6

Molecules as a Basis for Modeling the Force Field of Silica

G. V. Gibbs, F. C. Hill, M. B. Boisen, Jr, and R. T. Downs

Departments of Geological Sciences, Material Science and Engineering and Mathematics Virginia Tech, Blacksburg, VA, USA

1 INTRODUCTION

More than fifty years ago, John C. Slater (1939), Institute Professor at MIT, noted that the bond lengths and angles of the C_6 skeletal ring of the cyclohexane molecule are strikingly similar to those observed for the C framework of diamond. Structural analyses have since revealed that the bond lengths and angles of the C skeletons of several other aliphatic molecules (neopentane, adamantine, congressane, anti-tetramantine) are also similar to those observed for diamond. As observed for the skeletal ring of cyclohexane, the skeletal pattern of the C atoms of any one of these molecules has only to be extended in three-dimensional space to generate the diamond structure. The close correspondence between these structures provides the basis for Slater's (1939) statement that 'A diamond is really a molecule of visible dimensions

held together by just the same forces acting in small molecules'. More recent studies indicate that a similar connection exists between the force field of silica and that of the Si–O–Si skeleton of small silicic acid and siloxane molecules, demonstrating that Slater's observations are more prescient and general than was perhaps originally thought. This paper examines the experimental and the theoretical evidence upon which these observations are based.

2   CONNECTION BETWEEN THE FORCE FIELD OF SILICA AND SMALL MOLECULES

2.1   Structural Evidence

There is a wealth of experimental data reported over the past 35 years for silica and silicate crystals and siloxane and silicic acid molecules that indicate that a close connection exists between the shape of an Si–O–Si unit in silica and the shape of the unit in small siloxane and silicic acid molecules. The data show, for example, that the average Si–O bond length and Si–O–Si angle observed for the crystals (1.63 Å and 144°) are virtually the same as those (1.63 Å and 142°) observed for the molecules. Almennigen *et al.* (1963) were possibly among the first to report this correspondence in a study of disiloxane H_6Si_2O, the simplest gas phase molecule to contain the skeletal Si–O–Si unit of a silicate crystal. Despite the small size of the molecule, they found on average that the shape of the unit closely resembles that observed for silicate crystals. From these results, they asserted that the bonding picture of the Si–O–Si unit of the molecule is similar to that in a silicate crystal. Additional evidence for this picture was provided by a structure analysis of an H_6Si_2O crystal formed by cooling a gas of disiloxane molecules. An X-ray diffraction study shows that the bond lengths and angles (R(SiO) = 1.632 Å; <Si–O–Si = 142.2°) of the crystal closely resemble those observed for the gas phase molecule (R(Si–O) = 1.634 Å; <Si–O–Si = 144.1°; Barrow *et al.*, 1979). This was an unexpected result considering the very compliant nature of the Si–O–Si angle and the expected difference between the force field of the gas phase molecule and that of the crystal.

For the silica polymorphs, a correlation has also been reported between Si–O bond length and Si–O–Si angle, with shorter bonds tending to involve wider angles (cf. Gibbs *et al.*, 1994). A similar correlation has also been reported for a variety of siloxane and silicic acid molecules (Chakoumakos *et al.*, 1981; Karle *et al.*, 1986; Bürgi *et al.*, 1993). The similarity of these correlations and the similarity of the structural properties of siloxane and silicic acid molecules and those of the silica polymorphs not only provide a basis for the observations made by Almennigen *et al.* (1963), but also a basis for explaining why molecular force fields have been successful in the reproduction of the structures

of the silica polymorphs (Gibbs, 1982; Lasaga and Gibbs, 1987). They also provide a basis for understanding why the scaled force constant of the Si–O bond (Hill *et al.*, 1994) and the electron density distribution, $\rho(r)$, recorded for the silica polymorphs and that calculated for the Si_2O_7 skeletal unit of the disilicic acid molecule are similar (Gibbs *et al.*, 1994).

