Polyhedral oligomeric silsesquioxanes (POSS) are nanometer-size molecules suitable for the production of organic–inorganic nanocomposite materials. These organic–inorganic nano-building blocks show promise for enabling the production of polymeric materials of exceptional mechanical properties as well as novel composite materials. While the experimental studies of these materials have rapidly evolved in the past decade, their theoretical investigation is still in its infancy. Toward the validation of force fields for the molecular simulation of POSS-containing systems, we present the charge-transfer reactive (CTR) force field for the molecular simulation of polyhedral oligomeric silsesquioxane (POSS) molecules and compare the ability of this, and several force fields taken from the literature, to predict the thermophysical properties of POSS-containing systems. The literature force fields compared include the universal force field (UFF) and the COMPASS and Hybrid-COMPASS force fields. Predictions from molecular dynamics simulations of the structural parameters (unit cell vectors), melting temperature, and FT-IR spectra of crystals of POSS monomers are presented. The POSS monomers investigated are octahydride, octamethyl, and octapropyl POSS. Predicted quantities are compared to experimental results where available and provide molecular-level physical insight into several aspects of the behavior of POSS molecules. While all the force fields tested perform reasonably well, our results indicate that the Hybrid-COMPASS and CTR force fields predict structural properties that are in good agreement with experimental data.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) are multifunctional molecules, with the chemical composition (RSiO₁.₅)ₙ (n = 4, 6, 8, 10...) which is intermediate between that of silica (SiO₂) and polysiloxanes (R₂SiO)ₙ. The most-studied members of the series are the octasilsequioxanes (n = 8), which have a cube-shaped Si₈O₁₂ core with organic groups R at each corner. Figure 1 shows the simplest member of the octasilsequioxane family, the polyhedral octahydridosilsesquioxane (H₈Si₈O₁₂), often referred to as T₈, in which the organic groups are hydrogen atoms. Because of the rich chemistry of these molecules, POSS-based systems have a wide range of potential applications, for example, as additives to paints, coatings, packaging materials, resins, elastomers, and advanced plastics, where they enhance the abrasion and temperature resistance, increase the glass transition temperature, and improve mechanical properties (without compromising processibility).¹,²

The first experimental studies on POSS-containing systems focused on determining the crystal structures of a variety of POSS monomers³–⁵ and was followed by work from several groups to solve the crystal structures of other octasubstituted silsesquioxanes R₈Si₈O₁₂, with R = –C₂H₅,⁶ –CH₃,⁷ –Cl,⁸ and –nC₃H₆I.⁹ More recently, Waddon et al. investigated the crystal structure of a cyclopentyl–POSS–norbornenyl monomer (containing seven cyclopentyl and one norbornyl groups),¹⁰,¹¹ which is a widely used POSS monomer in composite applications; the seven chemically inert cyclopentyl groups help dissolve the POSS unit into a polymer matrix, while the one chemically reactive norbornyl group acts as a site for further polymerization or grafting reactions.

In recent years, significant research efforts have focused on the development of POSS molecules as molecular nanoscale building blocks for the production of nanocomposite materials. The outstanding feature of polyhedral silsesquioxanes, in
mental studies have examined the effect of POSS monomers
expensive and produced in small quantities. Several experi-
tion, invoking their aggregation.
properties to the bulkiness of the POSS monomers without
while others attribute the enhancement of the composite
of the POSS units is due to their aggregation into microdomains,
while others attribute the enhancement of the composite
properties to the bulkiness of the POSS monomers without
invoking their aggregation.

To properly understand and control the aggregation and
crystallization of monomers in POSS-based nanocomposites, it
is necessary to fully understand the thermodynamic and me-
chanical properties of POSS cubes and the interactions that occur
between POSS monomers at a molecular level. Given the limited
availability of experimental techniques that probe such details,
molecular simulation appears to be the ideal tool to gain this
understanding. However, while powerful algorithms to study
thermodynamic and mechanical properties of polymeric materi-
als have been developed, the results obtained are only reliable
if realistic expressions for the force fields that describe the
interactions between the atoms and molecules in the system are
included in the calculations. To permit the study of POSS
monomers by molecular simulation, we have developed a new
force field and compare this force field to others taken from
the literature in the prediction of the crystal structures of several
POSS monomers. X-ray diffraction patterns computed from the
simulation results are compared to experimental data where
available. In addition, we have calculated densities and diffusion
coefficients for POSS monomers as a function of temperature
and estimated the melting temperature. The remainder of the
paper is organized as follows: in Section 2, we provide a
detailed description of the force fields used in this work, and
in Section 3, we give details of the simulations performed. In
Section 4, we discuss the simulation results obtained with the
different force fields studied, and compare our predictions to
the available experimental data. Finally, in Section 5, we
summarize our findings.

