

## NIRT: Multiscale Simulation of the Synthesis, Assembly and Properties of Nanostructured Organic/Inorganic Hybrid Materials

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PIs: Peter Cummings<sup>1</sup>, Sharon Glotzer<sup>2</sup>, John Kieffer<sup>2</sup>, Clare McCabe<sup>3</sup>, Matthew Neurock<sup>4</sup>,

<sup>1</sup>Vanderbilt University, <sup>2</sup>University of Michigan

<sup>3</sup>Colorado School of Mines, <sup>4</sup>University of Virginia

Polyhedral oligomeric silsesquioxane (POSS) molecules (see Figure 1) are unique nanometer-size inorganic/organic hybrid structures. POSS molecules have a polyhedral core which can be multifunctional and serve as platforms that can be synthetically modified to contain groups for copolymerization, adhesion, light sensitization, binding catalyst species, and improved solubility. The ability to independently functionalize each corner of a POSS cage with different organic or inorganic groups confers a nearly infinite array of possible nanostructures made of assemblies of POSS molecules. Depending on the functionalization of the POSS cages, the resulting systems can be solid or liquid, or, upon crosslinking turned into a network. They are a truly nano-structured building block, which, through self- and guided-assembly, can be transformed into a remarkable array of products, which are just now becoming available to industry on a large scale.

While much is known experimentally about the chemical synthesis of POSS systems, very little theoretical understanding exists at the molecular level or beyond. In particular, the way in which individual POSS molecules can be assembled and manipulated at the nanoscale to form meso- and macro-scale systems has not been investigated previously. In this project, our overall goal is to develop a multiscale computational framework to simulate the synthesis and self- and guided-assembly of POSS systems. We employ a variety of methods: *ab initio* quantum chemistry methods (such as Gaussian 98), *ab initio* molecular dynamics (particularly the VASP code), atomistic molecular dynamics (MD) and Monte Carlo (MC) simulation methods (using codes developed within our research groups as well as commercial codes - Accelrys' Cerius II and Materials Studio – and the public domain code DL\_POLY), mesoscale molecular dynamics and MC simulations using coarse-grained models developed within this project, and the statistical associating fluid theory (SAFT), a molecular-based theory for describing complex molecular systems (including polymers).

*Molecular Color Centers.* Our first-principle density functional theoretical studies show that the smallest size cube,  $\text{Si}_8\text{O}_{12}\text{R}_8$ , is quite interesting in that it has various excited states whereby the electron density is centered inside of the cavity. At least two of these states are below the vacuum level indicating that the potential inside the cage is lower than that of the vacuum. These states take on characteristics of an "electron in a box". The POSS cage, therefore, behaves like a quantum box. By fluorinating the ends of the cages, we were able to dramatically increase the electron affinity of the POSS cage, thus making it energetically favorable for the  $\text{POSS}(\text{F})_8$  to capture an extra electron inside the cube. Calculations on the effect of adding an alkali metal atom in the presence of the  $\text{POSS}(\text{F})_8$  cube show that the electron favorably transfers from Cs and is isolated in the center of the POSS cube. The  $\text{POSS}(\text{F})_8$  system, therefore, behaves as a

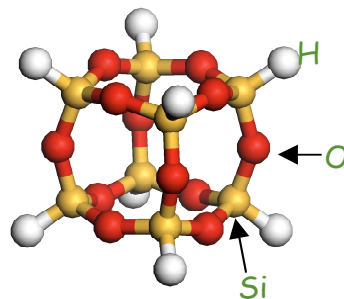


Figure 1. POSS core molecule with hydrogens at corners ( $\text{Si}_8\text{O}_{12}\text{H}_8$ ). This fundamental POSS cube can be functionalized at one or more of the eight corners by substituting the hydrogens with various oligomers.

molecular color center. The addition of alkali promoters alter its optical properties whereby it would absorb different wavelengths of light. By changing the nature of the POSS cube, the end group substituents or the specific metal atom we can begin to tune the wave length. These molecular color centers could be used in the creation of optical fibers or lasers.

*Degradation dynamics of tethered POSS molecules.* Using VASP, the core POSS cage with 1-2 ethyl tethers was bombarded with atomic oxygen with incoming energies of 4 and 7 eV. At 4eV, oxygen inserts into the Si-H and Si-C bonds to form a silanol or siloxy intermediates, leading to an increased oxygen ratio consistent with model experimental studies. Subsequent oxygen collisions lead to fragmentation of neighboring C-C bonds ultimately forming CO<sub>2</sub>. This is a primary degradation path seen experimentally. These studies are relevant to the proposed use of POSS-based coatings on spacecraft, which are exposed to atomic oxygen in the ionosphere.

