1 Supplementary methods

1.1 GASP

All simulations were carried out using the program GASP [1, 2, 3, 4], which models the rigid-unit motion of tetrahedral frameworks. The GASP algorithm models the structure simultaneously with a collection of atoms (Si, O) and a set of geometric templates with ideal tetrahedral angles and a center – vertex (Si–O) bond length appropriate to the system (1.61 Å for silica). The offset between an atom and a template vertex is decomposed into components representing stretching of the bond and bending of the tetrahedral angles, as illustrated in Supplementary figure 1, and harmonic springs are applied to constrain each of these components. In an iterative process of relaxation, the atoms and templates move together so as to minimise the distortion in the structure. The algorithm includes hard-sphere interactions between atoms, so as to forbid two atoms from approaching each other more closely than the sum of their radii. However no other long-range interaction, attractive or repulsive, was included, as the objective was to determine whether or not the atoms can be made to match the templates exactly; the bridging (Si–O–Si) angle was unconstrained.

Simulations at different densities were carried out by taking an initial set of fractional coordinates for the atoms (e.g. from a crystal structure), setting the cell parameter to produce a given density, then geometrically relaxing the system. We found that there was a sharp distinction between cases where the atoms could be made to match the templates exactly, and those where some distortion remained. We defined a perfect match using the very strict criteria that bond lengths should differ from the ideal by no more than 0.001 Å, and that the internal angles of the tetrahedron should vary by no more than 0.001°, which is close to the numerical limit of accuracy of the algorithm. A small random perturbation of about 0.01 Å was applied to the atomic positions before relaxation. The relaxed atomic coordinates therefore correspond to an instantaneous snapshot of the system rather than to the crystallographic average positions.

1.2 Free boundary conditions simulations

The only real cubic zeolite structure that did not display a window when simulated with *periodic* boundary conditions was the clathrasil **MTN**. This dodecasil consists of cages (*i.e.* it is a foam in that every point in space can be assigned to a single polyhedra or cage) and has multiple interlocking 5-rings. Simulations with periodic boundary conditions always displayed a small degree of tetrahedral distortion. Simulations of supercells of increasing size of 136, 1088, 3672 and 8704 polyhedra with periodic boundary conditions still displayed the distortion. We then simulated free boundary conditions by severing those bonds that crossed the boundaries of the simulation cell and placing the resulting truncated structure in a larger simulation box. The density of the truncated structure was controlled by fixing the coordinates of selected polyhedra at the corners. The density was calculated by systematically sampling points, using a Voronoi type construction, in the simulation cell, so as to obtain a density for the central bulk-like region while ignoring the surface region. This was tested against results for **FAU** where it was not necessary, and shown to be a reliable procedure as we obtained very similar results with either periodic or free boundary conditions.

These supercells were all perfect with free boundary conditions; simulations at different densities showed a window as found for the other real cubic zeolites. On inspection of the periodic and non-periodic relaxed structures, it was clear that in the non-periodic structures, each 5-ring relaxed with a different pattern of tetrahedral tilts, whereas the regularity introduced by periodic boundary conditions required each 5-ring to have the same pattern of tilts.

This implies that periodic simulations of this clathrasil using any method — not only our geometric approach — would tend to introduce an extra degree of strain in the structure.

This is in line with the recent observation by O'Keefe (private communication) that the crystallographically symmetric positions for the atoms in **MTN** are not consistent with perfectly tetrahedral SiO_4 geometry. Similar to this cubic framework, we found that several non-cubic structures were nearly perfectible with periodic boundary condition, but fully perfectible with free boundary conditions. Those were **MEI**, ***BEA**, **IST**, **MWW** and **DOH**.

We have also investigated models of silica glass generated by the WWW bond-swapping algorithm [5] and described as 'large well-relaxed [silica structures]', as a means to study very large unit cells. We used structures containing 1000 and 4062 tetrahedra, both of which gave similar results; those for the 1000-tetrahedron model are discussed here. The structure as provided contained a great deal of tetrahedral distortion, with bond lengths of 1.61 ± 0.04 Å and O–Si–O angles of $109.46 \pm 5.79°$. Given the method of generating these structures, by relaxation with a potential, this could represent intrinsic strain of the tetrahedra (*i.e.* the bonding in the structure is not compatible with geometrically perfect tetrahedra); or it could represent distortion of an otherwise ideal tetrahedral network by the long-range interaction terms in the potential. Geometric simulation with periodic boundary conditions reduced the degree of distortion but still left the tetrahedra imperfect (bond lengths of 1.61 ± 0.01 Å, bond angles of $109.47 \pm 1.92°$). Geometric simulation with free boundary conditions, however, as for the case of **MTN**, did indeed produce a perfect structure, albeit over an extremely narrow window. The narrowness of the window is understandable since the distribution of bridging angles covers a full range from near 180° at some parts of the solid (so that further extension creates tension in a bond) to around $120°$, so that further compression leads to a steric collision in some parts of the solid, while at other parts the framework is expected to be jammed. This occurs because all possible kinds of allowed local conformations are present at some location in the glass when the system is large enough, using a Lifshitz type argument [6].