2. Methods and Force Fields

Several force fields have been evaluated for describing POSS
molecules: the universal force field (UFF), the condensed-
phase optimized molecular potentials for atomic simulation
studies force field (COMPASS), a simplified version of
COMPASS, referred to as Hybrid-COMPASS (HC), and
the new charge-transfer reactive (CTR) force field. In earlier
work, on the basis of ab initio calculations, we demonstrated
that when an alkane tether is substituted for one organic group
R on the POSS cage, the geometrical features of both the POSS
cage and the alkane tether do not significantly change when
compared to the isolated molecules. Thus, we concluded that
it should be possible to describe the properties of alkane-
substituted POSS monomers by combining force fields inde-
pendently developed to describe alkane chains and siloxane
molecules. Hence, for simulations of alkyl-functionalized
POSS cages, we have combined the force fields chosen to
described silsesquioxane molecules with a well-established
alkane force field, namely the transferable potential for phase
equilibria united atom force field (TraPPE UA). In what
follows, we briefly summarize the main features of each of the
force fields used in this work.

2.1. Universal Force Field (UFF). In the UFF force field,
total potential energy $U$ is given by

$$U = U_b + U_\theta + U_\psi + U_{vdw}$$  \hspace{1cm} (1)

where $U_b$ represents the bond-stretching interactions, $U_\theta$
represents the angle-bending interactions, $U_\psi$ represents the
torsional interactions, and $U_{vdw}$ represents the nonbonded
interactions. The bond-stretching interaction can be described
either as a harmonic oscillator or as a Morse function. In this
work, the harmonic oscillator formulation is used:

$$U_b = 1/2k_I(r - r_{eq})^2$$  \hspace{1cm} (2)

where $r_{eq}$ is the equilibrium bond length between atoms $I$ and $J$,
$r$ is the actual bond length between atoms $I$ and $J$, and $k_I$
is the force constant. The angle-bending term is described as a
harmonic cosine oscillator:

$$U_\theta = 1/2k_{\theta}(\cos \theta - \cos \theta_0)^2$$  \hspace{1cm} (3)

where $\theta_0$ is the equilibrium angle, $\theta$ is the actual angle, and $k_{\theta}$
is the force constant. The torsional interactions are given by a
cosine potential,

$$U_\psi = A[1 + \cos(m\Phi - \delta)]$$  \hspace{1cm} (4)

where $A$ is a constant, $m$ the periodicity coefficient, $\Phi$
the dihedral angle, and for the force field considered here, $\delta = 0$.
The nonbonded interactions between atoms in different mole-
cules and between atoms in the same molecule but separated
by three or more bonds are described by a 12–6 Lennard–
Jones potential:

$$U_{vdw} = \epsilon_{IJ}\left[\frac{1}{r_{IJ}^6} - \frac{1}{r_{IJ}^{12}}\right]$$  \hspace{1cm} (5)

where $\epsilon_{IJ}$ represents the depth of the potential well, $r_{IJ}$
is the distance between the atoms when the energy is a minimum (i.e.,
$U_{vdw} = -\epsilon_{IJ}$), and $r$ is the actual distance between the atom
pair $I–J$. The parameters $\epsilon_{IJ} \equiv \epsilon_I$ and $r_{IJ} \equiv r_I$
are tabulated for like atom pairs, while the unlike atom interactions are
determined by using the geometric combining rules

$$r_{IJ} = (r_I r_J)^{1/2}$$  \hspace{1cm} (6)

$$\epsilon_{IJ} = (\epsilon_I \epsilon_J)^{1/2}$$  \hspace{1cm} (7)

In Table 1, we report all the parameters used to implement
the UFF force field for the POSS systems studied.

