

Hyperbolic Surfaces in the Solid State and the Structure of ZSM-5 Zeolites

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In this paper we discuss the importance of periodic minimal surfaces to the processes of diffusion and confinement of interstitial charges within a charged lattice. It has been suggested that the hyperbolic geometry of aluminosilicate networks in zeolites can be understood within this context, since the aluminosilica species are confined onto or close to these surfaces, owing to the field set up by the templating ions. This model is applied to the ZSM-5 zeolite framework, where an orthorhombic periodic minimal surface of genus 9 per unit cell can be traced in the aluminosilicate network.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

The observation of hyperbolic (saddle-shaped) surfaces in the solid state by Sten Andersson (and, independently, Alan Mackay), has spawned much fundamental research into the application of these surfaces to the solid state. Andersson's original insight into a possible connection between minimal surfaces and crystalline structures came about when he saw an image of the three-horned "monkey saddle", in Ref. 1. (Minimal surfaces are the simplest hyperbolic surfaces. Their mean curvature is identically zero, so that they are equally concave and convex everywhere.)

Andersson and Fälth had proposed earlier a simple explanation of the large inorganic structure, zeolite N, which they suggested was an intergrowth of fragments of the smaller ZK5 and sodalite structures.² The hyperbolic form of the monkey saddle seemed to describe perfectly the local shape of the interface between these two sub-structures. The global geometry of this interface fits well the D-surface, which bisects space into two interpenetrating diamond lattices.^{3,4} This example remains a superb illustration of the importance of these surfaces in atomic crystals. Subsequently, it was found that many other structures can be described by curved nets, which are folded onto, or close to, periodic minimal surfaces.^{5,6}

Periodic minimal surfaces and the electronic field in atomic crystals

In what sense can (or should) an atomic structure be understood in terms of a hyperbolic surface? After all, we must agree that a crystal is no more than a periodically varying electric field, described by a field vector at all points in three-dimensional space. Along with Democritus, we may

perhaps insist that the point singularities (zero-dimensional) of this field (the atoms) are paramount. However, most chemists would feel more comfortable with the addition of the concept of chemical bonds, which define the extremal trajectories (one-dimensional) within the electric field, linking atoms. We can also extract a (two-dimensional) critical surface from the electric field, and invoke a surface description of crystalline form. The hyperbolic geometry of this surface arises naturally, since we are describing extended framework structures, without bound in any direction. The origins of the apparent vanishing mean curvature of the atomic net, which is due to the underlying minimal surface, are less easy to understand.

Calculations of the equipotential surfaces within charged lattices by von Schnering and Nesper⁶ have revealed the presence of similar hyperbolic surfaces to those seen in zeolites. Just as the mirror plane lying between a single cation and an anion is the zero equipotential surface for the charged pair, surfaces similar to periodic minimal surfaces define the location of a "zero" of potential within interpenetrating cation and anion arrays, the surface lying halfway between cation–anion pairs.⁷ It can be demonstrated that if the equipotential surface for a certain lattice (consisting of cations and anions) is a minimal surface, that surface defines the collection of open orbits for mobile ions diffusing within a geometrically identical lattice built up of cations (or anions) alone.⁸ Thus, minimal surfaces arise as tangen-

⁷ Although the average value of the mean curvature of these equipotential surfaces vanishes over a unit cell of the lattice, the magnitude of the mean curvature fluctuates over the surface. The coordinates of the equipotential surface can be expressed exactly in terms of products of transcendental Jacobi θ -functions.⁷

tial field surfaces within charged lattices. Presumably, if the equipotential surface approximates a periodic minimal surface, as found in charged lattices interacting via the Coulomb potential, the tangential field surface for the related charge distribution is also similar to a periodic minimal surface.

This link between hyperbolic surfaces and crystalline arrays explains the observation that mobile ions in solid electrolytes seem to move along these surfaces.⁹ For example, the classical solid electrolyte, α -AgI, consists of a mobile cation distribution, with the anions frozen in a body-centred cubic lattice. In this material, the silver ions are expected to diffuse along tangential field surfaces created by the b.c.c. array of iodine ions, which include the P- and D-periodic minimal surfaces. Another solid electrolyte, β -PbF₂, exhibits high conductivity owing to the mobility of the fluorine ions within the f.c.c. lead matrix. Here, the T-surface describes the trajectories of the conducting species well.^{6,8} It is tempting to suggest that these surfaces also describe the locations of free electrons within metals, where the cation lattice determines the geometry of the surface.

Many open questions remain to be answered in this area. For example, is there a unique equipotential surface for a given value of the potential? After all, the magnitude of the potential is ill-defined in an ideal lattice. Further, the convergence of the infinite series describing the (Coulomb) potential within the lattice is assured only for rapidly decaying charge distributions about each site, so that the solution may depend on the order of summation of the series.^{7,10} The implications of such a multiplicity are wide. Do multiple solutions of distinct genus (a quantised topological index) occur for this array? Unfortunately, standard calculation techniques (such as the Ewald procedure) necessarily avoid this possible degeneracy of equipotentials, so that answers to these questions are lacking.