2 Supplementary notes

2.1 Effective framework density

The effective framework density is defined as the number of tetrahedrally coordinated atoms (T-atoms) per 1000 $Å^3$. For non-zeolitic framework structures, values of at least 19 to 21 T/1000 $Å^3$ are generally obtained, while for zeolites with fully crosslinked frameworks the observed values range from about 10 for structures with the largest pore volume to around 20.6. The framework density is obviously related to the pore volume but does not reflect the size of the pore openings. For some more flexible zeolite structure types, the framework density values can vary appreciably.

A framework type is independent of chemical composition. Therefore, idealized framework data (cell parameters, coordinates of atoms at the center of the tetrahedra etc.) were obtained from a distance-least-squares refinement [7] in the given (highest possible) symmetry for the framework type and we call it an effective density. The refinement was carried out assuming a (sometimes hypothetical) SiO_2 composition and with the prescribed interatomic distance for Si–O = 1.61 Å. In each case, the coordinates were first optimized within an approximate unit cell, and then the unit cell was refined.

The space group, the cell dimensions and the atomic coordinates of a real material will depend upon its chemical composition, but they will be related to the crystallographic data listed for the framework type. If the symmetry is different, it will be a subgroup of this space group, and the unit cell parameters will be related by relatively simple geometric considerations.

2.2 Classification by Baur

Baur in 1992 [8] classified zeolites as *collapsible* if all the bridging angles co-rotate, or *non-collapsible* if some angles anti-rotate. By this criterion we would classify **FAU**, **LTA**, **TSC**, **KFI**, **PAU**, **LTN** and **-CLO** as non-collapsible. We note that the frameworks classified as ‘non-collapsible’ due to their antirotating angles do nonetheless collapse on compression, as shown by the example of **FAU**.

2.3 Hypothetical zeolites

We have looked at several hypothetical zeolite structures. Supplementary figure 2 shows one of the hypothetical zeolites 229_4_60312. This structure was generated by Treacy et al [9] as a hypothetical zeolite. To the eye, the structure looks acceptable though there are slight distortions of some of the tetrahedra. However, geometric simulation does not show any window in which the tetrahedra can be made perfect, with either periodic or free boundary conditions. Since the structure has no flexibility window and cannot support geometrically perfect tetrahedra, we would predict that it cannot be synthesised and would reject it as a candidate pure-silica zeolite structure.

3 Supplementary figures

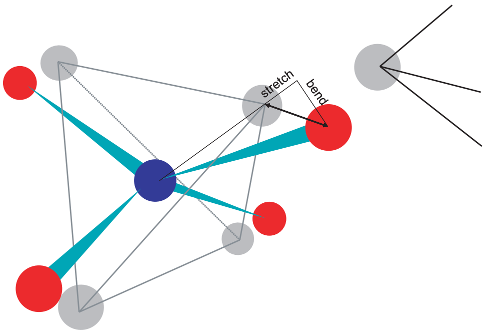

Figure Supplementary figure 1: GASP overlays a bonded group of atoms with a template representing the ideal local tetrahedral geometry. The template is fitted to the atoms by a least-squares procedure. The mismatch between an atom and its template vertex is decomposed into components of bond stretching and tetrahedral angle bending, which are constrained by harmonic springs. Over multiple iterations of fitting templates and atoms, the structure is brought to perfect tetrahedral geometry; if not, some residual distortion remains. Red atoms represent oxygens, blue – silicon. Templates are represented by gray lines. Gay circles represent positions of template vertices. Tetrahedra have ideal shape when actual atom positions match the atom positions of templates, i.e. red atoms overlay gray circles.

References

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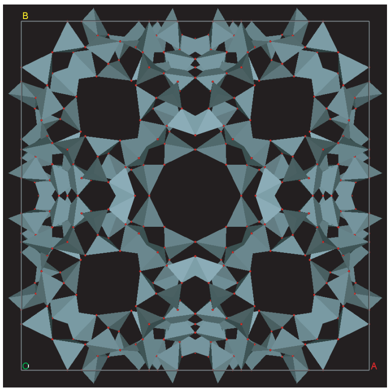

Figure Supplementary figure 2: Structure of 229_4_60312 hypothetical zeolite in tetrahedral view. This structure is from the hypothetical zeolite database at http://www.hypotheticalzeolites.net [9]

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