2.2   Evidence Provided by Electron Density Distributions

The electron density distribution of molecules and crystals is an observable property that can be determined experimentally and theoretically, in sharp contrast to wave functions which are unobservable. As the forces in molecules and crystals are closely connected to their electron density distributions, Geisinger *et al.* (1987) completed a mapping of the deformation electron density distribution, $\Delta\rho(r)$, for coesite, a high-pressure polymorph of silica, and compared the distribution with deformation density distributions calculated for several molecules. The experimental $\Delta\rho(r)$ maps were found to be in rough agreement with those calculated for the Si–O–Si skeletal units of the siloxane and silicic acid molecules H_6Si_2O, $H_6Si_2O_7$ and $H_8Si_4O_4$. However, because of the qualitative and arbitrary nature of such maps, Downs (1995) used the data recorded by Geisinger *et al.* (1987) to represent $\rho(r)$ for coesite with a generalized X-ray scattering factor model. He then located the $(3, -1)$ critical points, r_c, along each Si–O bond, determined the value of the electron density and the Laplacian of $\rho(r)$ at each of these points, $\rho(r_c)$ and $\nabla^2\rho(r_c)$, respectively, and mapped $\nabla^2\rho(r)$ in a plane of each Si–O–Si skeletal unit.

A mapping of $\rho(r)$ for a molecule or a crystal and its topological properties has a distinct advantage over a mapping of $\Delta\rho(r)$ in that 'The derivation of a unique and physically meaningful difference (deformation) electron density is a problem that cannot be solved since the choice of the promolecular reference density always implies some arbitrariness' (Cremer, 1987). This statement is consistent with the observations (a) that the heights of the peaks in the $\Delta\rho(r)$ maps recorded along the Si–O bonds of coesite fail to show any obvious trends with the observed bond lengths and (b) that the peaks in deformation maps calculated for the Si–O bridging bonds of the $H_6Si_2O_7$ molecule used to model the Si–O–Si units in the mineral were actually found to increase in height as the lengths of the bonds increased (and as the Si–O–Si angle decreased). On the other hand, the value of $\rho(r_c)$ provided by calculations of the total electron density distribution for the molecule shows that the value of $\rho(r_c)$ increases in a regular way as the Si–O bond decreases (and as the Si–O–Si angle widens) (Gibbs *et al.*, 1997). In other words, some sense can be made of the bond length variation when examined in terms of the value of $\rho(r)$ at each critical point. However, little or no sense can be made of the bond length variations when examined in terms of the heights of the peaks in $\Delta\rho(r)$ maps.

For purposes of comparison, $\rho(r)$ of a minimum energy conformer of $H_6Si_2O_7$, has been generated using the wave functions obtained in a Becke3LYP/6-311G(2d,p) level calculation which models electron correlation and exchange effects (Gibbs, in preparation). Earlier calculations of the $\rho(r)$ properties for the $H_6Si_2O_7$ molecule obtained at Hartree–Fock/6-311++G** level have yielded values that departed from those observed for coesite by as much as $\sim$30 % (Gibbs *et al.*, 1994). This is not surprising inasmuch as $\nabla^2\rho(r)$ is very sensitive to slight differences in $\rho(r)$ and as model HF calculations neglect electron correlation and exchange effects. The total electron density distribution measured for coesite attains an average value of 1.05 e/$\mathring{A}^3$ at an average distance of 0.936 $\mathring{A}$ measured along the Si–O bond from the oxide ion to the critical point r_c (the average bonded radius of the oxide ion), with an average $\nabla^2\rho(r_c)$ value at this point of +20.4 e/$\mathring{A}^5$. These observations together with the average bonded radius of the oxide ion (Gibbs *et al.*, 1994) and the negative value of the local energy density, $H(r_c)$, at r_c (Cremer and Kraka, 1984) suggest that the Si–O bonds in coesite have a substantial component of covalent character. The curvatures of $\rho(r_c)$, λ_1 and λ_2, measured at r_c, perpendicular to the Si–O bonds, are on average −7.2 and −6.8 e/$\mathring{A}^5$, respectively, while the average curvature of $\rho(r)$ at r_c along the bond path, λ_3, is observed to be 34.4 e/$\mathring{A}^5$ (Downs, 1995), resulting in an average $\nabla^2(r_c)$ value of 20.4 e/$\mathring{A}^5$.

