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Emergence of Zeolite Analogs and other Microporous Crystals in an Atomic Lattice Model of Silica and Related Materials

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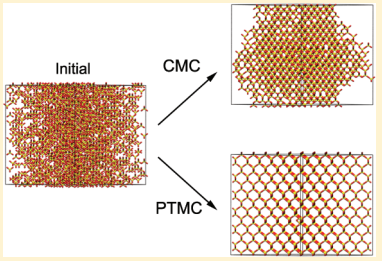
Supporting Information

ABSTRACT: The potential of tailored nanopores to transform technologies such as drug delivery, biofuel production, and optical-electronic devices depends on fundamental knowledge of the self-assembly of ordered nanoporous solids. Atomic-level geometries of critical nuclei that lead to such solids have remained hidden in the nanoscale blind spot between local (<0.5 nm) and collective (>5 nm) probes of structure. Heroic efforts at molecular simulation of nanopore formation have provided massive libraries of hypothetical structures;[1−5] however, to date no statistical simulation has generated a crystallization pathway from random initial condition to ordered nanoporous solid, until now. In this work, we show that a recently developed atomic lattice model of silica and related materials can form ordered nanoporous solids with a rich variety of structures including known chalcogenides, zeolite analogs, and layered materials. We find that whereas canonical Monte Carlo simulations of the model consistently produce the amorphous solids studied in our previous work, parallel tempering Monte Carlo gives rise to ordered nanoporous solids. The utility of parallel tempering highlights the existence of barriers between amorphous and crystalline phases of our model. Moreover, the self-assembly or nanoporous crystalline phases in the model open the door to detailed understanding of nanopore nucleation.



SECTION: Nanoparticles and Nanostructures

Nanoporous materials such as zeolites have been studied extensively for over 50 years because of their myriad applications in shape-selective catalysis and separations.[6] In addition, zeolite-like electronic materials such as nanoporous chalcogenides have also received substantial attention[7−9] because of their potential for photocatalysis and chemoselective sensing. Synthetic routes for fabricating zeolites and nanoporous chalcogenides have been discovered,[10] although mostly through trial-and-error sampling of reaction conditions, generating precious little insight into how such framework structures form. With the promise of tailored nanoporous materials[11,12] to revolutionize energy, health, and environmental technologies,[10,13] there is thus a tremendous need for atomic-level understanding of the processes that lead to ordered nanoporous solids. Molecular modeling is uniquely poised to generate such insights[14] but is hampered by the need to sample long lengths and times and by the complex interplay of physical and chemical interactions involved in nanopore formation. To address these issues, we report below for the first time the self-assembly of ordered nanoporous materials through statistical simulation of a versatile atomic lattice model.

Deem and coworkers have reported ingenious algorithms for sampling the large space of hypothetical zeolite structures,[1−5] generating databases with millions of possible frameworks that stimulate efforts in material synthesis. Their computational approach involves Monte Carlo sampling of randomly generated structures with imposed symmetries, accepted or rejected based on a fictitious Hamiltonian that measures whether a given new structure exhibits Si−Si lengths, Si−Si−Si angles, and so forth, typical of known zeolites. Whereas this approach has enjoyed great success in finding new frameworks, it does little to show how zeolites actually form during sol−gel processing.

Several atomistic molecular dynamics simulations of silica polymerization from aqueous orthosilicic acid have been reported,[14−17] all producing disordered 3-D networks of various sizes and shapes. These studies generally aim to match ^{29}Si NMR data expressed as the so-called Q_n distribution,[18] which probes the fraction of silicons bound to n bridging oxygens. Such bridges are formed from the following condensation reaction: $2{\equiv}Si{-}OH \rightarrow {\equiv}Si{-}O{-}Si{\equiv} + H_2O$. Because of length- and time-scale limitations in these simulations, they typically consider temperatures or densities much higher than in the NMR experiments, causing the computed Q_n distributions to differ widely from experiment. Wu and Deem addressed the limitations of molecular dynamics by performing Monte Carlo simulations of silica cluster formation.[15] However, because of the computational expense of the forcefields involved, their simulations were relegated to only a couple hundred silica tetrahedra. These results suggest that some degree of coarse graining is necessary to push molecular modeling toward nanopore formation.