2.2. Condensed-Phase Optimized Molecular Potentials
( COMPASS) and Hybrid-COMPASS Force Fields (HC).
In the COMPASS force field, the total potential energy $U$
is given by,

$$U = U_b + U_\theta + U_\psi + U_z + U_{bb} + U_{b\theta} + U_{b\psi} + U_{\theta\phi} +
U_{b\theta\phi} + U_{coa} + U_{vdw}$$  \hspace{1cm} (8)

The terms on the right-hand side of eq 8 can be divided into
two categories: valence terms, which include bond-stretching
(U_b), bond-angle-bending (U_\theta), torsion (U_\psi), out-of-plane angle-
bending (U_z), cross-coupling terms (bond-bond (U_{bb}), bond-
 interaction, etc.)

TABLE 1: Parameters Used in the UFF Force Field for the POSS Monomers Studied

<table>
<thead>
<tr>
<th></th>
<th>(E_0) (k) (kcal/mol)</th>
<th>(r_0) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–H</td>
<td>345.4464</td>
<td>1.4705</td>
</tr>
<tr>
<td>Si–O</td>
<td>879.8471</td>
<td>1.5917</td>
</tr>
<tr>
<td>H–Si–O</td>
<td>104.06</td>
<td>109.47</td>
</tr>
<tr>
<td>Si–O–Si</td>
<td>140.91</td>
<td>146.0</td>
</tr>
<tr>
<td>O–Si–O</td>
<td>300.08</td>
<td>109.47</td>
</tr>
</tbody>
</table>

TABLE 2: Parameters Used in the Hybrid-COMPASS Force Field for the POSS Monomers Studied

<table>
<thead>
<tr>
<th></th>
<th>(E_0) (b_0) (Å)</th>
<th>(k_2) (kcal/mol Å(^2))</th>
<th>(k_3) (kcal/mol Å(^3))</th>
<th>(k_4) (kcal/mol Å(^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–O</td>
<td>1.64</td>
<td>350.1232</td>
<td>-517.3424</td>
<td>673.7067</td>
</tr>
<tr>
<td>Si–H</td>
<td>1.478</td>
<td>202.78</td>
<td>-305.36</td>
<td>280.27</td>
</tr>
<tr>
<td>Si–C</td>
<td>1.899</td>
<td>189.65</td>
<td>-279.42</td>
<td>307.51</td>
</tr>
<tr>
<td>Si–O–Si</td>
<td>159.0</td>
<td>8.500</td>
<td>-13.4188</td>
<td>-4.1785</td>
</tr>
<tr>
<td>O–Si–O</td>
<td>110.7</td>
<td>70.3069</td>
<td>-6.9375</td>
<td>0</td>
</tr>
<tr>
<td>H–Si–O</td>
<td>107.4</td>
<td>57.6643</td>
<td>-10.6506</td>
<td>4.6274</td>
</tr>
<tr>
<td>C–Si–O</td>
<td>114.9</td>
<td>23.0218</td>
<td>-31.3993</td>
<td>24.9814</td>
</tr>
</tbody>
</table>

angle (\(U_{\theta 0}\)), bond–torsion (\(U_{\theta 0}\)), and bond–angle–torsion (\(U_{\theta 0}\)) interactions), and nonbonded interaction terms, which include the Coulombic function (\(U_{\text{coul}}\)) for electrostatic interactions and the Lennard–Jones 9–6 function (\(U_{\text{vdw}}\)) for van der Waals interactions. The full COMPASS force field was used in this work as implemented in Materials Studio.\(^a\) A simplified version of the COMPASS force field, in which the out-of-plane angle-bending and the cross-coupling interaction terms are neglected, has also been tested. We refer to this latter force field as Hybrid-COMPASS (HC). In the HC potential, the bond-stretching \(U_b\) and angle-bending \(U_\theta\) terms are described by quartic functions

\[
U_b = k_2(b - b_0)^2 + k_3(b - b_0)^3 + k_4(b - b_0)^4
\]

(9)

\[
U_\theta = H_4(\theta - \theta_0)^2 + H_5(\theta - \theta_0)^3 + H_6(\theta - \theta_0)^4
\]