Unlike the topological properties calculated at the Hartree–Fock/6-311++G** level, the properties calculated for the molecule at the Becke-3LYP/6-311G(2d,p) level are in good agreement with those observed on average for coesite (Gibbs *et al.*, 1998). The value of $\rho(r_c)$ calculated for bridging bonds of the molecule is 1.00 e/$\mathring{A}^3$ ($\sim$5 % less than that observed, on average, for coesite) at a distance of 0.943 $\mathring{A}$ from the bridging oxide ion ($\sim$1 % larger than observed on average for coesite). The curvatures of $\rho(r)$, λ_1, λ_2 and λ_3, for the bridging bonds of the molecule, evaluated at r_c, are −7.41, −7.35 and 35.6 e/$\mathring{A}^5$ respectively, resulting in a $\nabla^2\rho(r_c)$ value of 20.9 e/$\mathring{A}^5$, $\sim$2 % larger than observed, on average, for coesite. In addition, the anisotropy of the electron density of the Si–O bond increases regularly as the Si–O–Si angle narrows, a feature that has been interpreted in terms of a weak π system (Gibbs *et al.*, 1994). As the curvature of $\rho(r)$ is a very sensitive probe of the topography of $\rho(r)$, as discussed above, the close connection between the topological properties observed for coesite and those calculated for the molecule indicates that the force fields and the properties of electron density distribution of the two systems are very similar, particularly in the vicinities of the critical points. In view of this result, it may not be surprising that considerable success has been made in modeling the structures, the force constants and the elastic properties of the silica polymorphs using potentials based on molecular force fields.

2.3 Evidence Provided by Molecular Modeling of the Structure of Silica

Lasaga and Gibbs (1987) were the first to show that a molecular force field can be used to reproduce the structures and volume compressibilities for the silica polymorphs with a simple covalent potential energy function derived for the Si_2O_7 skeleton of the disilicic acid molecule, $H_6Si_2O_7$. The model structure generated for low quartz was found to agree with that observed to within $\sim$2 %, with the zero-pressure compressibility calculated for the structure being only 5 % smaller than that observed. However, the calculated zero-pressure derivative of the compressibility, K_0', which can be difficult to determine experimentally, was found to have a negative sign, in poor agreement with the experimental value. The negative K_0' value of the model structure indicates that quartz should actually soften rather than stiffen with increasing confining pressure which, of course, is contrary to the experimental observation (Levien *et al.*, 1980). However, when the potential energy function of the disilicic acid molecule was derived with a more robust basis set, not only was the K_0' value of the model structure found to be positive in sign, but it was also found to be in better agreement with the experimental value (2.7 versus 6.4 obs.). In addition, the dynamic properties of the $Si-O$ bonds of the model structure were found to be in reasonable agreement with the values observed for the bonds in quartz and silica glass (Lasaga and Gibbs, 1987, 1988).

With the success of these calculations, a myriad of other molecular-based potential energy functions were derived. For example, Stixrude and Bulowinski (1988). Tsuneyuki *et al.* (1990). Gibbs *et al.* (1988), van Beest *et al.* (1990). Purton *et al.* (1993) and Boisen and Gibbs (1993) have since derived potential energy functions based on a variety of molecules ranging in size from that of an SiO_4^{+4} anion embedded in an array of neutralizing point charges to that of the Si_5O_{16} skeleton of the pentasilicic acid molecule. These functions were not only used with varying degrees of success in the reproduction of the quartz structure at room pressure and at high pressures, but they were also used in the successful generation of the photon spectra, NMR spectra and quadrupole parameters and chemical shifts, the force constants of the $Si-O$ bond and the $Si-O-Si$ angle, the correct distribution of the infrared and Raman vibrational modes, the shifts of the modes with pressure, the elastic constants, the piezoelectric properties of quartz and the observed trends in photoelectron, X-ray emission and UV excitation energies recorded for silicate glasses (cf. Tossell and Vaughan, 1992).

Structures generated for these silica polymorphs with the geometry and force field calculated for the molecule at the Becke3lyp/6-311G(2d,p) level are in better agreement, as may be expected, with the observed structures than those calculated with the HF force field. For example, the cell dimensions generated for low-quartz agree with those observed to within $\sim$0.5 %, on average, while those generated for low cristobalite and coesite agree to within $\sim$1 %, on