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Toward this end, we and others have developed lattice models that capture many features of amorphous dense[20−23] and mesoporous silica.[24−27] For example, we developed an atomic lattice model for silica polymerization based on Si and O atoms occupying the sites of a body-center cubic (bcc) lattice,[23] with all atoms arranged in SiO_4 tetrahedra similar to the rigid unit model of Dove and coworkers.[28] Condensation reactions are represented within this model by allowing two oxygens to occupy a common bridging lattice site, with an accompanying stabilization ($-\varepsilon \approx -3$ kcal/mol[29]) that drives network formation. It is worth noting that in contrast with the activation relaxation technique[30] in which attempted moves are chosen from a catalog with existing and possible local topology based on free-energy barriers, in this model, the energy barrier for condensation reaction is neglected. The free-energy barriers in our model are associated with the collective rearrangements of the network topology. On the basis of our recent work on silica polymerization, this appears to be a major component in the self-assembly and stability of silica structures.[23,31,32] This bcc lattice provides the simplest model that allows for variation in the Si−O−Si angle, which is largely responsible for the versatility in silica polymorphs. Canonical Monte Carlo (CMC) simulations of this atomic lattice model at experimentally relevant temperature and density produce amorphous silica with Q_n distributions in excellent agreement with NMR results and ring-size distributions in good agreement with X-ray and neutron diffraction data.[33] In the present work, we apply parallel tempering Monte Carlo (PTMC) to this model and show below the self-assembly of a rich array of crystalline nanoporous materials, from known chalcogenides to zeolite- and clay-analogs. Other advanced simulation techniques, such as metadynamics,[34,35] explore free-energy landscapes via pathways chosen through particular selections of collective variables. PTMC[36] allows simultaneous studies of phase space at various values of temperatures without putting bias into the system. The present study uses PTMC not to determine pathways but simply to overcome the barriers associated with the network topology in the model and to facilitate an unbiased search for ground states of the model. A remarkable feature of our work is that the resulting structures include nanoporous crystalline structures resembling zeolite frameworks, chalcogenides, and clays. The determination of pathways to these ground states that would model the pathways in experimental syntheses of crystalline nanoporous materials is part of the next phase of our work.

Generalizing the application of this bcc lattice model to materials with tetrahedral (T) and bridging (B) atoms, this lattice geometry produces three T-B-T angles, as shown in Figure 1: 70, 109.47, and 180°. We exclude structures with 70° angles because these arise from two-membered rings with cyclic geometry T-B-T-B- (Figure 1a), which experience substantial ring strain and are observed only in silica at 850 °C and above.[37] For chalcogenides, two-membered ring structures do exist in 1D chain structures.[38] However, in this Letter, we are more interested in open-framework 3D structures, and the T-S-T angle lies generally within 10° of 109°.[39] We have also investigated applying energy penalties on three- and four-membered rings to determine how such penalties influence the structures that emerge. For the first set of results presented here, we applied penalties of 0.6ε and 0.3ε on three- and four-rings, respectively, to a system with 1728 TB_4 tetrahedra in a 24^3 simulation box (i.e., a mole fraction $x = 0.0625$, considering two sites per bcc unit cell). This choice of parameters was used in our previous study of silica polymerization to form amorphous silica.[23]

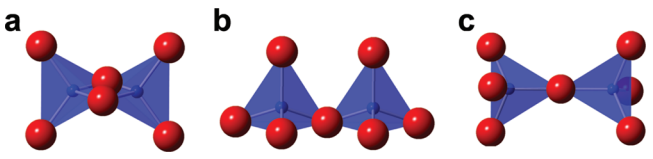

Figure 1. Possible arrangements of two tetrahedra. (a) Edge-sharing tetrahedra with $\angle_{TOT} = 70°$. (b) Corner-sharing tetrahedra with $\angle_{TOT} = 109°$. (c) Corner-sharing tetrahedra with $\angle_{TOT} = 180°$.

