Modelling the deformation mechanisms, structure–property relationships and applications of auxetic nanomaterials

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Analytical and Molecular Mechanics methods have been used to study the structure and deformation mechanisms acting at the molecular level in the auxetic polymorph of crystalline silica (α-cristobalite). The Molecular Mechanics simulations indicate a stress-induced phase transition from α-cristobalite to ‘ordered’ β-cristobalite occurs for uniaxial loading along the x₃ direction. This is in reasonable agreement with the previous prediction from an analytical model assuming deformation is by concurrent dilation and cooperative rotation (about axes in the x₁-x₂ plane, passing through the midpoints of opposing edges – the a-axes) of the SiO₄ tetrahedral molecular sub-units, previously shown to predict the Poisson’s ratio for loading in the x₃ direction. The analytical models have been extended to include cooperative rotation of each tetrahedron about its axis (the c-axis) mostly closely aligned with the principal unit-cell x₃-axis. The new models enable significantly improved prediction of the Poisson’s ratios of α-cristobalite when loaded in one of the transverse (x₁ or x₂) directions. Parametric fitting of the analytical models indicate that the deformation mechanism for transverse uniaxial loading of α-cristobalite is by concurrent dilation and cooperative rotation about the local a and c-axes of the SiO₄ tetrahedra.

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1 Introduction

Negative Poisson’s ratio (ν) materials and structures expand transversely when stretched axially, and also undergo transverse contraction under axial compression. This is shown in Fig. 1, along with the classic example of a re-entrant honeycomb structure deforming by hinging of the cell walls leading to negative Poisson’s ratio behaviour. There is increasing interest in the development of these novel materials, known as auxetic materials [1], due to their counter-intuitive behaviour and also in applications where the auxetic property itself, or enhancements in other materials properties due to a negative Poisson’s ratio, may be exploited. For example, auxetic honeycomb and foam materials have been shown to offer enhanced de-fouling or tunable size selectivity when employed as filter materials, due to the characteristic high volume change (and hence permeability variation) which they undergo upon mechanical loading [2].

The development of auxetic nanomaterials is expected to lead to high modulus auxetic materials as well as leading to potential applications in sensor, molecular sieve and separation technologies. For example, we have recently reported that a number of zeolitic cage structures are predicted by molecular modelling calculations to be auxetic [3]. Zeolites are polyhedral aluminosilicate framework nanostruc-
Fig. 1 (a) Schematic of a material displaying negative Poisson’s ratio (auxetic) behaviour; (b) a re-entrant honeycomb undergoing deformation by hinging of the cell walls, leading to negative Poisson’s ratio behaviour.

Figures commonly used as molecular sieves because of their availability and well-defined molecular-sized cavities and pathways. Zeolite MFI was predicted by the force-field simulations to have both positive and negative ν’s for loading in the z-direction (νzx = –0.35 and νzy = +0.38). Combined molecular modelling and Monte Carlo simulations for the strain-dependent sorption of benzene and neopentane molecules onto the MFI all-silica zeolite nanostructure undergoing uniaxial loading along the z-direction were performed, and demonstrated that the benefits in separation applications due to auxetic functionality were predicted to persist down to the nanoscale [3].

One of the first attempts to design materials displaying negative Poisson’s ratio behaviour at the molecular level was based on an idealised 2D system of hard cyclic hexamers [4]. This was followed by the modelling of auxetic behaviour in molecular networks designed by scaling down geometries known to lead to auxetic behaviour at the macroscale. An example of this approach is the design of nanoscale macrocyclic hydrocarbons based on the re-entrant honeycomb geometry known to lead to auxetic behaviour at the macroscale [2, 5] (Fig. 2). Molecular modelling has been used to predict auxetic behaviour in these theoretical nanomaterials [1]. Analytical models have also been developed, extending the cell wall flexure model of honeycomb deformation [5], to include cell wall hinging and stretching acting concur-

Fig. 2 (online colour at: www.pss-b.com) Re-entrant honeycomb networks: (a) macroscale polymeric honeycomb [2]; (b) microscale metallic honeycomb structure; (c) theoretical polycrylylene molecular honeycomb network sub-unit [1].
rently with cell wall flexure, and also taking account of the inhomogeneity (atomic bond structure) that exists in the honeycomb cell walls at the nanoscale [6]. These more advanced analytical models for honeycomb deformation were shown to lead to excellent agreement with the molecular model calculations which, when used in combination with the molecular modelling approach, enable an efficient route to the design of this family of network nanostructures with tailored mechanical properties.