average. The two non-equivalent Si–O bond lengths in quartz are 1.602 and 1.614 Å while the Si–O–Si angle is 143.7°. The Si–O bond lengths of the model structure of quartz are both 1.612 Å and the Si–O–Si angle is 145.0°. A correction of the Si–O bond lengths of quartz for thermal motion, using a strategy devised by Downs *et al.* (1992), yields lengths of 1.611 and 1.619 Å, respectively, with an average value of 1.615 Å, slightly longer than that generated for the model structure. Although there are two non-equivalent Si–O bond lengths in cristobalite, they are both observed to be identical in length (1.603 Å), with an observed Si–O–Si angle of 145.5°. A correction of the observed bond lengths for thermal motion yields a value of 1.615 Å for both bond lengths compared with 1.612 Å calculated for the model structure. Like the quartz model, the Si–O–Si angle in the cristobalite model is 145.0°, 0.5° narrower than observed. The observed Si–O bond lengths in coesite range between 1.595 and 1.621 Å. The shorter of these two is involved in a 180° Si–O–Si angle and the longer one is involved in the narrowest Si–O–Si angle (137.2°) in the structure. A thermal correction of the bond lengths yields values of 1.598 and 1.626Å, respectively, for these two bonds. The corresponding bond lengths in the coesite model structure are 1.602 and 1.614 Å, respectively, with the shorter of the two again involved in the 180.0° angle and the longest bond length involved in the narrowest angle, 141.9°. However, the model structure, when generated with the HF force field, was found to be significantly softer than that observed (Boisen and Gibbs, 1993). On the other hand, the structures, volume compressibilities and K_0' values generated for low quartz, low cristobalite and coesite, with a potential energy function based on an SiO_4^{+4} molecule embedded in a tetrahedron of four e^+ point charges, were found to be in reasonably good agreement with observed values (Tsuneyuki *et al.*, 1990). Even though the potential energy function observed by Tsuneyuki *et al.* (1990) is based on a molecule with four-coordinated Si, it was used with reasonable success in the generation of the structure and the volume compressibility of stishovite, a natural form of silica with six-coordinated Si. The success of these calculations provoked Cohen (1994) to exclaim that 'The versatility of these potentials is quite astounding'. Accordingly, it may not be surprising that a derivation was recently undertaken of a large number of stable and metastable structure types for silica, starting with a random arrangement of Si and O atoms and using the geometry and a penalty function based on the force field of the disilicic acid molecule (Boisen *et al.*, 1994).

3   GENERATION OF SILICA STRUCTURE TYPES USING A MOLECULAR-BASED POTENTIAL

As observed by Hawthorne (1994), the derivation of the structure types of such a material as silica starting with a random arrangement of atoms is a stubborn

problem that has yet to be solved even for a relatively simple system like NaCl. Despite the challenging nature of the problem, Deem and Newsam (1992) made important progress in this direction when they derived model structures for a large number of zeolite framework structures together with several high-silica, porous zeolite structures. Their goal was to build a catalogue of viable framework structure types as well as to design structures with channels and large pore space architectures. With the availability of a catalogue of calculated powder patterns for these structures, workers in the field could more easily identify and characterize the structures of new zeolites which are often too fine grained for single-crystal structural analyses. In their study, a generation of the known structure types was completed using simulated annealing strategies and a penalty function based on histograms of TT separations (T represents either tetracoordinated Si or Al) and TTT angles recorded for the structures. The calculations, completed using the observed cell dimensions with the T atoms randomly distributed in the given unit cell arranged to conform with the observed space group symmetry, resulted in the generation of more than 60 known four-connected T atom framework structures and several silica structure types. To complete the derivation of each of the tetrahedral frameworks, an oxide anion was placed at the mid-point between each pair of adjacent T atoms and the structure was refined using distance least squares methods. In addition to the known framework structure types, more than 5000 new, low-symmetry framework structures with their cell dimensions were derived. The addition of these structures to the catalogue resulted in a wealth of viable framework structure types for the zeolites and silica. In a related paper, Wood and Price (1992) also used simulated annealing strategies to generate periodic two-dimensional, three-connected nets of T atoms that replicated the layers of a number of known zeolite structure types.

More recently, Boisen *et al.* (1994, 1999) derived a large number of structure types for silica with a penalty function based on a force field and a geometry calculated for the Si_2O_7 skeleton of the disilicic acid molecule with simulated annealing strategies. However, unlike previous studies, the derivations were completed starting with a random arrangement of atoms in a periodic structure with triclinic symmetry. In other words, no assumptions are made about the starting atomic arrangement, nor about the symmetry other than that the unit cell contains a given number of SiO_2 formula units and that periodic boundary conditions are imposed on the structure by *P*1 translational symmetry.