Figure 2a−c on the left shows initial, intermediate, and final configurations of CMC simulations at $T = 300$ K or $T^* = k_BT/\varepsilon = 0.15$. Figure 2d,e on the right shows the same for PTMC from the same random initial configuration; these snapshots are at $T^* = 0.15$, which is the lowest temperature in the PTMC grid. CMC was found in all cases to produce disordered structures resembling amorphous silica, whereas PTMC was found to produce an ordered solid identical to the structure of "idealized" β-cristobalite with all T-B-T angles equal to 180° and composed entirely of six-rings. The utility of PTMC to produce the crystalline β-cristobalite phase indicates roughness in the free-energy landscape of our model, which PTMC is able to overcome.

Repeating these PTMC calculations with successively lower maximum temperatures (T^*_{max}) provides an estimate of the free-energy barrier in our model for crystalline network formation from amorphous silica to β-cristobalite. Note that this barrier lacks the intrinsic contribution from the microscopic condensation process. We have found that the crystalline silica phase emerges from PTMC only for T^*_{max} values above 0.2 ($T = 400$ K), suggesting a network free-energy barrier of 3.3 kJ/mol. Our PTMC simulations help explain experiments by Broge and Iler,[40,41] who studied silica particle growth for long heating times and at high temperatures and pressures. They found that when alkali-stabilized sols were heated above 300 °C (573 K, 4.8 kJ/mol), quartz crystals were produced instead of stable colloids.

Microporosity in framework structures usually involves eight-rings, larger rings balanced by smaller rings to produce mechanically stable solids, or both. The previous calculations shown in Figure 2 biased against the formation of smaller three- and four-rings through energetic penalties, yielding the relatively dense β-cristobalite phase. To investigate the self-assembly of ordered microporous materials within the present lattice model, we thus removed such ring penalties and ran PTMC with a variety of mole fractions (i.e., silica densities) less than or equal to the β-cristobalite value $x_\beta = 0.0625$. A rich variety of structures emerges from this approach, including known chalcogenides, zeolite analogs, and layered materials.

Figure 3 shows the evolution of PTMC from a random initial condition to a structure denoted as a "zeolite analog" in an $8 \times 8 \times 8$ bcc lattice with $x = 0.75x_\beta = 0.04688$. The resulting structure contains two interpenetrating 12-ring channels, as shown in Figure 3c,d, and exhibits both allowed T-B-T angles of 109.5 and 180°. Figure 4 shows the self-assembly of two known chalcogenide structures by PTMC from random initial conditions. The actual materials are sulfides and selenides with promising photocatalytic and chemosensing properties.[7−9] Both of these chalcogenides are large-pore materials comprised of 12- (Figure 4c) and 16-ring (Figure 4f) channels. These

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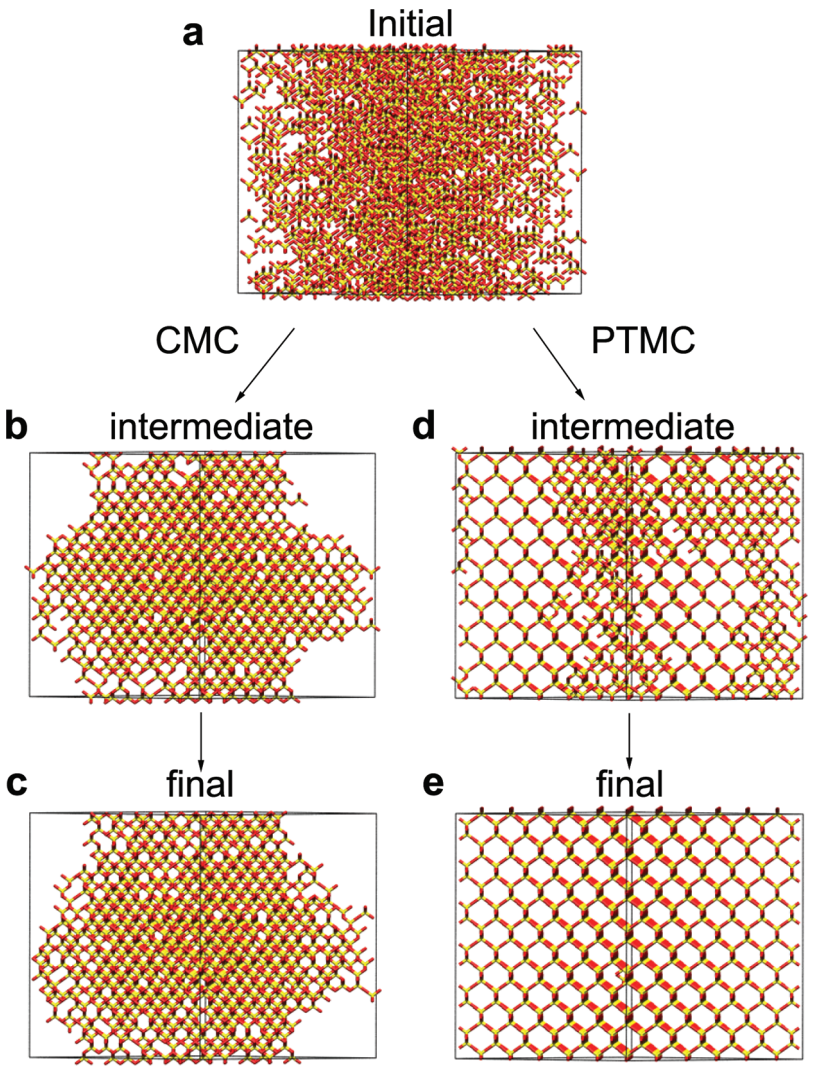

