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The importance of odd circuits in covalent glasses

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Abstract
Amorphous silicon and covalent glass are represented structurally and physically as a random, regular graph of degree 4. Odd circuits form extended structures, called odd loops or R-loops, the topological defects surviving the absence of translation and rotation symmetries in the material. Odd loops are responsible for the topological entropy frozen into the disordered structure, and for the tunneling modes, the generic low-energy excitations of non-crystalline materials. They are identified and characterized from a graph theoretical viewpoint.

1. Introduction

This paper illustrates the essential contribution of odd circuits (circuits with odd numbers of edges) to the physics of glass (entropy and elementary excitations) and to the geometry and combinatorics of random, regular graphs of degree 4. In fact, odd circuits do not occur individually, but are traversed by continuous lines that close as loop or terminates at the surface of the material. These odd lines or R-lines (Rivier 1979) are topological defects in covalent glasses. They are configurations to be counted when evaluating the entropy. Moreover, each has two distinct ground states, corresponding to the two classes of odd permutations of the edges incident on a vertex, when it is carried around an odd circuit. The R-line is a source of frustration: the structure of the graph around it cannot be labeled (edge-colored) once and for all, because it undergoes an odd permutation every time around. Two turns around the R-line restores the original structure. In this respect, the R-line resembles a 2π-disclination in a random elastic continuum. Rotation by 2π entangles the structure, but in a unique way independent of the axis of rotation. Rotation by 4π is the identity.

A covalent glass (e.g. amorphous silicon, or silicate glass SiO_2) can be represented as a regular graph of degree 4, called continuous random network by physicists. Each vertex of the graph represents a silicon atom. It has $z = 4$ incident edges, a perfect short-range order imposed by chemistry (in the absence of dangling bonds), and each edge represents one (in elementary glass like amorphous Si) or two covalent bonds, separated by an oxygen atom (in silicate glass). The oxygen atom only decorates the edge and plays no topological part. We count edges and call a circuit or ring odd if it has an odd number of edges. The identical vertices and identical edges of the graph are physical objects. Thus, incidence and adjacency matrices are well defined, and local elementary transformations, such as an edge- or bond switch (eq.1 below), can be performed to disorder the graph. The only connection between two vertices is a covalent bond (whether decorated by an oxygen atom or not), which has some rigidity: it costs some, decreasing, energy to stretch, bend or twist it. This enables us to calculate the ground state (of lowest energy) of the graph, and its elementary excitations. We can also relax its elastic energy after performing a bond switch. In real glasses, there are a few dangling (not connecting) bonds. They will be ignored here. In amorphous silicon, the covalent bond fluctuates in length by only a few percent from the nearest neighbor distance of 0.235 nm in the diamond cubic structure of crystalline Si, and the angular deviation from perfect tetrahedral bonding of $\cos^{-1}(-1/3) = 109.5°$ is of the order of 10%.

The graph is defined unambiguously by the sets of vertices, of edges, and by an incidence relation between vertices and edges (Biggs, 1974). These are also physical elements. However, odd circuits turn out to be important physically, because they constitute topological, line defects in the graph.

2. Topological defects in glass

Real solids deform plastically, permanently, and the necessary yield stress is much weaker than an estimate given for one row of atoms slipping over another. Gliding extended line defects, the dislocations, account for the discrepancy. They also explain other mechanical properties of materials, such as work-hardening (c.f. Mott 1958, Friedel 1964). Dislocations are topological defects, resulting from upsetting the translation symmetry locally. Other lines, the disclinations, are sources of rotation, e.g. in liquid crystals.

In amorphous materials such as glass, where there is no lattice to *dis*locate, only one topological defect survives the absence of any translation or rotation symmetry, the R-line. One can pass a thread through the odd circuits of a graph, such that each odd ring is threaded through only once. The thread returns to the starting point to complete a loop or terminates at the surface of the material (and repeats periodically in a network with periodic boundary conditions). The process is repeated until each odd ring has been threaded once and only once. This can be done algorithmically (Wooten, 2002). Figure 1 shows the R-lines (black ribbons) threading the odd rings for a 216-atom random network model of amorphous Si subject to periodic boundary conditions (Wooten et al., 1985). The model was constructed by randomizing and relaxing a cell of 6^3 silicon atoms that was initially in the diamond structure, with only six-fold (irreducible) rings. Randomizing was done through edge-switch between two neighboring vertices, i.e. a local change in the incidence or in the adjacency matrix of the graph: here, the two neighboring vertices are 4 and 5, and edges 34 and 65 are switched to 35 and 64 (eq. (1)),