The first set of calculations was undertaken for four SiO_2 formula units with the Si and O atoms randomly distributed in a unit cell. Of the 400 calculations completed, 106 resulted in viable model framework structures of corner-sharing silicate tetrahedra, where each Si atom is linked to four O atoms and each O atom is linked to two Si atoms. The remaining structures were of higher energy and exhibited such features as five- and six-coordinated Si and two- and three-coordinated O, and four-coordinated planar and pyramidal Si. Also,

numerous molecular crystal structures were generated including silica-w. These and other less stable framework structures were often found to contain edge- and face-sharing SiO_4 tetrahedral groups. Despite the lack of any formal charges on Si and O, the shared edges of the tetrahedra were found to be significantly shorter ($\sim$2.25 Å) than the unshared ones ($\sim$2.74), in conformity with Pauling's third rule. Because of the electrostatic neutrality of the resulting structures, it is difficult to ascribe this feature to the electrostatic repulsion between highly charged Si cations in adjacent edge-sharing tetrahedra. As observed by Boisen et al. (1994), the short shared edges can be ascribed to the tendency of the Si–O–Si angle formed between two edge-sharing Si_2O_6 dimers to relax and adopt a wider angle at the bridging O, which in turn is balanced by a destabilization of the system induced by a narrowing of the O–Si–O angles opposite the shared edge.

Of the viable framework structures derived by Boisen et al. (1994), an analysis of their space group symmetries, structures, coordination sequences, X-ray powder diffraction patterns and calculated enthalpies resulted in more than 20 distinct stable and metastable structure types for silica. Despite the assumption made in the calculations of a random arrangement of four Si and eight O atoms in a triclinic unit cell for the starting assemblage, less than a third of the local minimum energy structures were found to possess triclinic symmetry, with the remaining two thirds exhibiting symmetries that ranged from Pc to $I\overline{4}2d$. The resulting structures exhibit symmetrically equivalent cell dimensions that agree with one another to within 0.0001 Å and equivalent interaxial angles that agree to within 0.0001°. Also, the fractional coordinates of the symmetrically equivalent atoms agree to within 0.0001. Even though the potential energy function for the disilicic acid molecule used in the calculations has a single minimum energy bridging Si–O bond length (R(Si–O) = 1.621 Å), a single Si–O–Si angle (Φ = 137.6°) and a single O–Si–O angle (Θ = 109.5°), the local minimum energy structures obtained in the calculations exhibit Si–O bond lengths that range from 1.55 to 1.68 Å, Si–O–Si angles that range from 105 to 180° and O–Si–O angles that range from 102 to 116°. From a crystal chemistry point of view, it is noteworthy that the correlation observed for coesite and the other silica polymorphs and for siloxane molecules with four-coordinated Si between R(Si–O) and f_s(O) $= \cos\Phi/(\cos\Phi - 1)$ is reproduced almost exactly by the bond lengths and bridging angles generated for the structures, despite the assumption of a single Si–O target bond length and Si–O–Si target angle in the calculations.

Five of the low-energy structure types generated in the calculations with $Z = 4$ exhibit the same coordination sequences as those exhibited by cristobalite with space group symmetries $I\overline{4}2d$, $P4_12_12$, $P4_32_12$, $Ima2_1$ and $C2/c$. The ones with $I\overline{4}2d$ symmetry were determined to possess the true high cristobalite structure, those with $P4_12_12$ and $P4_22_12$ symmetries were determined to possess the left- and right-handed low cristobalite structures

and those with $Ima2_1$ symmetry were determined to possess a stuffed derivative structure of low cristobalite (O'Keeffe and Hyde, 1976). Of the structures generated, the one with the lowest energy, denoted BGB1 by O'Keeffe (1995), is of particular interest. It is tetragonal with space group symmetry $I\bar{4}$, with a coordination sequence that is different from that of cristobalite and from those generated in the study for the remaining structure types. However, the sequence matches that observed for the silicate tetrahedra in moganite out to the tenth sphere. BGB1 has a structure that consists of four- and eight-membered rings of silicate tetrahedra that are linked into a framework by six-membered rings. However, the coordination sequence of the structure and the ring statistics match those of the tetrahedral atoms in monoclinic structure type $CaAl_2Si_2O_8$ which also contains four- six- and eight-membered rings (O'Keeffe, 1995). Thus, the topology of the BGB1 framework conforms exactly with that observed for $CaAl_2Si_2O_8$. The network defined by the Si atoms of BGB1 also corresponds to net number 4 enumerated by Smith (1977) which he derived from a planar 6^3 net. According to O'Keeffe (1995), the symmetry of BGB1 would be $I4/mmm$ if the BGB1 topology were allowed to adopt its highest possible symmetry provided no bonds were broken.