(10)

where \(b_0\) is the equilibrium bond length and \(\theta_0\) the equilibrium bond angle, \(b\) the actual bond length, \(\theta\) the actual angle, and \(H_2, H_3, H_4\) and \(k_2, k_3, k_4\) are constants. The torsion term \(U_\theta\) is given by the triple cosine function,

\[
U_\theta = V_1(1 - \cos(\Phi)) + V_2(1 - \cos(2\Phi)) + V_3(1 - \cos(3\Phi))
\]

(11)

where \(\Phi\) is the actual value of the dihedral angle, and \(V_1, V_2,\) and \(V_3\) are constants. The electrostatic interactions are described by the Coulombic function,

\[
U_{\text{coul}} = \sum_{I,J} \frac{q_Iq_J}{r_{IJ}}
\]

(12)

where \(q_I\) and \(q_J\) represent the partial charges of atoms \(I\) and \(J\), respectively, and \(r_{IJ}\) is the distance between atoms \(I\) and \(J\). The partial charges on each atom are computed using the method of bond increments, as implemented in COMPASS by Sun.\(^b\) For atom \(i\), the partial charge is given by

\[
q_I = \sum_J \delta_{IJ}
\]

(13)

where the sum is of all charge bond increments \(\delta_{IJ}\) (which are tabulated values) for atoms \(J\) that are valence bonded to atom \(I\). The van der Waals interactions are described by the Lennard–Jones 9–6 potential function,

\[
U_{\text{vdw}} = \epsilon_{IJ} \left\{ 2 \left( \frac{r_{IJ}^9}{r} - \frac{3}{2} \left( \frac{r_{IJ}^6}{r} \right)^2 \right) \right\}
\]

(14)

where \(\epsilon_{IJ}\) represents the depth of the potential well, \(r_{IJ}\) is the distance between the atoms where \(U_{\text{vdw}} = -\epsilon_{IJ}\), and \(r\) is the actual distance between the atom pair. The van der Waals potentials are calculated for every nonbonded atom pair within a cutoff radius, usually 10 Å, and for atoms separated by two or more bonds on the same chain. The Lennard–Jones parameters \(\epsilon_{IJ}\) and \(r_{IJ}\) are tabulated for like atom pairs. For unlike atom pairs, a 6th order combining rule is used to calculate the parameters,

\[
r_{IJ} = \left( \frac{r_{IJ}^6 + r_{IJ}^6}{2} \right)^{1/6}
\]

(15)

\[
\epsilon_{IJ} = \left( \frac{2r_{IJ}^6}{r_{IJ}^6 + r_{IJ}^6} \right)^{1/2} \epsilon_{IJ}
\]

(16)

where \(r_I, r_J, \epsilon_I,\) and \(\epsilon_J\) represent the like atom interaction parameters for atoms \(I\) and \(J\), respectively. In Table 2, we report all the parameters used to implement the Hybrid-COMPASS force field in this work.

2.3. Charge-Transfer Reactive (CTR) Force Field. The CTR force field was originally conceived for the study of inorganic materials with mixed ionic and covalent bonding, and an earlier version has proven successful in reproducing the
structural transition between various silica polymorphs with a single parametrization. The use of this potential in the present context was motivated by the inorganic character of the core of the polyhedral octahydridosilsequoxane (H2SiO12) building blocks. The CTR force field has been parametrized to reproduce the stable crystal structure and vibrational properties of the POSS cage. The CTR force field includes a Coulomb term, $U_{CB}$, a Born–Huggins–Mayer repulsive term, $U_{BMH}$, a three-body term, $U_{3B}$, and an attractive van der Waals term $U_{vdw}$ giving the following expression for the total energy:

$$U_{total} = U_{CB} + U_{BMH} + U_{3B} + U_{vdw}$$

The Coulomb interaction between point charges is expressed as

$$U_{CB} = \frac{1}{4\pi\varepsilon_0} \sum_{j=1}^{N} \frac{q_i q_j}{r_{ij}}$$

where $q_i$ is the total amount of transferable charge, $a$ and $b$ are constants, and $r_{ij}$ is the distance between atoms $i$ and $j$. The van der Waals interactions are given by,