Little progress has been reported on the synthesis of the molecular re-entrant sub-units required for auxetic behaviour. However, whilst the synthesis of auxetic nanomaterials remains a challenge, it is likely that advances in supramolecular chemistry and crystal engineering will soon overcome this. Perhaps the most promising route to date in the development of man-made auxetic nanomaterials is proposed to be due to site-connectivity-driven rod orientation in a main-chain liquid crystalline polymer [7].

An alternative approach is to model the behaviour of naturally-occurring molecular-level auxetic materials in order to improve the design of chemically synthesisable auxetic nanomaterials. We have reported [8] the development of analytical expressions for the Poisson’s ratios of certain silica polymorphs which reproduce the experimental values for loading in the $x_3$ direction remarkably well, explaining in the process the dichotomy between negative and positive values of Poisson’s ratio in $\alpha$-cristobalite [9] and $\alpha$-quartz [10], respectively. The models consist of deformation due to cooperative rotation (described elsewhere as a ‘rigid unit mode’ (RUM) [11, 12]) and dilation of the SiO$_4$ tetrahedra making up the framework nanostructure of these materials. Most recently, the analytical models have been extended to predict a uniaxial stress-induced second phase, and Molecular Mechanics simulations have been performed to investigate the effects of uniaxial stress and pressure on the structure and mechanical properties for $\alpha$-cristobalite [13].

This paper reports further results from our recent modelling investigations into the structure, deformation mechanisms and mechanical properties of $\alpha$-cristobalite in order to develop an increased understanding of auxetic deformation mechanisms acting in a nanomaterial.

## 2 Models

### 2.1 Molecular mechanics model

The Cerius$^2$ Molecular Modelling software (Accelrys) was employed on a Silicon Graphics O2 workstation. The starting structure for $\alpha$-cristobalite was as provided within the Cerius$^2$ structure database derived from experimental data. The modelling protocols for the structure and mechanical properties simulations were as described in detail in Ref. [3]. For the work reported here, the Burchart force-field [14], developed specifically for silicas and aluminophosphates, was employed in the structure and mechanical properties simulations. The Burchart force-field assumes the frameworks are largely covalent and interactions were parameterised using experimental data. Whilst this force-field does not reproduce the negative on-axis Poisson’s ratios known to occur in $\alpha$-cristobalite, it does predict low positive values and also gives reasonable agreement with the experimental on-axis Young’s moduli. The stiffness matrix $C$ was computed from the second derivative of the energy expression, and the on-axis Poisson’s ratios and other elastic constants were obtained directly from the compliance matrix, $S = C^{-1}$, since, for example, $v_{ij} = s_{ij}/s_{ii}$.

Structure and mechanical properties simulations were performed for uniaxial loading along each of the mutually orthogonal principal axes $x_1$, $x_2$ and $x_3$.

### 2.2 Analytical models

The basic molecular “building block” for $\alpha$-cristobalite is the SiO$_4$ tetrahedron consisting of an O atom at each of the four corners surrounding a central Si atom. The molecular structure consists of a framework of corner-sharing SiO$_4$ tetrahedra in which each O atom is shared between two adjacent tetrahedra. Figure 3(a) shows the cartesian coordinate system and unit cell (space group P4$_2$2$_1$2) for $\alpha$-cristobalite, which is characterized by a ‘tilt’ (by an angle $\delta = 23.5^\circ$) of the tetrahedra about the local axis passing...
through the midpoints of opposing tetrahedron edges and lying within the $x_1$-$x_2$ plane for each tetrahedron (Figs. 3(b) and 3(c)).

Figure 4(a) shows the projection of the unit-cell in the $x_2$-$x_3$ plane, again with the tilt axes in the $x_1$-$x_2$ plane indicated. The projection of the ‘untilted’ ($\delta = 0$) structure in the $x_1$-$x_2$ plane is shown in Fig. 4(b) and corresponds to the ‘idealised’ $\beta$-cristobalite structure (space group Fd3m) originally proposed by Wyckoff [15] for the high temperature phase of cristobalite. However, the idealised $\beta$-cristobalite structure contains collinear Si–O–Si bonds which are unusual in silica polymorphs. The actual structure of $\beta$-cristobalite remains a topic of some debate in the literature. One view is that $\beta$-cristobalite has a dynamically disordered framework in which the oxygen atoms precess about the Si-Si axes in the idealised structure [16]. Another suggestion is that the $\beta$-cristobalite structure is a dynamic average of domains of $\alpha$-cristobalite [17]. Yet another suggestion for the structure of $\beta$-cristobalite proposes a locally ordered structure (‘ordered’ $\beta$-cristobalite) [18–20]. The ‘ordered’ $\beta$-cristobalite structure (space group I42d) is derived from the idealized $\beta$-cristobalite structure by rotation of each tetrahedron by an angle $\phi (= 19.8^\circ)$ about a tetrahedral axis aligned along the $x_3$ direction (i.e. perpendicular to the $x_1$-$x_2$ plane) – Fig. 4(c).