A first principle LDA pseudopotential crystal calculation of the model structures and the $P-V$ equations of state for polymorphs quartz, cristobalite, stishovite and BGB1 predicts that the bulk modulus (21.5 GPa) of BGB1 is intermediate between that of quartz and that of cristobalite with a pressure derivative that is close to that observed for cristobalite (Teter *et al.*, 1995). The total energy calculated for BGB1 is lower than that calculated for stishovite, but it is the same as that calculated for quartz and cristobalite. Since BGB1 qualifies as a porous high-silica zeolite, it may well exist in nature, particularly in volcanic and hydrothermally active areas such as geysers and hot springs.

The BGB6 structure matches that observed for the tetrahedral framework of the synthetic zeolite Li–A(BW), $Li_4[AlSiO_4]_4 \cdot H_2O$ (O'Keeffe, 1995). Despite the differences in composition, the cell edges predicted for BGB6 ($a = 10.217$ Å; $b = 7.958$ Å; $c = 4.956$ Å) are only 1–2 % smaller than those observed ($a = 10.3$ Å; $b = 8.2$ Å; $c = 5.0$ Å) for Li–A(BW). The network defined by the Si atoms in BGB6 matches the net 4 enumerated by Smith (1977). The highest symmetry that the BGB6 topology can assume is $Imma$, while that adopted by the derived structure is $Ima2$, a subgroup of the higher symmetry group.

Calculations have also been completed for six SiO_2 formula units with the Si and O atoms randomly distributed again in a unit cell with $P1$ symmetry, including quartz and moganite (Boisen *et al.*, 1999). Of the more than 2000 framework structure types generated, more than half have distinct structures. Despite the assumption of $P1$ symmetry in the calculations, more than three quarters of the structures display space group symmetries other that $P1$ symmetry, ranging from $P\bar{1}$ to $R32$. These structures and others being derived

in our laboratories at Virginia Tech are currently being analyzed and compared with known and model structure types for silica.

4 DISCUSSION

The successful modeling of the properties and structures of silica not only provides support for the observations made by Slater (1939) and Almennigen *et al.* (1963), but also lends credence to the statement that a silica polymorph like quartz can be viewed as a giant molecule bound together by essentially the same forces that bind the atoms of the Si–O–Si skeleton into a small siloxane molecule (Gibbs, 1982). It also provides a basis for understanding the close structural similarities that exist between silicates and organosiloxanes. As observed by Noll (1968), it is possible to pass from the polymeric silicate anions of a silicate to the polymeric molecules of an organosiloxane by replacing the non-bridging oxide ions of the silicate anions with methyl groups. The structures that result from this replacement closely resemble the silicate anions exhibited by the silicates with polymethylsiloxanes containing polymeric units that correspond to the basic building blocks of a silicate: monomers, dimers, trimers, etc., rings, chains, sheets and frameworks of corner-sharing silicate SiO_4 groups. Indeed, this correspondence is complete to the extent that the polymethylsiloxanes can be classified with the same classic scheme used by Bragg to classify the silicates. In addition, the close correspondence of the bond lengths and angles and the structures of the polyanions in silicates and polymethysiloxane molecules indicates that the force field that governs the structure of the silicate frame of an organosiloxane molecule is likewise virtually the same as that in a silicate crystal. In other words, the argument that the force field of a molecule can be used to mimic that in silica seems to be more general and to hold for silicates, aluminosilicates and aluminophosphates as well. Nicholas *et al.* (1992), for example, completed MO calculations on several structural analogs of disiloxane, H_6T_2O (T = Si, Al, B, P): the force constants and the relative acidities of the hydroxyl groups calculated for the molecule used to model surface and defect sites of a number of substituted zeolite crystals agree with the experimental values. The success of their calculations in the reproduction of the data observed for the zeolites led them to conclude that the molecules themselves are but very small fragments of the crystal structure of a chemically similar zeolite crystal.