Hyperbolic surfaces in ZSM-5 zeolites

Zeolites are routinely synthesised in the laboratory by dissolving aluminosilicate species in an aqueous solution of cationic "templating ions", such as tetra-alkylammonium ions (plus, it seems, sodium).¹¹ These ions have generally been regarded as providing large sites around which the proto-aluminosilicate species can crystallise, resulting in a zeolite "cage" which encapsulates these ions. The cages are linked by tunnels, forming the three-dimensional microporous crystalline array.

These ions create an electric field within the solution, which is sensed by the silicate species. If it is assumed that the templating ions remain locally ordered in solution, the aluminosilicate net is expected to be (approximately) confined to periodic minimal surfaces, since these are the tangential field surfaces set up by the templating ions.¹² In this model of zeolite formation and resulting structure, the distinction between tunnels and cages is artificial, since the network can be viewed as a single-sheeted hyperbolic layer.

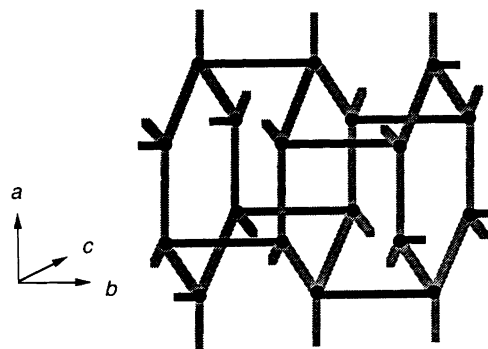


Fig. 1. Simplified topological view of the narrower tunnel network surrounded by four-, five-, and six-membered rings in the ZSM-5 structure. The hexagonal rings are normal to the *b*-axis, and are skew in the actual structure. This labyrinth is topologically equivalent to the wurtzite structure.

An important member of the zeolite family, ZSM-5, can be synthesised in this fashion, using tetrapropyl ammonium salts as the templating species. This zeolite can be made with a variety of Si:Al ratios, ranging from the pure silicon form, silicalite, to the ZSM-5 pentasil containing up to eight Al atoms per unit cell, which comprises 96 T atoms.¹³

The atomic structure of silicalite is complex, and dominated by an orthorhombic network of the ten-membered ring channels.¹⁴ The most natural surface description of this structure is expected to invoke a surface containing tunnels which match the interconnected straight tunnels parallel to the *b*-axis, spanned by ten-membered rings. Since these channels are linked by staggered ten-membered rings (normal to the *b*-axis), they must lie on the same side of the surface (since they are not shielded from their neighbours by a portion of the silicate network).

Close examination of a vertex model of the silicalite network reveals the presence of narrow convoluted tunnels which separate these large ten-membered ring tunnels. The former tunnels are made up of four-, five-, and six-membered rings joined four-by-four at their nodes, resulting in an array which is topologically identical to the wurtzite structure, albeit orthorhombically distorted. This network consists of distorted skew hexagonal rings (lying roughly normal to the [010] direction of the lattice, defined by the large straight channels), with every alternate hexagonal vertex joined via a short vertical tunnel to the next layer above/below along the *b*-axis (Fig. 1). The nodes of this network are defined by small polyhedra, consisting of six skew pentagonal faces. A single embedded hyperbolic interface can then be traced out within the T-atom network, with all T-O-T bonds lying on the interface, with the exception of four bonds in six-membered rings within each orthorhombic unit cell. (These six-membered rings are in the middle of a set of three edge-shared six-membered rings, aligned parallel to the *a*-axis.) If a single atom is removed from these rings (O-23 in the numbering system of Olson *et al.*¹⁵), extra tunnels of high elliptical eccentricity

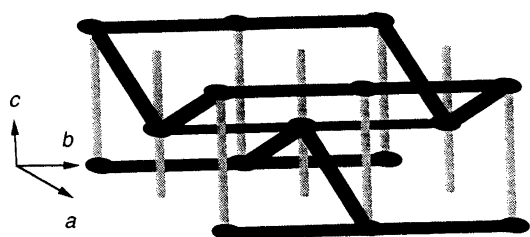


Fig. 2. A schematic picture of the topology of the larger tunnel labyrinth within the ZSM-5 network. The lighter links denote the flattened tunnels, while the darker tunnels correspond to those enclosed by ten-membered rings. The a , b and c -axes of the network are also shown.

are generated between ten-membered rings, so that every node of this network contains two (10-membered ring) tunnels running along the b -axis, two (10-membered ring) tunnels in $\{101\}$ directions and two smaller tunnels, along the $\langle 001 \rangle$ direction (Fig. 2). The smaller tunnels are threaded by severely flattened 10-membered rings.