A local tetrahedral co-ordinate system is defined in Fig. 5(a), comprising of 3 orthogonal axes, each passing through the midpoints of two opposing edges. The $a$-axis in the local coordinate system lies in the $x_1$-$x_2$ plane of the cartesian coordinate system for $\alpha$-cristobalite (Figs. 3(b), 3(c) and 4(a)). The local $c$-axis is aligned along the $x_3$ cartesian axis for the idealised/ordered $\beta$-cristobalite structures. In $\alpha$-cristobalite, the local $c$-axis is rotated away from the $x_3$ axis due to the rotation of each tetrahedron by an angle $\delta$ about the $a$-axis (Fig. 5(b)).

Previously [21], analytical models have been developed which assume that the tetrahedral framework for $\alpha$-cristobalite deforms by tetrahedral dilation (i.e. the O–O bond distance, $l$, varies – the Dilating Tetrahedra Model (DTM)), cooperative tetrahedral rotation about the local $a$-axes ($\delta$ varies – the Rotating

Fig. 3 a) Unit cell and cartesian coordinates for $\alpha$-cristobalite. b) $x_3 - [\overline{1}10]$ projection of the unit cell, showing tetrahedral axes and ‘untilted’ tetrahedron (B) to define tilt angle $\delta$. c) $x_3 - [110]$ projection of the unit cell.

Fig. 4 $x_1-x_3$ projections of: a) $\alpha$-cristobalite, b) idealised $\beta$-cristobalite and c) ordered $\beta$-cristobalite.
Tetrahedra Model 1 (RTM1)) and concurrent tetrahedral dilation and $a$-axis rotation ($l$ and $\delta$ vary simultaneously – the Concurrent Tetrahedra Model 1 (CTM1)). Molecular mechanics simulations have confirmed that the mechanisms acting in the CTM1 occur for uniaxial loading of $\alpha$-cristobalite in the $x_3$ direction [13]. However, molecular mechanics simulations for uniaxial loading of $\alpha$-cristobalite in one of the transverse ($x_1$ or $x_2$) directions suggest an alternative tetrahedral rotation mechanism acts [13], resulting in 2 distinct values of the Si–O–Si intertetrahedral angle ($\theta$) at any given stress level. We consider this is due to cooperative rotation of the tetrahedra about the local $c$-axes, shown in Fig. 5(b).

We have, therefore, recently developed 3 new analytical models incorporating cooperative rotation of the tetrahedra about the local $c$-axes [22]: cooperative tetrahedral rotation about the local $c$-axes ($\phi$ varies – the Rotating Tetrahedra Model 2 (RTM2)); concurrent tetrahedral dilation and $c$-axis rotation ($l$ and $\phi$ vary simultaneously – the Concurrent Tetrahedra Model 2 (CTM2)); concurrent tetrahedral dilation, $c$-axis rotation and $a$-axis rotation ($l$, $\phi$ and $\delta$ vary simultaneously – the Concurrent Tetrahedra Model 3 (CTM3)). Full details are given in Ref. [22], but the method is summarized here.

The lengths of the unit cell, $X_1$, $X_2$, and $X_3$ along the $x_1$, $x_2$, and $x_3$ directions, respectively, are related to the tetrahedral size ($l$) and orientation angles ($\delta$ and $\phi$) by [22]

\[ X_1 = \sqrt{2}l \left[ \sin (45 + \phi) + \cos (45 + \phi) \cos \delta \right] , \]  
\[ X_2 = \sqrt{2}l \left[ \cos (45 + \phi) + \sin (45 + \phi) \cos \delta \right] , \]  
\[ X_3 = 2\sqrt{2}l \cos \delta . \]  