However, as observed by Noda *et al.* (1990), the results obtained for the silica polymorphs using first principles crystal calculations are much more meaningful than those generated with potential energy functions based on a molecular force field. Without a doubt, such calculations are unsurpassed as models for generating the structures and properties for crystals for a variety of conditions (see Bukowinski, 1994, for an excellent review of these calculations).

Although they have been successful in reproducing the structures and compressibilities of the known structure types for silica, they have failed for the most part in the discovery of new viable structure types, primarily because of the immense computer costs that would be involved. On the other hand, as discussed above, a large number of viable structure types for silica has been derived using molecular-based potential energy functions, demonstrating the efficacy and power of molecular-based calculations. Indeed, a first principles calculation of the structure and properties of one of the derived structures of silica such as moganite would be very time consuming and an expensive undertaking. When it comes to clarifying and providing a quantum mechanical basis for understanding the local structure of a silicate crystal, molecular model calculations have been quite successful in providing meaningful interpretations of a large number of experimental phenomena and principles in crystal chemistry, interpretations that have yet to be forthcoming from high-level crystal calculations (see Gibbs *et al.*, 1994). The calculations have also provided important insights into the field of heterogeneous kinetics by delineating reaction pathways and energetics in systematizing the available experimental data on the dissolution of quartz by H_2O (cf. Lasaga and Gibbs, 1990).

In conclusion, it is clear that MO calculations on molecules have advanced our understanding of bonding, the crystal chemistry and the properties of silica and silicate crystals. They have also provided potentials that can be used to derive viable structure types that are often far too costly and difficult to obtain with first principle crystal methods. Moreover, the close correspondence that exists between the bond length data generated in MO calculations for oxide, sulfide, nitride and fluoride molecules and those observed for crystals indicates that molecular force fields can be used not only to generate crystal structures for oxide, sulfide, nitride and fluoride crystals but also to generate their thermodynamic and mechanical properties as well (Gibbs *et al.*, 1987; Bartelmehs *et al.*, 1989; Buterakos, *et al.*, 1992; Wendel and Goddard, 1992; Nicoll *et al.*, 1994).

5 REFERENCES

Almennigen, A., Bastiansen, O., Ewing, V., Hedberg, K. and Traetteberg, M. (1963) *Acta Chem. Scand.* **17**, 2455–2460.

Barrow, M. J., Ebsworth, E. A. V. and Harding, M. M. (1979) *Acta Crystallogr.* **B35**, 2093–2099.

Bartelmehs, K. L., Gibbs, G. V. and Boisen, M. B. (1989) *Am. Miner.* **74**, 157–168.

Boisen, M. B. and Gibbs, G. V. (1993) *Phys. Chem. Miner.* **20**, 123–135.

Boisen, M. B., Jr, Gibbs, G. V. and Bukowinski, M. S. T. (1994) *Phys. Chem. Miner.* **21**, 269–284.

Boisen, M. B., Gibbs, G. V., O'Keefe, M. and Bartelmehs, K. L. (1999) *Microporous and Mesporous Materials* **29**, 219–266.

Bukowinski, M. S. T. (1994) *Annu. Rev. Earth Planet Sci.* **22**, 167–205.

Bürgi, H. B., Törnroos, K. W., Calzaferri, G. and Heribert, B. (1993) *Inorg. Chem.* **32**, 4914–4919.

Buterahos, L. A., Gibbs, G. V. and Boisen, M. B. (1992) *Phys. Chem. Miner.* **19**, 127–132.

Chakoumakos, B. C., Hill, R. J. and Gibbs, G. V. (1981) *Amer. Miner.* **66**, 1237–1249.

Cohen, R. E. (1994) in *Silica*, eds Heaney, P. J., Prewitt, C. T. and Gibbs, G. V., Mineralogical Society of America, Washington, DC, pp. 369–402.

Cremer, D. and Krakar, E. (1984) *Croatic Chem. Acta* **57**, 1259–1281.

Cremer, D. (1987) in *Modelling of Structures and Properties of Molecules*, ed. Z. B. Macsić, pp. 128–144.

Deem, M. W. and Newsam, J. M. (1992) *J. Am. Chem. Soc.* **114**, 7189–7198.

Downs, J. W. (1995) *J. Phys. Chem.* **99**, 6849–6852.

Downs, R. T., Gibbs, G. V., Bartelmehs, K. L. and Boisen, M. B. (1992) *Am. Miner.* **77**, 751–757.