The sixfold coordinated tunnel structure is topologically equivalent to the smaller forefold coordinated tunnel labyrinth, since the two labyrinths are "maximally interpenetrating" in the sense of Wells:¹⁶ every loop of one network encloses a link of the other. This means that one labyrinth can be continuously inflated, via the partitioning surface, finally to enclose the other labyrinth. Thus, it is reasonable to suppose that the dividing interface may adopt vanishing mean curvature, forming a triply periodic minimal surface.

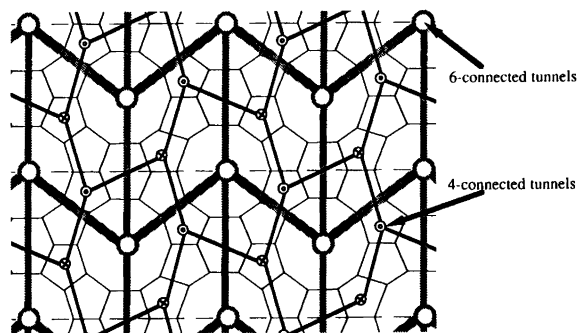


Fig. 3. $\langle 010 \rangle$ projection of the T-atom framework in ZSM-5 zeolites. The two labyrinths enclosed by the partitioning hyperbolic surface (on which the framework sits) are fourfold-connected (similar to the D-surface) and sixfold-connected (P-like). The open circles in the P-like labyrinth indicate the straight tunnels down the b -axis. The thick and thin zig-zag lines denote the larger (ten-membered ring) tunnels and the smaller flattened tunnels. The D-like network contains short channels running along the b -axis, with every second node in the skew, distorted hexagonal rings linked to the parallel layer above/below. Two parallel layers of both labyrinths occur per unit cell, and the up/down and thick/thin nature of the labyrinths are reversed in each successive layer.

The topological description of this partitioning surface is remarkably simple. On one side of the surface, the tunnel network can be viewed as a distortion of the simple cubic array tunnels of the P-surface, such that one pair of straight tunnels adopts a zig-zag conformation. There are two sets of staggered tunnels: $\langle 101 \rangle$, $\langle \bar{1}01 \rangle$ and $\langle 10\bar{1} \rangle$, $\langle \bar{1}0\bar{1} \rangle$ related by the twofold axes of the space group, both lying in $[001]$ planes, separated by $b/2$. On the other side of the atomic net, the tunnel network is an orthorhombic distortion of the wurtzite network. The distorted P-surface labyrinth consists of six tunnels meeting at a common node (Fig. 2), and the wurtzite labyrinth consists of four tunnels meeting at a common vertex (Fig. 3). The presence of two distinct tunnel diameters in the P-like labyrinth results in a doubling of the unit cell dimensions along the $\langle 100 \rangle$ and $\langle 010 \rangle$ directions relative to the P-surface. Thus, a single unit cell of this surface (which corresponds to a unit cell of the silicalite framework) contains four P-like nodes (as well as eight wurtzite nodes). The genus per unit cell of this hyperbolic surface is 9 (Euler characteristic four times that of the P-surface).

This surface description of the ZSM-5 framework naturally accounts for all of the 96 aluminium/silicon sites (the T atoms) and 188 of the 192 O atoms within a unit cell of the ZSM-5 family of pentasils. Thus the surface provides a natural manifold for a hypothetical network containing 88 fourfold-coordinated T-atoms, and eight threefold-coordinated T-atom sites, of composition $T_{96}O_{188}$. If these eight threefold-coordinated sites are occupied by aluminium atoms, we have a natural explanation for the observed maximum of eight aluminiums per unit cell.

This assumes that the aluminium atoms are all threefold-coordinated, with an inherent barrier to the presence of the more usual fourfold-coordinated sites within the aluminosilicate framework. Note that the presence of threefold-coordinated sites in the silicalite net is expected from the surface description. (The most symmetric embedding of the sodalite and faujasite frameworks within the P- or D-surfaces results in all sites being fourfold-coordinated.) Within this picture, some features of the aluminium/silicon exchange behaviour of ZSM-5 can be explained. Experiments indicate that freshly prepared ZSM-5 contains a fraction of aluminium (up to eight atoms per unit cell).¹³ Since the freshly prepared zeolite is a product of the electric templating effect of the large cations, which means that the framework is confined to the surface set up by the electric field of these ions, some (threefold-coordinated) aluminium must be present. However, these sites, which are neighbours to the large straight channels, are very reactive, and liable to be exchanged for silicon (since the pairs of adjacent aluminiums cannot be simply bridged by an oxygen ion to satisfy their preferred coordination without violating Loewenstein's rule). Hence the dealumination behaviour of ZSM-5 upon steam treatment, and its ability to form a pure silicate framework.

Conclusion

It appears that ZSM-5 can be simply described in terms of a hyperbolic surface, consistent with the tangential field surface created by templating ions during zeolite crystallisation. Within this picture, the framework geometry of ZSM-5 is intermediate to those of the simpler zeolites, sodalite and faujasite, containing both four- and six-connected tunnel systems. The sodalite T-atom framework can be described by the P-surface (six-connected), while that of faujasite decorates the D-surface (four-connected).

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