Figure 2. Effect of parallel tempering on the Monte Carlo evolution of the lattice model with penalties on three- and four-rings in a bcc lattice of size 24^3 and $x = 0.0625$. Both CMC and PTMC start with the same random initial configuration, as shown in panel a. (b,c) Intermediate and final configurations from CMC. (d,e) Intermediate and final configurations from PTMC, all at $T = 300$ K or $T^* = 0.15$. (e) Idealized β-cristobalite with $\angle$T-B-T = 180° [inorganic crystal structure database (ICSD) collection code 77459]. Snapshots are generated using Visual Molecular Dynamics.[19]

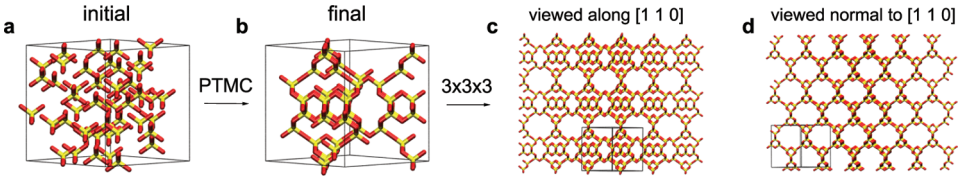

Figure 3. Self-assembly of a crystalline microporous zeolite-analog with two interpenetrating 12-ring channels formed via PTMC in an $8 \times 8 \times 8$ unit bcc lattice with $x = 0.75x_\beta = 0.04688$. (a,b) Initial (random) and final configurations from PTMC. (c,d) $3 \times 3 \times 3$ periodic extensions of that in panel b, viewed along and normal-to the [110] direction, respectively. The black lines indicate the unit cell boundaries.

materials exhibit all T-B-T angles of 109.5°, to be contrasted with the idealized β-cristobalite in Figure 2 (all 180°) and the zeolite-analog in Figure 3 (a mix of 109.5 and 180°).

Applying PTMC to this lattice model has produced a great many more crystalline microporous structures beyond those shown in Figures 2 and 3. These fall into three general classes: layered materials such as those shown in Figure S1, chalcogenide analogs shown in Figure S2 (all T-B-T angles equal to 109.5°), and zeolite-analogs shown in Figure S3 (mix of 109.5 and 180° T-B-T angles) in the Supporting Information. The two additional chalcogenides shown in Figure S2 have also been experimentally synthesized by Feng and coworkers.[7] This atomic bcc lattice model is thus capable of generating a rich diversity of ordered microporous materials found in nature.