$$U_{vdw} = \sum_{j=p}^{N} C_{ij}$$

where $C_{ij}$ is a constant. The repulsion between atomic cores is modeled by the Born–Mayer–Huggins term according to

$$U_{BMH} = \sum_{j=p}^{N} A_{ij} \left( \frac{z_i}{n_i} + \frac{z_j}{n_j} \right) e^{\left(\alpha_3 r_{ij} - r_0\right) n_i n_j}$$

where $A_{ij}$ is the preexponential energy scaling factor, $\rho_0$ is the hardness parameter, $z_i$ is the valence electron number, and $n_i$ is the number of outer shell electrons. The parameter $\alpha_3$ provides a measure of the atom size. The three-body term accounts for the directionality of covalent bonds by constraining the angle between two adjacent bonds. This term is conditional upon the existence of covalent attraction between atoms and is given by

$$U_{3B} = \sum_{i=1}^{NC-1} \sum_{j=k+1}^{NC} \left( \phi_{ij} + \phi_{jk} \right) e^{-\gamma \left( \theta_{ij} - \theta_0 \right)^2}$$

where $\theta$ is the angle formed by the $i-j$ and $i-k$ bonds, and $\phi$ is an angular spring constant,

$$\phi_{ij} = -A_{ij} \left[ 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j} \right] \kappa_{ij} \gamma_{ij} e^\beta e^{-\gamma \phi_{ij}}$$

where $\gamma_{ij}$, $\lambda_{ij}$, and $\kappa_{ij}$ are empirical constants. For torsional interactions, the expression for $U_{\Phi}$ given by eq 11 has also been implemented in this force field. In Table 3, we report the parameters used to implement the CTR force field.

2.4. TraPPE Force Field. The TraPPE UA force field specifies that the total energy $U$ has the same functional form as the UFF model (eq 1). The bond-stretching and bond-angle-bending interactions are modeled as harmonic oscillators, as given by

$$U_b = \frac{1}{2} k_{ij} (r - r_{ij})^2$$

$$U_{\Phi} = 1/2 k_{\Phi} (\theta - \theta_0)^2$$

The terms in eq 23 are defined as in eq 2. In eq 24, $\theta_0$ is the equilibrium value of the angle, $\theta$ is the actual value, and $k_{\Phi}$ is a constant. The torsional potential $U_{\Phi}$ is given by a triple cosine function,

$$U_{\Phi} = c_1 [1 + \cos(\Phi)] + c_2 [1 - \cos(2\Phi)] + c_3 [1 + \cos(3\Phi)]$$

where $\Phi$ is the actual value of the dihedral angle, and $c_1$, $c_2$, and $c_3$ are constants. The nonbonded interaction term $U_{vdw}$ is given by the Lennard–Jones 12–6 LJ potential function

$$U_{vdw} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6\right]$$

The unlike atom interactions are determined by using the Lorenz–Berthelot combining rules,

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$$

For alkyl-functionalized POSS molecules, the cross nonbonded van der Waals interactions are treated by following the work of Frischknecht and Curro.22 The Si–C bond-stretching potential from the HC force field was used to determine the Si–CH3 and Si–CH2 bond-stretching potentials. Similarly, the O–Si–C HC angle-bending potential was used for the O–Si–CH3 and O–Si–CH2 interactions, and the HC X–Si–C–X torsion potential was used to represent the O–Si–CH2–CH2 torsional potential. In Table 4, we report the parameters used to implement the TraPPE force field in this work, and in Table 5, the van der Waals nonbonded cross interactions for alkyl-POSS systems.

3. Simulation Details

Molecular dynamics simulations were carried out using the public domain DL_poly 2 code, the Accelrys Materials...
correction 25 when using DL molecules in the (CH$_3$)$_8$Si$_8$O$_{12}$ case. The structures were first the H$_8$Si$_8$O$_{12}$ case, and 3