$$\begin{pmatrix} 0&0&0&1&0&0&0&0\\ 0&0&0&1&0&0&0&0\\ 0&0&0&1&0&0&0&0\\ 1&1&1&0&1&0&0&0\\ 0&0&0&1&0&1&1&1\\ 0&0&0&0&1&0&0&0\\ 0&0&0&0&1&0&0&0\\ 0&0&0&0&1&0&0&0 \end{pmatrix} \rightarrow \begin{pmatrix} 0&0&0&1&0&0&0&0\\ 0&0&0&1&0&0&0&0\\ 0&0&0&0&1&0&0&0\\ 1&1&0&0&1&1&0&0\\ 0&0&1&1&0&0&1&1\\ 0&0&0&1&0&0&0&0\\ 0&0&0&0&1&0&0&0\\ 0&0&0&0&1&0&0&0 \end{pmatrix} \tag{1}$$

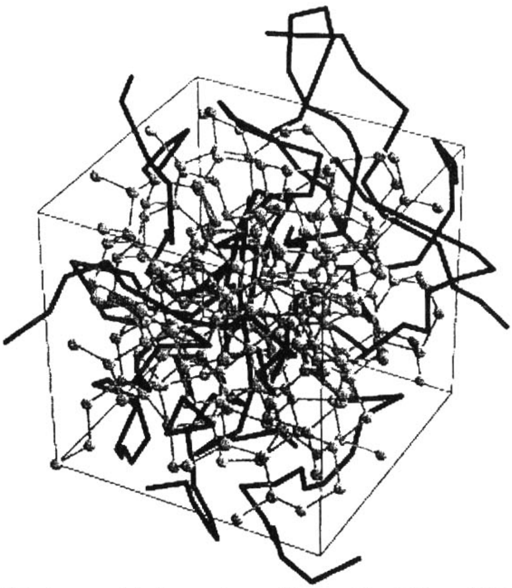

Fig. 1. A 216-atom model of amorphous silicon, with odd lines (R-lines: thick).
From Wooten (2002)

This process introduces fivefold and sevenfold rings in the structure, then larger ones and some fourfold rings, unless explicitly excluded. The model was subsequently relaxed by simulated annealing.

Theorem (Rivier 1979): Odd lines close as loops, or terminate at the surface of the material (or repeat periodically in a network with periodic boundary conditions), without passing through any irreducible even rings. Proof: Consider an arbitrary, closed surface S, bounded by circuits (rings) in the network. There is an even number of odd rings on S, thereby providing an exit for any odd line (R-line) entering S. Associate (−1) to any edge on S. Define a ring index as the product of its edges. An even/odd ring has index +1/−1. The product of all ring indexes on S equals +1, simply because each edge is counted twice, as it borders two rings on S. Thus, odd rings never occur in isolation, but form loops.

3. Elasticity of regular, z = 4, random networks

Odd lines have important physical effects. They count as configurations in the evaluation of the entropy; each loop is the seat of one tunneling mode, or two-level system, the very simple elementary excitations of glasses and amorphous materials; their motion is blocked at the glass transition (cf. Rivier 1987).

We now describe the classical elasticity of continuous random networks (Rivier 1990, 1993). The elastic energy is carried by the edges of the graph, the chemical bonds connecting two Si atoms. This potential energy consists of two terms, a strong, bond stretching V_1 and a weaker, bond-bending contribution V_2. The bond-twisting energy is negligible. Set $V_2 = 0$ as a first approximation. The normal modes are a band of N phonons flanked by two sets of N degenerate modes (Alben et al. 1975, Sen and Thorpe 1977). One set has zero frequency and energy, for any value of V_1. These N normal modes involve unstretched edges and constitute the ground state and lowest energy excitations of the network. The network is wobbly in the absence of bond-bending forces.

Let us now stiffen the network by bond-bending forces V_2 0, and evaluate the energy of a ring configuration. The energy is measured by comparing the orientation of two neighboring atoms i and i α connected by a bond α, through a congruent transformation of the atom with its four incident bonds, a local frame (tetrapod), from its orientation at i to that at i α. The connecting bond imposes a mirror reflection fixing its midpoint. Thus, the congruent transformation is a rotation-reflection (the other three non-shared bonds may rotate).

The tetrapod must be returned to its original orientation (or an equivalent one) after being carried around the ring. The configuration of an n-fold ring is the product of n rotation-reflections, which is a covering transformation of the tetrapod, namely a permutation of the labels (colors) of its four bonds. If the ring is even, the permutation (a product of n reflections) is even for $z = 4$ (given that a rotation about the shared bond, a cyclic permutation of the $z-1 = 3$ others, has parity $(-1)^z$). If the ring is odd, the permutation is odd.