Geisinger, K. L., Spackman, M. A. and Gibbs, G. V. (1987) *J. Phys. Chem.* **91**, 3237–3244.

Gibbs, G. V. (1982) *Am. Miner.* **67**, 421–450.

Gibbs, G. V. and Boisen, M. B. (1986) *Mater. Res. Soc. Symp. Proc.* **73**, 515–527.

Gibbs, G. V., Finger, L. W. and Boisen, M. B. (1987) *Phys. Chem. Miner.* **14**, 327–331.

Gibbs, G. V., Boisen, M. B., Downs, R. T. and Lasaga, A. C. (1988) *Mater. Res. Soc. Symp. Proc.* **121**, 156–165.

Gibbs, G. V., Downs, J. W. and Boisen, M. B. (1994) in *Silica*, eds Heaney, P. J., Prewitt, C. T. and Gibbs, G. V., Mineralogical Society of America, Washington, DC, pp. 331–368.

Gibbs, G. V., Hill, F. C. and Boisen, M. B. (1997) in *Modelling of Minerals and Silicated Structures*, eds Silvi, B. and D'Arco, Ph., John Wiley & Sons, pp. 167–178.

Gibbs, G. V., Boisen, M. B., Hill, F. C., Tamada, O. and Downs, R. T. (1998) *Phys. Chem. Min.* **25**, 574–584.

Hawthorne, F. C. (1994) *Acta Crystallogr.* **B50**, 481–510.

Hill, F. C., Gibbs, G. V. and Boisen, M. B. (1994) *Struct. Chem.* **5**, 349–355.

Karle, I. L., Karle, J. M. and Nielson, C. J. (1986) *Acta Crystallogr.* **C42**, 64–67.

Lasaga, A. C. and Gibbs, G. V. (1987) *Phys. Chem. Miner.* **14**, 107–117.

Lasaga, A. C. and Gibbs, G. V. (1988) *Phys. Chem. Miner.* **16**, 29–41.

Lasaga, A. and Gibbs, G. V. (1990) *Am. J. Sci.* **290**, 263–295.

Levien, L., Prewitt, C. T. and Weidner, D. J. (1980) *Am. Miner.* **65**, 920–930.

Nicholas, J. B., Winans, R. E., Harrison, R. J., Iton, L. E. and Curtiss, L. A. (1992) *J. Phys. Chem.* **96**, 10247–10257.

Nicoll, J. S., Gibbs, G. V., Boisen, Jr, M. B., Downs, R. T. and Bartelmehs, K. L. (1994) *Phys. Chem. Miner.* **20**, 617–624.

Noda, R., Catlow, C. R. A., Dovesi, R. and Pisani, C. (1990) *Phys. Chem. Miner.* **17**, 353–369.

Noll, W. (1968) *Chemistry and Technology of Silicones*, Academic Press, London.

O'Keeffe, M. and Hyde, B. G. (1976) *Acta Crystallogr.* **B32**, 2923–2936.

O'Keeffe, M. (1995) *Phys. Chem. Miner.* **22**, 504–506.

Purton, J., Jones, R., Catlow, C. R. A. and Leslie, M. (1993) *Phys. Chem. Miner.* **18**, 389–392.

Slater, J. C. (1939) *Introduction to Chemical Physics*, McGraw-Hill, New York, NY, 521 pp.

Smith, J. V. (1977) *Am. Miner.,* **62**, 703–709.

Stixrude, L. and Bukowinski, M. S. T. (1988) *Phys. Chem. Miner.* **16**, 199–206.

Teter, D. M., Gibbs, G. V., Boisen, M. B., Allan, D. C. and Teter, M. P. (1995) *Phys. Rev.* **B52**, 8064–8073.

Tossell, J. A. and Vaughan, D. J. (1992) *Theoretical Geochemistry: Applications of Quantum Mechanics in the Earth and Mineral Sciences*, Oxford University Press, New York.

Tsuneyuki, S., Aoki, H., Tsukada, M. and Matsui, Y. (1990) *Phys. Rev. Lett.* **64**, 776–779.

van Beest, B. W. H., Kramer, G. J. and van Santen, R. A. (1990) *Phys. Rev. Lett.* **64**, 1955–1958.

Wendel, J. A. and Goddard, III, W. A. (1992) *J. Chem. Phys.* **97**, 5048–5062.

Wood, I. G. and Price, D. P. (1992) *Zeolites* **12**, 320–326.