Poisson’s ratio is defined by:

\[ \nu_{ij} = -\frac{\partial e_j}{\partial e_i} = -\frac{\partial X_j}{X_i} \frac{\partial X_i}{\partial X_j} , \]  

where $e_i$ is the strain in the $x_i$ direction and $i, j = 1, 2, 3$ ($i \neq j$). The infinitesimal changes in the lengths of the unit cell are given by:

\[ \mathrm{d}X_i = \frac{\partial X_i}{\partial l} \mathrm{d}l + \frac{\partial X_i}{\partial \phi} \mathrm{d}\phi + \frac{\partial X_i}{\partial \delta} \mathrm{d}\delta . \]  

In Eq. (5), $\mathrm{d}l = \mathrm{d}\delta = 0$ for the RTM2, and $\mathrm{d}\delta = 0$ for the CTM2.
Table 1       Analytical model Poisson’s ratio expressions for α-cristobalite. $\kappa = l (d \delta dl)$ and $\lambda = l (d \phi dl)$.

<table>
<thead>
<tr>
<th>model</th>
<th>$\nu_{12} = \nu_{21}$</th>
<th>$\nu_{13} = \nu_{32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTM (l varying) [21]</td>
<td>−1</td>
<td>−1</td>
</tr>
<tr>
<td>RTM1 (δ varying) [21]</td>
<td>$\frac{1 + \cos \delta}{\cos \delta}$</td>
<td>$\frac{1 + \cos \delta}{1 + \cos \delta}$</td>
</tr>
<tr>
<td>CTM1 (l and δ varying) [21]</td>
<td>−1</td>
<td>$\frac{\cos \delta - \kappa \sin \delta}{\cos \delta}$</td>
</tr>
<tr>
<td>RTM2 (φ varying)</td>
<td>+1</td>
<td>0</td>
</tr>
<tr>
<td>CTM2 (l and φ varying)</td>
<td>$\frac{[1 + \cos \delta + \lambda (\cos \delta - 1)]}{[1 + \cos \delta + \lambda (1 - \cos \delta)]}$</td>
<td>$\frac{1}{1 + \lambda (1 - \cos \delta)}$</td>
</tr>
<tr>
<td>CTM3 (l, φ and δ varying)</td>
<td>$\frac{[1 + \cos \delta + \lambda (\cos \delta - 1) - \kappa \sin \delta]}{[1 + \cos \delta + \lambda (1 - \cos \delta) - \kappa \sin \delta]}$</td>
<td>$\frac{\cos \delta - \kappa \sin \delta}{1 + \cos \delta + \lambda (1 - \cos \delta) - \kappa \sin \delta}$</td>
</tr>
</tbody>
</table>

Table 1 contains the Poisson’s ratio expressions for uniaxial loading in the transverse directions ($x_1$ and $x_2$) of α-cristobalite for the 3 models described above, and also for the DTM, RTM1 and CTM1 models developed previously [21].

3 Results

3.1 $\sigma_3$-induced phase change for cristobalite

Figure 6a shows the calculated unit-cell parameter variations with loading along $x_3$ predicted from the molecular model simulations. The unit-cell dimension along the loading direction ($X_3$) decreases smoothly for compressive loading. The unit-cell length $X_1$ remains nearly constant for compressive loading, consistent with the low positive (near zero) value of $\nu_{13}$ calculated previously using the Burchart force-field [3]. In the case of tensile loading, $X_3$ increases smoothly along the same gradient as for compressive loading, and $X_1$ remains approximately unchanged, for $\sigma_3 < 1$ GPa. At a stress value within the range of $1$ GPa < $\sigma_3$ < $1.2$ GPa the unit-cell dimension variations with stress depart from the rate of change

![Fig. 6](online colour at: www.pss-b.com) Molecular mechanics simulation data: (a) unit-cell lengths $X_1$ and $X_3$ versus $\sigma_3$ – inserts show $x_1$-$x_2$ plane projections of unit-cell corresponding to α-cristobalite and ‘ordered’ β-cristobalite; (b) $\nu_{ij}$ versus $\sigma_3$. 

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Table 2  Experimental, calculated analytical model and force-field simulation Poisson’s ratios for transverse loading of α-cristobalite. Force-field simulation data are shown for the Burchart [14], BKS [26], Universal [27, 28] and CVFF [29] force-fields.