Studio software package, and an in-house code, FLX. Crystal structures were simulated by using the Berendsen constant pressure algorithm$^{26}$ with the Rahman–Parrinello anisotropy correction$^{25}$ when using DL$_{\text{POLY}}$ 2, and the Rahman–Parrinello constant pressure algorithm when using FLX and Materials Studio. In both cases, not only the volume, but also the shape of the simulation box, is allowed to vary. In all the simulations, an integration time step of 1 fs was used. For simulations performed with Materials Studio and FLX, bonded and nonbonded interactions were evaluated at every time step. To increase computational efficiency in DL$_{\text{POLY}}$ 2, a multiple time step method was employed in which the bonded interactions were evaluated at every time step, and the nonbonded interactions evaluated every five time steps. The starting unit cell fractional coordinates were obtained from Larson$^{3,26}$ using X-ray diffraction analysis. X-ray diffraction analysis, in agreement with experimental data.$^5,10$

### 4. Results

We first focus on the results of the structural calculations. We computed via molecular mechanics simulations the molecular structure of the POSS cage predicted from the different force fields to compare with experimental data and ab initio calculations.$^{17}$ Bond lengths and angles were measured and averaged over the course of each molecular mechanics simulation for the different force fields considered. The results are presented in Table 6 for polyhedral octahydridosilsesquioxane, T8. The results indicate that the predictions obtained by using standard force fields satisfactorily reproduce the available experimental data. Because of the computationally intensive nature of electrostatic interactions in a force field, we also performed calculations using the Hybrid-COMPASS force field with the electrostatic interactions turned off (referred to as HC w/o). We note from the results that the prediction of the molecular structure of octahydridosilsesquioxane monomers (H$_8$Si$_8$O$_{12}$) with the HC force field is in good agreement with the experimental data both with and without the inclusion of electrostatic interactions in the force field. This is perhaps not unexpected, given that the partial charges in the HC force field are small. Because the calculation of electrostatic interactions is computationally expensive, this is an advantageous feature of the HC force field.

Although no experimental data is available to confirm our findings, it is instructive to study the POSS cage with alkyl tethers through molecular mechanics simulations to study the impact of the tethers on the cage structure.$^{17}$ The effect of substituting all eight hydrogen atoms with propyl chains is presented in Table 7 for the UFF, COMPASS, and HC w/o force fields. As suggested by previous ab initio calculations of monomethyly POSS cages, this has minimal impact on the cage structure. Furthermore, we note that the results from the three different force fields are consistent in that the Si−O bond lengths and the Si−O−Si angle show a slight increase, while the O−Si−O angle shows a slightly decrease in propyl POSS compared to T8 POSS in all cases.

Having validated the use of UFF, COMPASS, HC, and CTR force fields to satisfactorily reproduce the intramolecular structural parameters of POSS monomers, we now turn to the prediction of the crystal structure. Crystalline structures were investigated for T8 POSS (H$_8$Si$_8$O$_{12}$) and polyhedral octamethyl silesquioxane ((CH$_3$)$_8$Si$_8$O$_{12}$). In Figure 2, we report representative simulation snapshots for the H$_8$Si$_8$O$_{12}$ crystal at 100 K and the (CH$_3$)$_8$Si$_8$O$_{12}$ crystal at 300 K. The hexagonal unit cell, used to initialize the simulations, was in each case conserved during the simulation, in agreement with experimental data.$^5,10$

It is noted that the results from the three different force fields are consistent in that the Si−O bond lengths and the Si−O−Si angle show a slight increase, while the O−Si−O angle shows a slight decrease in propyl POSS compared to T8 POSS in all cases.

**Table 6:** Molecular Structure Predictions for H$_8$Si$_8$O$_{12}$ from the CTR, UFF, COMPASS, HC, HC w/o Force Fields Compared with Experimental Values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CTR</th>
<th>UFF</th>
<th>COMPASS</th>
<th>HC</th>
<th>HC w/o</th>
<th>exp$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si−O (Å)</td>
<td>1.620</td>
<td>1.5896</td>
<td>1.624</td>
<td>1.6702</td>
<td>1.6383</td>
<td>1.619</td>
</tr>
<tr>
<td>Si−H (Å)</td>
<td>1.4760</td>
<td>1.4637</td>
<td>1.473</td>
<td>1.4819</td>
<td>1.4761</td>
<td>1.4805</td>
</tr>
<tr>
<td>Si−O−Si (deg)</td>
<td>146.80</td>
<td>147.00</td>
<td>146.95</td>
<td>146.7</td>
<td>146.86</td>
<td>147.54</td>
</tr>
<tr>
<td>O−Si−O (deg)</td>
<td>109.73</td>
<td>109.92</td>
<td>110.19</td>
<td>110.26</td>
<td>110.09</td>
<td>109.6</td>
</tr>
</tbody>
</table>