In fact, it is not the permutation that labels the configuration, but only its conjugacy class. (If one goes around two different rings in succession, starting from a common vertex, the resulting permutation depends normally on the order of the trips, but not the physical configuration). Permutations belonging to the same class are physically identical. The ground state of even rings clearly belongs to the identity class of the permutation group S_4. It is non-degenerate, and a graph containing only even rings can be labeled consistently (coloring all its edges with four colors). Even rings can be edge-colored without permuting the labels. The configurations of odd rings are labeled by the two classes of odd permutations of S_4 (containing six elements each). Odd rings have two distinct lowest energy configurations (characterized by one permutation in the class, selected by labeling a spanning *tree* of the graph; odd *rings* cannot be edge-colored). One odd ring is the sole representative of an entire R-line, because the other odd rings of the line are linked to the first by even rings, consistently labeled, and their bonds are permuted in concert.

The physical attributes of the random network are $z = 4$, edges shared by two neighbor atoms, and the impossibility of edge-coloring an odd circuit. Change of permutation class leaves invariant the physical properties of the network, a gauge transformation. Labeling is just a metaphor for bonds shared between tetrapods. It is not the actual labeling which matters physically, since bonds are identical, but whether consistent coloring is possible and in how many essentially distinct ways, i.e. no and two for every R-line. These are the two-level systems, characteristic excitations of amorphous materials. Because a change of permutation is not a physically observable transformation, the gauge-invariant, physical configuration is a tunneling mode, a linear combination of the two configurations determined by the permutation classes, per R-line. Tunneling modes have been identified in the 1970's as the generic elementary excitations in glasses (see Hunklinger and Raychaudhari 1986, Phillips 1981).

4. Irreducible circuits or rings

We have seen that odd rings are important physically. We would like to find them, to draw algorithmically the network of odd lines (R-lines), and use them to calculate the topological entropy of disorder. Wooten (2002) has developed an algorithm for these purposes. It is based on partitioning the continuous random network into cells bounded by irreducible rings. One such cell is represented in Fig. 2. It is bounded by four odd rings, one 7-fold and three 5-fold, and by one irreducible 6-fold ring, the "basis" of the cell. The "meridian" of the cell, a 6-fold ring, is reducible. It is reduced into two 5-fold rings by the shortcut 167-187-173. The cell gathers two R-lines, and constitutes a vertex of the network of odd lines represented in Fig. 1. If the meridian 6-ring had been irreducible, it would have split the cell into two, and constituted an impenetrable wall for the odd lines.

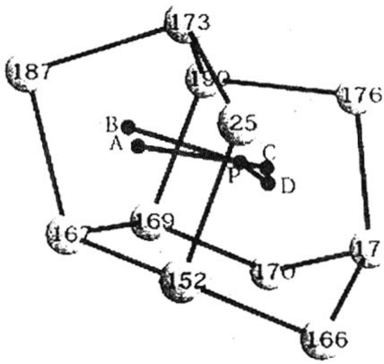

Fig. 2. A cell belonging to the model of Fig. 1, bounded by four odd rings: A,B,C,D, and by one even ring. The 6-fold meridian circuit is reducible. From Wooten (2002).

This is a genuine partition of space into cells. Any general point in space lies inside one cell bounded by irreducible rings. The difficulty lies in the facts that irreducible rings are not planar, and that two edges incident on one vertex usually define more than one, overlapping irreducible rings. An example of overlapping rings is given in Fig. 3. (By contrast, froths are partitions of space into cells that are convex polyhedra. All irreducible rings (faces) are planar, determined uniquely by two edges incident on a vertex. Generic froths are also regular graphs of minimal degree z = 4, but with the regularity imposed by randomness, rather than by chemistry. Reducibility is just a one-edge long shortcut across the ring.)

<u>Definition</u>:

1. A ring is <u>irreducible</u> if there is no shorter path between any two vertices on the ring than a path on the ring itself. (Ring and circuit are synonymous).

(The naive picture of a reducing shortcut holds: Consider the three n-, m- and p-fold rings of Fig. 4 (called p-ring hereafter). They share segments i, j, and k, with $n = i + j$, $m = i + k$ and $p = j + k$. If the path k is a shortcut for the n-ring ($k < i$ and j), then $n > m$ and p. The n-ring is reducible. The two rings, m- and p- are irreducible in this situation. Moreover, since $n + m + p = 2(i + j + k)$, either all three rings are even, or two are odd.)