<table>
<thead>
<tr>
<th>model</th>
<th>$\nu_{12}$</th>
<th>$\nu_{13}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment [9]</td>
<td>+0.06</td>
<td>-0.10</td>
</tr>
<tr>
<td>DTM</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>RTM1</td>
<td>-1</td>
<td>-2.09</td>
</tr>
<tr>
<td>CTM1 ($\kappa = 5.18$) [8]</td>
<td>-1</td>
<td>-16.17</td>
</tr>
<tr>
<td>RTM2</td>
<td>+1</td>
<td>0</td>
</tr>
<tr>
<td>CTM2 ($\lambda = 35$)</td>
<td>+0.20</td>
<td>-0.40</td>
</tr>
<tr>
<td>CTM3 ($\lambda = 15.1, \kappa = 2.02$)</td>
<td>+0.06</td>
<td>-0.10</td>
</tr>
<tr>
<td>Burchart [3]</td>
<td>+0.20</td>
<td>+0.02</td>
</tr>
<tr>
<td>BKS [3]</td>
<td>+0.16</td>
<td>+0.07</td>
</tr>
<tr>
<td>Universal [3]</td>
<td>+0.11</td>
<td>+0.14</td>
</tr>
<tr>
<td>CVFF [3]</td>
<td>+0.09</td>
<td>-0.16</td>
</tr>
</tbody>
</table>

observed for $\sigma < 1$ GPa, indicating a phase transition has occurred. The inserts in Fig. 6a show the $x_1-x_2$ projections for the unit-cell and correspond to the α-cristobalite and ‘ordered’ β-cristobalite structures for the low tensile and high tensile stress regions, respectively. Figure 6b shows the predicted $\sigma_3$-dependent Poisson’s ratio behaviour from the molecular modeling simulations. The Poisson’s ratios show a clear change in magnitude from one phase to the other, and include a change in sign of $\nu_{12}$ from positive (α-cristobalite) to negative (‘ordered’ β-cristobalite).

3.2 Deformation mechanisms for transverse loading of α-cristobalite

Table 2 summarises the Poisson’s ratios calculated for transverse loading of α-cristobalite for the analytical models developed to date. Experimental values and values from previous force-field simulations are also included in Table 2 for comparison. The analytical model calculations employed the experimentally determined value of $\delta = 23.5^\circ$ for α-cristobalite [23] ($\phi = 0$ for α-cristobalite). The CTM1 values were calculated assuming a ‘strength’ parameter of $\kappa = 5.18$ from the parametric fit to the Poisson’s ratio for loading along $x_3$ ($\nu_{31}$), for which the CTM1 has been shown to be a valid model. A value of the strength parameter $\lambda = 35$ was found to give the best agreement of the CTM2 to the combined experimental $\nu_{12}$ and $\nu_{13}$ values. The CTM3 gives the exact values for both $\nu_{12}$ and $\nu_{13}$ when $\lambda = 15.1$ and $\kappa = 2.02$.

4 Discussion

The experimental unit-cell dimensions for α-cristobalite are $X_1 = 4.978$ Å and $X_3 = 6.948$ Å [24], which compare with the predicted undeformed values of $X_1 = 4.982$ Å and $X_3 = 6.658$ Å from the simulations reported here (Fig. 6a). The predicted value for $X_1$ is, therefore, in excellent agreement with experiment. The value of $X_3$ is underestimated in the simulations by 5%. The predicted values are similar to those from the pair potential calculations of Keskar and Chelikowsky [25] who reported predicted values of $X_1 = 4.96$ Å and $X_3 = 6.68$ Å.

Experimental unit-cell dimensions for ordered β-cristobalite have been reported by Peacor [30]: $X_1 = 5.07$ Å and $X_3 = 7.17$ Å, which compare with the predicted values of $X_1 = 4.84$ Å and $X_3 = 7.47$ Å from the simulations reported here (Fig. 6a). The predicted values are, therefore, accurate to ±5% of the experimental values, which is consistent with the level of agreement found in the simulations for the α-phase ($X_3$ dimension). However, the predicted values correspond to an applied stress of 1.2 GPa along the $X_3$.
direction, and so it is expected that the predicted $X$ value should be greater than the undeformed value. In fact, at an applied load of 1.2 GPa along $x_3$, the predicted Young’s modulus in the loading direction was calculated to be $E_3 = 112$ GPa. The molecular model simulations showed linear stress-strain behaviour for both the $\alpha$ and $\beta$ phases over the strain ranges considered here (a few % strain). Hence, the combination of stress and Young’s modulus for $\beta$-cristobalite at the predicted transition stress of 1.2 GPa yield a strain of ~1% with respect to undeformed $\beta$-cristobalite (assuming linear elastic behaviour as shown in the molecular model simulations). This implies an undeformed value of $X_3 = 7.39$ Å is predicted from the force-field simulations, which is in better agreement with the experimental value.