$^a$ Reference 26.
of the crystal structure is good, with the UFF force field again giving the least accurate description compared to experiment. We note that the observed shift of diffraction peaks toward higher 2θ values is a direct consequence of a higher density in the simulations compared to experiment; the relative intensities and spacing between peaks is similar in all diffraction patterns, indicating that the placement of the atoms in the unit cell is adequately reproduced by all the force fields. In Figure 5, simulated X-ray diffraction patterns are compared to experiment for (CH₃)₈Si₈O₁₂ at 300 K. The simulated crystal structures are in excellent agreement with experiment, with the results obtained by using the UFF potential model again showing the greatest deviation from the experimental data.

Finally, in determining the suitability of different force fields to model the POSS cage, we have studied their melting properties to compare with the experimental data reported by Larsson and co-workers. At the melting point, the thermodynamic properties of the system, such as density, enthalpy, and self-diffusion coefficients, show discontinuous behavior due to the first-order nature of the transition. Thus, the melting point,
where $D$ is the center of mass self-diffusion coefficient, $\mathbf{r}(0)$ are the positions of the centers of mass at the time origins, and $\mathbf{r}(t)$ are the positions of the centers of mass at time $t$. The self-diffusion coefficient for a solid is on the order of $10^{-13}$ m$^2$/s, whereas for a liquid, it is on the order of $10^{-9}$ m$^2$/s. We have also determined the translational order parameter $\rho(\mathbf{k})$: 

$$
\rho(\mathbf{k}) = \frac{1}{N} \sqrt{\left( \sum_{i=1}^{N} \cos(\mathbf{k} \cdot \mathbf{r}_i) \right)^2 + \left( \sum_{i=1}^{N} \sin(\mathbf{k} \cdot \mathbf{r}_i) \right)^2}
$$

where $N$ is the number of molecules in the system, $\mathbf{k}$ is a reciprocal lattice vector and $\mathbf{r}_i$ are the positions of the centers of mass of the POSS molecules. The translational order parameter $\rho(\mathbf{k})$ has a value of 1 for a perfectly ordered crystal and a value of 0 for a disordered liquid.

In Figures 6–8, we report results for the density (Figure 6), the translational order parameter (Figure 7), and the self-diffusion coefficient (Figure 8) as a function of temperature for the $\text{H}_8 \text{Si}_8 \text{O}_{12}$ crystal obtained from the different force fields studied. We first note that for each of the properties studied, the UFF force field indicates the melting temperature to be in excess of 1000 K, which significantly overestimates the experimental value of 523 K. The results from both the HC and HC w/o force fields are generally in close agreement with each other and overestimate the experimental value. The CTR force field yields a significantly lower melting temperature than that of the other force fields, despite the fact that it overestimates the density. Presumably, the long-range electrostatic interactions, which include attraction and repulsion, dominate when the crystal expands, and a symmetry-breaking perturbation that favors the long-range repulsive interactions leads to the collapse of the structure. Similar calculations have been performed to determine the melting temperature of the $(\text{CH}_3)_8 \text{Si}_8 \text{O}_{12}$ and $(\text{CH}_2\text{CH}_2\text{CH}_2)_8 \text{Si}_8 \text{O}_{12}$ crystals with the HC w/o force field; the melting point is observed to decrease as the chain length of the alkane tether increases, in agreement with experimental measurements. A simple interpretation of this melting point behavior is that the tethers increasingly screen the electrostatic interactions between the cubes as the tether length increases. We are currently performing additional simulations to confirm this conclusion.