2. If the new path k has the same length as one path, j, on the n-ring, then the two paths join to form a $2k$ = p-ring, and the rings n and m <u>overlap</u> ($n = m$). If $n = m < p = 2k$, the two overlapping n- and m-rings are irreducible. If $n = m \quad p = 2k$, and the p-ring is reducible by another path, all three rings are reducible. (This corresponds to a reducible circuit enclosing

smaller rings, like the equatorial 10-ring of a dodecahedron.) But if the $2k = p$-ring is irreducible, then all three rings are irreducible. One can lift the apparent ambiguities associated with irreducible, overlapping rings, by introducing a pseudo-bond, thereby defining 3 pseudo-rings. In the example of Fig. 3, the two overlapping 7-rings and the 6-ring are resolved into one 5-fold pseudo-ring and two 4-fold pseudo-rings by one pseudo-bond (dashed line)

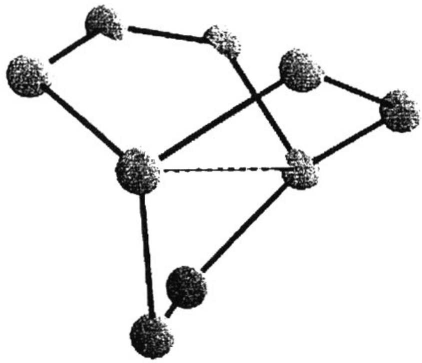

Fig. 3. Two overlapping 7-fold rings and a 6-fold ring, all irreducible, bounding three cells. A pseudo-bond (dashed line) resolves the boundaries of the three cells and locates the R-line by creating a pseudo 5-fold ring and two pseudo 4-fold ring. From Wooten (2002).

An irreducible even ring acts as a barrier for the R-lines. An odd ring forces an R-line through, whether it is reducible or not. If it is reducible, the R-line goes through the irreducible odd ring that shortens it. If the two overlapping rings are odd, the common pseudo-ring is odd, and it forces the R-line through. If the two overlapping rings are even, the three pseudo-rings are even: a pseudo-bond cannot be introduced to force a small odd loop through even, irreducible rings. Reducible circuits are irrelevant to the partition of the graph into cells, and to the R-lines.

In Fig. 4, an n-ring is split into two, p/m, by a new path with k edges. The split is physically possible if m and p $k+1$, i.e. i and j   1. Thus, sup $\{3, k + 1\}$ m $\lfloor n/2 \rfloor + k$, m $p = n + 2k - m$. The n-ring is reducible if $n > m$ and p. Larger circuits are more likely to be reducible. Indeed, in the model of Fig. 1, there are no even irreducible rings for n   8, and therefore no concealed barriers for odd lines. A $k = 1$ path would reduce any ring (except $n = 3$). This is the case in froths. 3-rings are irreducible for any value of k. They never occur in covalent glasses.

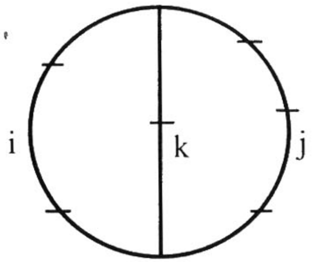

Fig. 4. An n-fold ring, split into two rings by a path with k edges ($n = i + j$). If $k < i$ and j, the n-ring is reducible, and the new rings are irreducible.

After identifying all irreducible rings, the algorithm builds the cells from corners (of three irreducible rings that share a common vertex, and each pair sharing a common edge), then pairs of corners with two rings in common, etc. (Wooten 2002). Segments of R-lines thread through irreducible odd rings, connecting adjoining cells. A cell bounded by four or more odd rings is a vertex in the network of R-lines (the network of thick lines in Fig.1, called R–network for short (Wooten 2002)). The R-network in Fig. 1 connects the centroids of 141 cells. For clarity, the loops have been separated at vertices. Of these 141 cells, 93 are bounded by two odd rings, 43 are bounded by four odd rings (vertices of degree 4 in the R-network), and 5 cells are bounded by six odd rings (vertices of degree 6).

5. Topological entropy

The topological entropy, remaining frozen in the glass at $T = 0$, is that of the R-network of odd loops. It has two contributions, one, combinatorial, associated with the vertices, and the configuration entropy, associated with the tortuous edges of the R-network. A good estimate (an upper bound) of the topological entropy can be obtained by assuming that each irreducible ring of the graph can be odd or even, independently of other rings, without restriction apart from the continuity of R-lines (Rivier and Duffy 1983).