It is interesting to compare the nature of our PTMC/lattice model simulations with real zeolite synthesis conditions. Zeolites are synthesized by tuning pH and temperature, largely to control the thermodynamic solubility and condensation kinetics of silica. Our model tunes silica solubility through the condensation energy parameter (ε) and assumes that condensation is instantaneous on the "time scale" of a Monte

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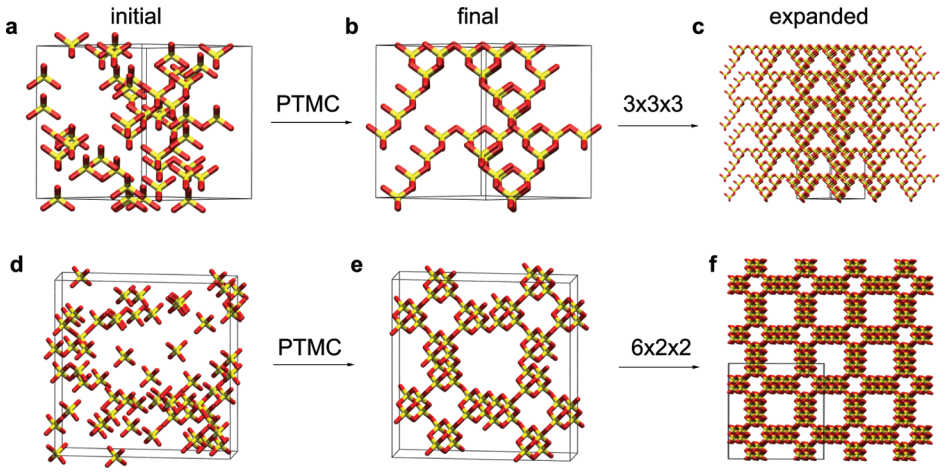

Figure 4. Crystalline microporous chalcogenides formed from PTMC. Two examples are shown with structures equivalent to experimentally synthesized materials. The first example started with random initial configuration shown in panel a, in an 8 × 8 × 8 bcc lattice with $x = 0.75x_\beta = 0.04688$. (c) 3 × 3 × 3 periodic extension of the final configuration in panel b. The structure shown in panels b and c is the decorated sodalite framework synthesized experimentally by Zheng et al. (ICSD collection code 281751[7]). The second example from PTMC is shown in panels d–f, initiated from a random initial configuration shown in panel d in a 4 × 12 × 12 bcc lattice with $x = 0.8889x_\beta$. (f) 6 × 2 × 2 periodic extension of the final configuration in panel e. The structure shown in panels e and f has also been synthesized experimentally[7] (ICSD collection code of 281749).

Carlo step, estimated in previous work to be 4 min.[23] Also crucial for zeolite synthesis is some structure directing agent to steer silica polymerization to cage-like structures. In our model, this steering may be accomplished through controlling density, the geometry of the lattice model, and, most importantly, by applying PTMC, which allows the system to evolve rapidly to ground states such as the ordered materials found herein. In future work, we will also investigate the incorporation of structure directing agents into the model.

In conclusion, we have reported Monte Carlo simulations of a simple but versatile atomic lattice model for silica and other T-B-T type materials, exhibiting self-assembly to an extremely rich variety of ordered microporous materials including known chalcogenides, layered materials, and zeolite analogs. This finding opens up myriad avenues for future research, including analysis of crystallization pathways to determine critical nuclei for formation of zeolites and related nanoporous materials.

COMPUTATIONAL METHODS

Our lattice model simulations include both rotational moves and translational moves of tetrahedra on the bcc lattice.[23] Three-dimensional periodic boundary conditions are used. The attempted moves are accepted or rejected according to the Metropolis criterion. One Monte Carlo step is defined as the attempts to move all tetrahedra in the system, including N rotational moves and N translational moves, where N is the number of tetrahedra in the simulation box. Twenty-seven temperature replicas were chosen for parallel tempering, with the lowest temperature, $T^* = 0.15$, corresponding to the room-temperature sol–gel synthesis from previous simulation of silica polymerization.[23] The highest temperature, $T^* = 0.28$, is sufficiently high to allow the system to overcome the energetic barriers to reach the ground states. Detailed illustrations of PTMC are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

Visualizations of additional chalcogenide structures and detailed illustrations of PTMC simulations.

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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