*Force field development.* We have confirmed that several *ab initio* methods accurately predict the structure of the non-functionalized POSS cage. In preliminary work, we have used the Rappé-Goddard universal force field (UFF) to study the structure and melting behavior of non-functionalized POSS molecules, and to obtain predictions from a “standard” force field for comparison with our own. Since we ultimately wish to study assembly and reaction into networks, we require explicit-atom large-scale reactive MD; for this, we use a charge-transfer potential designed for systems that exhibit mixed covalent-ionic interactions. This potential is capable of simulating dynamical polarization of electronic configuration as well as charge redistribution upon formation and breaking of chemical bonds. The design of this potential is based on input from experiments and *ab initio* density functional calculations. We optimized potential parameters to reproduce experimentally observed structures and properties of POSS. For example, we can now stably simulate non-functionalized POSS units in their trigonal crystalline structure. In this structure, nearest neighbor POSS cages are not positioned so as to minimize energy between them. Instead, the balance in this crystal is achieved through a delicate combination of long-range attractive electrostatic forces and short-range repulsive forces between atoms at the extremities of neighboring POSS cages. Our interaction potential also reproduces the infrared spectra of this POSS crystal. Density functional theory calculations and *ab-initio* quantum mechanical simulations have been used to fine-tune the charge distributions in the various chemical bonds of the non-functionalized POSS cage, as described by our reactive interaction potential. This was accomplished by mapping out the inter POSS cage interactions. A weak van der Waals attractive interaction appears to be present when the two cages are 7.82 Å apart (centers between the two cages). The optimal orientation is one in which the first cage is rotated 45 degrees with respect to orientation of the second one.

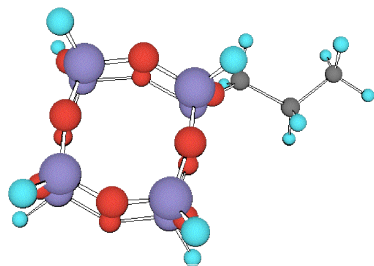


Figure 2. T-butyl POSS.

In addition, potential energy surfaces for the interaction of H<sup>+</sup> and dipolar molecular structure (NaCl) with the cage have been carried out to test the intermolecular potentials used in the dynamics. The charge distributions in the classical interaction potential have been optimized to produce the same results as the *ab initio* calculations. We are also investigating the application of symmetry adapted perturbation theory (SAPT) as a direct route to calculation of the van der Waals dispersion interaction.

*Force fields for tethered POSS molecules.* We performed *ab-initio* quantum mechanical calculations to evaluate the impact of side chains (e.g., see Figure 2) on the conformation of the POSS cage and vice versa (i.e., the impact of the POSS cage on the side chain). Geometry optimization and single point energy calculations indicate that adding

alkane tethers has minimal impact on the structure of the POSS cage, and that the POSS cage has minimal impact on the chain structure and interaction. This suggests that in atomistic simulations of alkane-tethered POSS cages existing high-accuracy force fields for alkanes can be used to model the tethers.

*Mesoscale model development.* Design and development of novel, hybrid organic/inorganic materials based on POSS technology requires a fundamental understanding of assembly processes that take place in these materials over time and length scales that span from atomistic to macroscopic scales. The investigation of directed self-assembly of POSS/polymer materials in particular requires the simulation of large, assembling systems containing thousands to hundreds of thousands of POSS cages functionalized with organic tethers, a task currently impossible using *ab initio* methods and even classical methods with chemically detailed force fields. We have developed a minimal model of  $\text{Si}_8\text{O}_{12}\text{H}_7\text{R}$  tethered POSS cages (see Figure 3) to expedite simulation of POSS/polymer assembly processes and enable rapid prototyping of phase diagrams and ordered structures. The model is constructed to retain the essential geometrical and energetic features of the tethered cubes and consequently the topological characteristics of the assembled structures. We have implemented the model in MD and off-lattice and on-lattice MC simulations. The model consists of rigid POSS cubes consisting of interaction sites at the eight cube corners and, for certain studies, at the center of the cube. *Ab initio* calculations and explicit atom MD simulations of the POSS cubes were used to parameterize the strength and range of POSS-POSS interactions. Hydrocarbon tethers on the cube corners are modeled as bead-spring-type chains, bead representing roughly three  $\text{CH}_2$  units. Cross-linking interactions between tether ends are achieved via thermoreversible, attractive interactions between terminal beads.

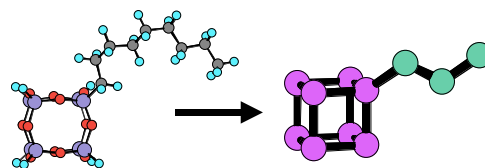


Figure 3: Minimal POSS model

*Assembly of monofunctional POSS cubes with nonane tethers.* Our MD simulations of POSS cubes functionalized with a single nonane tether using a chemically detailed reactive force field predict an ordered, highly porous structure with stable, nanoscopic POSS-rich and polymer-rich domains. Such a porous nanostructured material could find important uses in sensing applications such as gas absorption and detection. To explore this on a larger scale, we have performed MD simulations of this system using the minimal model described above, in which the corner beads of the rigid POSS cages interact via soft-sphere interactions and cage centers interact via a standard (Lennard-Jones) interaction parameterized to reproduce the minimal energy distances predicted by *ab initio* calculations. Preliminary results show the hierarchical formation of micelle-like structures with cores composed of aggregated POSS cages.

*Assembly of octafunctional POSS cubes tethered by organic linkers.* Crosslinked networks of tethered octafunctional POSS cubes represent a novel class of hybrid organic/inorganic materials. Experiments on these systems have demonstrated that the length and rigidity of tethers strongly affects the network structure and material properties. To gain a fundamental understanding of the role of tether length on the ordering and network properties of thermally reversible, crosslinked POSS networks, we performed lattice MC simulations up to 4500 octafunctional propyl-, hexyl-, nonyl- and dodecyl-POSS cubes using the minimal model described above. Our simulations predict that when the weak POSS-POSS van der Waals forces are screened by the polymer tethers, the porosity of the network decreases with increasing tether length. Our simulations also predict an optimum tether length to balance steric hindrance and flexibility in order to maximize the degree of crosslinking and thus network connectivity.