The maximum number of equivalent configuration $\Omega = \Omega_{comb}. \Omega_{conf}$ of an arbitrary number of odd loops in any position, shape or length, is simply two (odd or even) per irreducible ring of the network, with one ring per cell as parity control to ensure continuity and provide an exit for an R-line entering that cell. The network has N_0 vertices (number of Si atoms), N_1 edges, $F = N_2$ irreducible rings, and $C = N_3$ cells (bounded by irreducible rings). There are thus $\Omega = 2^{F-C}$ configurations in the network. Euler's relation for a graph in three dimensions on a torus T_3 (three-dimensional solid with periodic boundary conditions) is $- N_3 + N_2 - N_1 + N_0 = 0 = \chi(T_d)$. $\chi(T_d) = 0$ is the Euler-Poincaré characteristic of a torus in any dimension d. The maximum topological entropy is therefore,

$$S/k = \ln \Omega = (N_2 - N_3) \ln 2 = N_0 (z/2 - 1) \ln 2 = N_0 \ln 2, \tag{2}$$

since $z = 4$ and $z\,N_0 = 2\,N_1$ (an edge is bounded by two vertices, on which z edges are incident), where k is the Boltzmann constant (Rivier and Duffy 1983). For $N_0 = 216$ atoms in the model, $S/k = 149.7$.

Euler's relation is valid for any graph, regular or not, and whether there are dangling edges and faces or not, as long as cells are defined as bounded by irreducible rings. (Euler's relation is usually given on a d-sphere S_d, as

$$\sum_{i=0}^{d}(-1)^i N_i = 1+(-1)^d = \chi(S_d).$$

A finite graph in Euclidean space E_d can be embedded on S_d by considering the whole exterior region as one further d-cell, and removing it from both sides of Euler's relation for S_d. The Euler-Poincaré characteristic of E_d is then $\chi(E_d) = \chi(S_d) - (-1)^d = 1$ for all d. The torus T_d is a topological hypercube E_d with its opposite faces identified, so that half of the boundary subgraph of E_d, a graph in E_{d-1}, is removed from the left-hand side of Euler's relation. On the right-hand side, the corresponding characteristics must be subtracted. One obtains $\chi(T_d) = \chi(E_d) - \chi(E_{d-1}) = 0$ for all d 1. This result can be obtained by combinatorics, and verified for d = 1, 2 and 3. In d = 2, this is the original Euler relation for polyhedra. In d = 1, compare trees (vertices) on one side of a road (E_1) or of a lake ($S_1 = T_1$).)

Let us now compute the combinatorial topological entropy of the model of Fig. 1, $S_{comb}/k = \ln \Omega_{comb}$, where Ω_{comb} is the number of distinguishable configurations of the R-lines inside the cells, i.e. of the vertices of the R-network. For one cell bounded by 2n odd rings, there are $\Omega_{2n} = 2n!/(n!2^n) = (2n-1)!!$ configurations for the n R-lines, not oriented. Cells bounded by 2, 4 and 6 odd rings have 1, 3 and 15 configurations, respectively, for the R-lines. In the model, there are $V_6 = 5$ cells with six odd rings, $V_4 = 43$ with four odd rings and $V_2 = 93$ with two odd rings. Thus, $\Omega_{comb} = \prod_{cell}\Omega_{2n} = (15)^5(3)^{43}(1)^{93}$ and $S_{comb}/k = \ln \Omega_{comb} = 60.8$ for 216 atoms.

The configuration entropy S_{config} is associated with the edges of the R-network. One expects S_{config} to be roughly equal to S_{comb}, for a semi-dilute R-network of loops, where one does not know whether the nearest (non-contiguous) segment belongs to the same loop or to another. The number L of edges segments in the R-network is given by $2L = 2V_2 + 4V_4 + 6V_6$, that is $L = 194$, which is the total length of the R-lines in units of an average cell size. But there are $E_{top} = 101$ topological edges in the R-network (edges linking the vertices in the R-network), given by $2E_{top} = 4V_4 + 6V_6$. There are, on average, two edge segments for each topological edge, which can be straight or bent. Notably, it passes over or under a straight line with equal probability $p = 1/2$, and the complexity or entropy of each topological edge is given by the Gibbs-Shannon expression $-\;\; p \ln p = \ln 2$ (Dupain et al., 1986). The 101 topological edges give the configuration entropy of the R-network, $S_{config}/k = 101 \ln 2 = 70.0$ for 216 atoms. It is indeed roughly equal to S_{comb}/k. The total topological entropy computed for the model is $S_{config}/k + S_{comb}/k = 130.8$ for 216 atoms. This is 87 % of the upper limit $216 \ln 2 = 149.7$ given by eq. (2), which shows that the model has been well randomized and relaxed.

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