The Molecular Mechanics prediction of a $\sigma_3$-induced transition from $\alpha$-cristobalite to ‘ordered’ $\beta$-cristobalite with tensile load along $x_3$ is consistent with the prediction of a phase transformation from consideration of the analytical CTM1 model. Figure 7 shows the normalised strain energy function ($U^* = 2U/E_3$, where $U$ is the strain energy and $E_3$ is the Young’s modulus in the $x_3$ direction) plotted against tetrahedral tilt angle $\delta$ for the DTM, RTM1 and CTM1 analytical models (taken from Refs. [13, 31]). The CTM1 model predicts a second stable phase exists with a tilt angle in reasonable agreement with that for ‘idealised’ and ‘ordered’ $\beta$-cristobalite ($\delta = 0$).

A change in the sign of the Poisson’s ratio $\nu_{21}$ is predicted in the Molecular Mechanics simulations to accompany the $\sigma_3$-induced phase change (Fig. 6(b)). A change in the sign of Poisson’s ratio at the phase transition has also been predicted using the analytical CTM1 model for the cristobalite structure [21], and has been observed in other materials (e.g. the Poisson’s ratio of poly(N-isopropylacrylamide)/water gel has been observed to flip from a negative to a positive value at the volume phase transition [31]).

Previously, the analytical model of concurrent tetrahedral $\alpha$-axes rotation and dilation (CTM1) has been found to be sufficient to predict the Poisson’s ratio for loading of $\alpha$-cristobalite in the $x_3$ direction, and in so doing contains the essential features of the deformation mechanisms in this case. However, the CTM1 cannot predict the Poisson’s ratio sufficiently well for transverse loading of $\alpha$-cristobalite, indicating that the CTM1 does not adequately describe the deformation mechanisms for loading along $x_3$ or $x_5$. The data in Table 2 clearly show improved agreement in the transverse Poisson’s ratios is achieved by incorporating the tetrahedral $c$-axes rotation mechanism into the models. The RTM2 model (deformation due to tetrahedral $c$-axes rotation only) correctly predicts the sign of $\nu_{21}$ to be positive, whereas the previously developed analytical models consistently predict $\nu_{21} = -1$. Incorporating tetrahedral $c$-axes rotation with concurrent dilation of the tetrahedra (CTM2) leads to an improved fit for both $\nu_{21}$ and $\nu_{13}$ to be possible (correct sign and improved agreement in the magnitude of the Poisson’s ratio values). However, an exact fit for both $\nu_{21}$ and $\nu_{13}$ can be achieved by incorporating tetrahedral $\alpha$-axes rotation to act concurrently with both tetrahedral $c$-axes rotation and dilation (CTM3).

In comparison, whilst the previous Burchart and BKS force-field simulations indicate low values of $\nu_{21}$, they (and the Universal force-field) predict positive values for both $\nu_{21}$ and $\nu_{13}$ (Table 2). Only the
CVFF force-field correctly predicts both a positive sign for \( \nu_{12} \) and a negative sign for \( \nu_{13} \), being in closer agreement with experiment than the analytical CTM2 model, but not as close as the analytical CTM3 model.

5 Conclusions

Analytical and Molecular Mechanics models have been used to investigate the structure-property relationships of the naturally-occurring auxetic nanomaterial \( \alpha \)-cristobalite. The Molecular Mechanics models indicate the presence of a \( \sigma_3 \)-induced second phase corresponding to the ordered \( \beta \)-cristobalite geometry. The phase transition is predicted to be accompanied by a significant change in the magnitude of the on-axis Poisson’s ratios, including a change in sign of at least one of the on-axis Poisson’s ratios. The phase change and associated Poisson’s ratio variations are in broad agreement with the predictions from the CTM1 analytical model (concurrent tetrahedral dilation and \( a \)-axes rotation).

Based on previous Molecular Mechanics simulations showing a divergence of the intertetrahedral angles with applied stress along the \( x_3 \) direction, analytical models have been developed to incorporate cooperative tetrahedral rotation about the local \( c \)-axes. Parametric fits of the new and previously developed analytical models suggest that \( \alpha \)-cristobalite deforms by:

- 1 RUM (cooperative \( a \)-axis rotation) and tetrahedral dilation for uniaxial loading along the \( x_1 \) direction,
- 2 RUMs (cooperative \( a \)-axis and \( c \)-axis rotations) and tetrahedral dilation for uniaxial loading along the \( x_3 \) direction.

Acknowledgements

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