.1. Computed pH values compared with experiments [Yang et al.\textsuperscript{1}] at composition 25TEOS:xSDAOH:480H\textsubscript{2}O.

We now compare our pH calculations with the findings of Yang et al.\textsuperscript{1}. They used a stirred hydrogen electrode to calculate the pH of the solution before the crystallization of silicalite-1 during the clear solution synthesis. Figure A.1 shows the comparison of pH obtained from our calculation with experiments. We observe good agreement of the slope of the data with the experiments, but there is significant difference in our calculation of pH with the experiments.
APPENDIX B

MICROPOROUS FRAMEWORKS OBSERVED IN THE PRESENCE OF QUASI-SPHERICAL STRUCTURE DIRECTING AGENTS

In our simulations we considered a bcc lattice with $8 \times 8 \times 8$ unit cells. It should be noted that we have studied systems with $16 \times 16 \times 16$ unit cells as well, however we were unable to obtain ordered microporous materials in PTMC simulations. Falcioni et al. [Marco Falcioni and Michael W. Deem, *The Journal of Chemical Physics*, 110.3 (1999), 1754-1766] predicted that the total number of PTMC temperature grid points increase as order $\sqrt{N}$ with increase in system size, where $N$ is the system size. Moreover, Katzgarber et al. proposed an optimized scheme for PTMC simulations, where they predicted that the average round trip time for a configuration increases linearly with system size [Katzgraber, H. G., Trebst, S., Huse, D. A., and Troyer, M. (2006), *Journal of Statistical Mechanics: Theory and Experiment*, 03, P03018]. The above studies indicate that to study a larger system size, a large number of PTMC simulations are required and a longer computational time is needed. We would address this issue in our future publication.

Figure S1 to fig. S5 show 3D connected materials, and fig. S6 to fig. S15 show 2D materials observed in our simulations. All structures shown in the text are $2 \times 2 \times 2$ periodic image of an $8 \times 8 \times 8$ bcc lattice.
3D materials

Figure B.1. 3D material with 40 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_{4}-T(OH)_{4}}$, and $T^* = 0.168$. (a) plane $\langle \bar{1}01 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 101 \rangle$.

Figure B.2. 3D material with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_{4}-T(OH)_{4}}$, and $T^* = 0.258$. (a) plane $\langle 110 \rangle$; (b) plane $\langle 101 \rangle$.

Figure B.3. 3D material with 56 T(OH)$_4$, 3 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_{4}-T(OH)_{4}}$, and $T^* = 0.15$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 100 \rangle$. 
Figure B.4. 3D material with 48 T(OH)$_4$, 2 large SDAs (\(D_{SDA} = 10.4 \text{ Å}\)), \(\epsilon_{O-SDA} = 0.1\epsilon_{T(OH)_{4}-T(OH)_{4}}\), and \(T^* = 0.156\). (a) plane \(\langle 001 \rangle\); (b) plane \(\langle 100 \rangle\).

Figure B.5. 3D material with 64 T(OH)$_4$, 4 medium SDAs (\(D_{SDA} = 6.4 \text{ Å}\)), \(\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_{4}-T(OH)_{4}}\), and \(T^* = 0.204\). (a) plane \(\langle 001 \rangle\); (b) plane \(\langle 100 \rangle\).

2D Materials

Figure B.6. 2D material with 40 T(OH)$_4$, 2 medium SDAs (\(D_{SDA} = 6.4 \text{ Å}\)), \(\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_{4}-T(OH)_{4}}\), and \(T^* = 0.174\). (a) plane \(\langle \bar{1}01 \rangle\); (b) plane \(\langle 101 \rangle\).
Figure B.7. 2D material with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.15$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 10 \rangle$.

Figure B.8. 2D material with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.156$. (a) plane $\langle 011 \rangle$; (b) plane $\langle 01 \rangle$.

Figure B.9. 2D material with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.4\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.168$. (a) plane $\langle 101 \rangle$; (b) plane $\langle 010 \rangle$. 
Figure B.10. 2D material with 32 T(OH)$_4$, 2 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.4\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.228$. (a) plane $\langle 0\bar{1}1 \rangle$; (b) plane $\langle 100 \rangle$.

Figure B.11. 2D material with 48 T(OH)$_4$, 4 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.168$. (a) plane $\langle 011 \rangle$; (b) plane $\langle \bar{1}11 \rangle$; (c) plane $\langle 100 \rangle$.