Determining melting transitions by using molecular simulation is not a trivial task. The results reported in this work used perfect, defect-free crystals, whereas real crystals have defects and surfaces that have been shown to initiate melting. Therefore, we would anticipate our simulations to overpredict the melting temperature by 20–30%, as seen in other work. In the literature, there have been several reports of more refined methods to determine the melting transition, such as finding the melting temperature as a function of the number of defects in the crystal, finding the melting temperature for nanocrystals of increasing size and extrapolating to infinite size, and introducing a solid—liquid interface in the system. To explore the effect of the periodicity imposed on the crystal lattice on the melting temperature predicted by the UFF and HC force fields, we have performed simulations on an isolated nanoparticle consisting of 54 T8 molecules. The same simulation procedure was followed as for the periodic systems, and the same initial configurations were used. The systems were equilibrated for 500 ps at 100 K, and then the temperature was gradually increased by 100 K for every 100 ps until melting was observed. The translational order parameter was used to monitor the melting transition, and the results are presented in Figure 9. We note from Figure 9 that for both the UFF and HC force fields, the predicted melting temperature is significantly lower than was observed in the periodic simulations, and for the HC force field, the predicted melting temperature is now in good agreement with the experimental value.

Finally, the ability to reproduce vibrational properties has been evaluated by calculating the infrared spectrum of $\text{H}_8 \text{Si}_8 \text{O}_{12}$ from...
the Fourier transform of the current–dipole time correlation function according to

$$I(\omega) = \frac{\hbar}{4\pi^2(1 - e^{-\hbar\omega/k_B T})} \text{Im}\int_{-\infty}^{\infty} \langle \mu(0)\mu(t) \rangle e^{-i\omega t} dt$$  \hspace{1cm} (31)$$

where $\mu$ is the total dipole moment of the simulated configuration. To evaluate eq 31, the force field needs to account for the fluctuations in the charge distribution in the simulated structure, therefore, we can only use the CTR force field for this calculation. We present our prediction, as well as the experimental data in Figure 10. We find that the peak positions in the simulated spectrum agree with experimental data to within less than 50 cm$^{-1}$, and the sequence of relative intensities matches that of the experiments well. Peak positions and relative intensities depend very sensitively on potential parameters. Changing the spacing between two spectral peaks invariably requires the adjustment of more than one potential parameter and vice versa; changing a single potential parameter affects the position and intensity of more than one spectral feature. This is why it is difficult to design interaction potentials that accurately reproduce vibrational spectra. In our experience, the agreement between simulated and experimental spectra shown in Figure 10 can be considered as very good. Moreover, on the basis of a simulated spectrum, it is straightforward to assign the vibrational modes of motion that correspond to the various spectral peaks. This can be done by Fourier filtering the underlying atomic trajectories.21 Accordingly, we were able to confirm that the 2280 cm$^{-1}$ peak corresponds to the Si–H stretching mode, the 1150 cm$^{-1}$ peak to the asymmetric Si–O–Si stretching mode, the 890 cm$^{-1}$ peak to rattling of Si in its tetrahedral coordination shell, and the three low-frequency peaks to various Si–O–Si rocking modes. We also note that, except for the highest-frequency mode, there is a strong similarity between this spectrum and that for cristobalite silica.21

Conclusions

In this work, we have presented the CTR force field$^{33-35}$ for the study of POSS molecules and provided evidence that this, as well as other force fields taken from literature, can be used to obtain reliable predictions for the structural properties of systems composed of POSS molecules. The literature
force fields compared include the universal force field, the COMPASS, and the Hybrid-COMPASS force fields. We predicted the structural parameters (fractional coordinates and crystal packing) of octahydridosilsesquioxane monomers and compared our predictions to available experimental data. Good agreement has been found between predicted and experimental data for all the force fields considered. We have found that the inclusion of electrostatic interactions does not significantly affect the ability of the HC force field to predict the near-range structural characteristics of silsesquioxanes, as no noticeable difference was found between the predicted properties when the electrostatic interactions were excluded. We note, however, that the melting behavior and the vibrational properties from the CTR potential are sensitive to the proper representation of the charge distribution. We have predicted the melting temperature of the perfect infinitely replicated crystal and a nanocrystal of octahydridosilsesquioxane monomers. The results provide an upper and lower bound on the predicted melting temperatures from each force field; for the CTR and HC force fields, the predicted values are in quantitative agreement with experiment. Our work provides the necessary justification for using the CTR and HC force fields for the calculation of properties of systems that contain POSS monomers via molecular simulation.

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References and Notes