Figure B.12. 2D material with 48 T(OH)$_4$, 4 medium SDAs ($D_{SDA} = 6.4$ Å), $\varepsilon_{O-SDA} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.192$. (a) plane $\langle \bar{1}10 \rangle$; (b) plane $\langle 110 \rangle$. 

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Figure B.13. 2D material with 48 T(OH)$_4$, 4 medium SDAs ($D_{SDA} = 6.4$ Å), $\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.222$. (a) plane $\langle 0\bar{1}1 \rangle$; (b) plane $\langle 01\bar{1} \rangle$.

Figure B.14. 2D material with 48 T(OH)$_4$, 3 medium SDAs ($D_{SDA} = 6.4$ Å), $\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.150$. (a) plane $\langle \bar{1}10 \rangle$; (b) plane $\langle 100 \rangle$.

Figure B.15. 2D material with 48 T(OH)$_4$, 4 medium SDAs ($D_{SDA} = 10.4$ Å), $\epsilon_{O-SDA} = 0.2\epsilon_{T(OH)_4-T(OH)_4}$, and $T^* = 0.150$. (a) plane $\langle 011 \rangle$; (b) plane $\langle 01\bar{1} \rangle$. 

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APPENDIX C

MICROPOROUS FRAMEWORKS OBSERVED IN THE PRESENCE OF TETERAMETHYLAMMONIUM STRUCTURE DIRECTING AGENTS

Figure C.1. 3D material with 40 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4\text{--}T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 01 \bar{1} \rangle$; (c) plane $\langle 011 \rangle$.

Figure C.2. 3D material with 40 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0$, $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_4\text{--}T(OH)_4}$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 01 \bar{1} \rangle$; (c) plane $\langle 011 \rangle$. 
Figure C.3. 3D material with 40 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, $\varepsilon_{O-R} = 0.025 \varepsilon_{T(OH)_4-T(OH)_4}$.  
(a) plane $\langle 001 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 01 \rangle$.

Figure C.4. 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2 \varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.  
(a) plane $\langle 010 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 110 \rangle$.

Figure C.5. 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2 \varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$.  
(a) plane $\langle 100 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 110 \rangle$. 
Figure C.6. 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane \langle 100 \rangle; (b) plane \langle 110 \rangle; (c) plane \langle 110 \rangle.

Figure C.7. 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane \langle 100 \rangle; (b) plane \langle 101 \rangle; (c) plane \langle 001 \rangle.

Figure C.8. 3D material with 56 T(OH)$_4$, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane \langle 100 \rangle; (b) plane \langle 101 \rangle; (c) plane \langle 100 \rangle.
Figure C.9. 3D material with 56 T(OH)₄, 2 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)₄-T(OH)₄}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 011 \rangle$.

Figure C.10. 3D material with 56 T(OH)₄, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)₄-T(OH)₄}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 100 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 110 \rangle$.

Figure C.11. 3D material with 56 T(OH)₄, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)₄-T(OH)₄}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 001 \rangle$. 
Figure C.12. 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 100 \rangle$; (b) plane $\langle 1\overline{1}0 \rangle$; (c) plane $\langle 110 \rangle$.

Figure C.13. 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0.2\varepsilon_{T(OH)_4-T(OH)_4}$, $\varepsilon_{O-R} = 0$. (a) plane $\langle 100 \rangle$; (b) plane $\langle 1\overline{1}0 \rangle$; (c) plane $\langle 110 \rangle$.

Figure C.14. 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)_4-T(OH)_4}$. (a) plane $\langle 001 \rangle$; (b) plane $\langle 101 \rangle$; (c) plane $\langle 101 \rangle$. 
Figure C.15. 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)4-T(OH)4}$.
(a) plane $\langle 010 \rangle$; (b) plane $\langle 0\bar{1}1 \rangle$; (c) plane $\langle 011 \rangle$.

Figure C.16. 3D material with 56 T(OH)$_4$, 4 TMAs, $\varepsilon_{O-N} = 0$, $\varepsilon_{O-R} = 0.025\varepsilon_{T(OH)4-T(OH)4}$.
(a) plane $\langle 100 \rangle$; (b) plane $\langle 110 \rangle$; (c) plane $\langle 110 \rangle$. 
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