

Class 12: Liquid metals, intermetallics, metallic glasses and quasicrystals

A great deal of insight into the structures of liquids, glasses and crystals, and phase transitions between them has been obtained by studies on colloidal (typical surface-modified polystyrene sphere) systems. For example, the critical density for crystallization of hard spheres is known to be 0.494 and between 0.494 and 0.545, liquid and crystal phases are stable. Additionally, hard spheres are known to crystallize because of *entropic* reasons. Crystals (*fcc*) have the best packing meaning that each hard sphere has the most room to rattle around in.

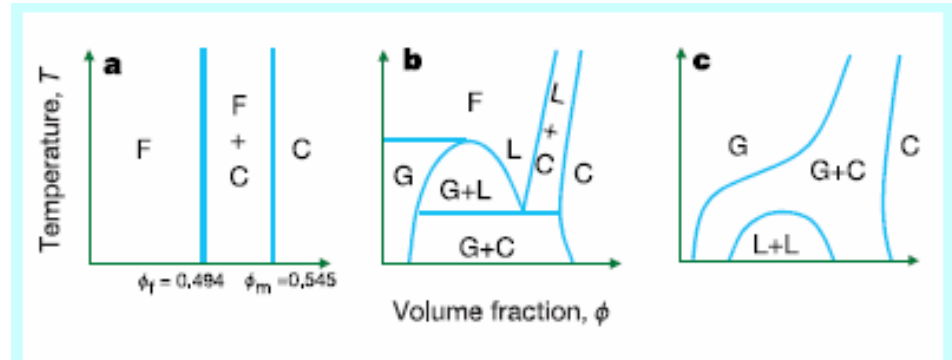


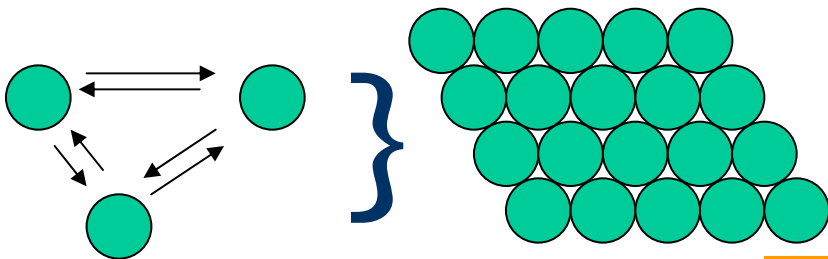
Figure 1 A wide range of phase diagrams occurs naturally. **a**, For a purely hard-sphere system the phase diagram shows only fluid (F) and crystal (C) phases. **b**, Atomic systems are often modelled by hard spheres with long-range attractions. This leads to equilibrium between gas (G), liquid (L) and crystal phases. **c**, In cases where the attraction is short-range, as in protein systems (important in physiology), equilibrium between gas and crystal is found, but the liquid–liquid transition becomes metastable.

From: Anderson and Lekkerkerker, *Nature* **416** (2002) 811 (see for a mini-review).

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If the density of the hard spheres is increased, whether a crystal is formed depends on boundary conditions. Peas in a cylindrical glass jar do not crystallize easily [an experiment performed by Stephen Hales in 1727; See R. Zallen, *The Physics of Amorphous Solids*, John Wiley, 1983.] Instead they form a random-close packed (rcp) structure which Bernal determined to have a packing efficiency of 0.63 (Cf. fcc at 0.74) Metallic glasses have structures that can be described by such packings. See the handout. The *dual* of this packing is *continuous random network*, found in SiO_2 glasses.

It is important to consider that packings in 2D are quite distinct from 3D. One way of looking at this is to consider an attractive potential between disks (2D) and spheres (3D). In 2D, three disks will form a triangle, and these triangles can eventually (in the crystal) lead to *hcp*.



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In 3D, three spheres will form a triangle, and the fourth one will attach to the three to form a tetrahedron. Many tetrahedra should come together to form the crystal, but in fact, what is formed is an icosahedron which does not pack crystallographically. This is *topological frustration*. The local bonding rule is incompatible with crystalline packing. Liquid-solid transitions in 3D are never continuous.

One of the consequences in 2D of the *crystal nucleus* existing in the liquid (the triangles) is that the nature of 2D crystals is quite unusual and intermediate phases called *hexatic* phases are possible in 2D. These are phases with long range six-fold orientational order, but no long-range translational order. See P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics*, Cambridge 1998, and K. J. Strandburg, *Rev. Mod. Phys.* **60** (1988) 161.

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One way that 2D crystals lose their long-range translational periodicity is through the formation of *disclinations*:

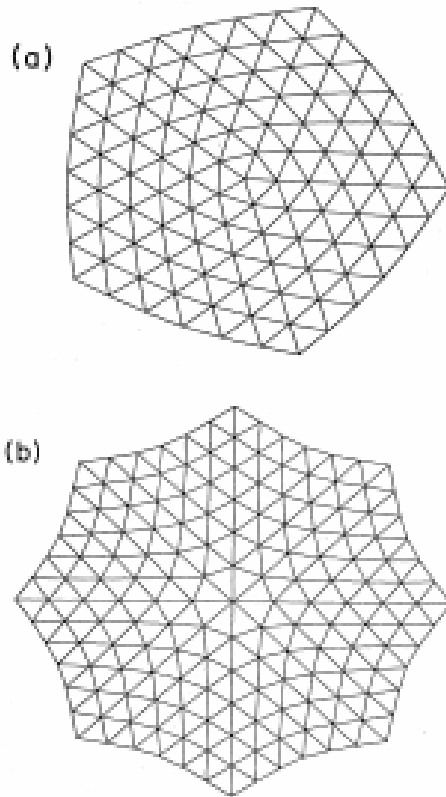


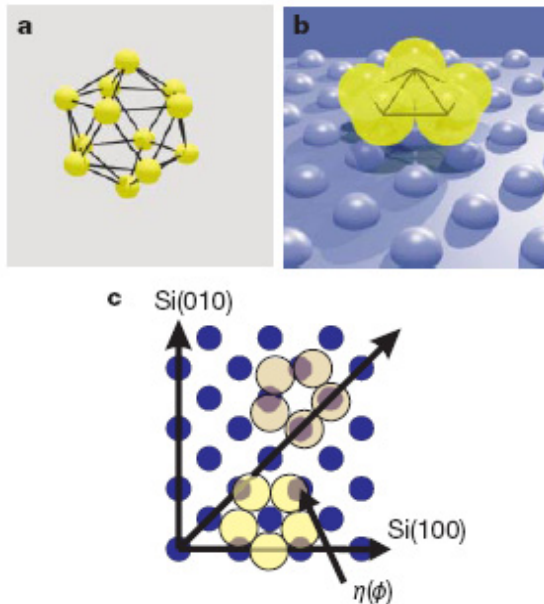
FIG. 4. Positive and negative disclinations in a triangular lattice. Note the rotation of the triangular cells by 60° (a) clockwise, and (b) counterclockwise, as a clockwise path around the disclination is traveled. Note that these disclinations may also be described as particles having (a) five, and (b) seven neighbors, respectively, rather than six.

(from Strandburg)

Disclinations become important for the structures of nanoparticles, liquid crystals, certain magnetic structures, block copolymer structures and liquid crystals.

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Liquid metals: Do they really have topological close packing ?



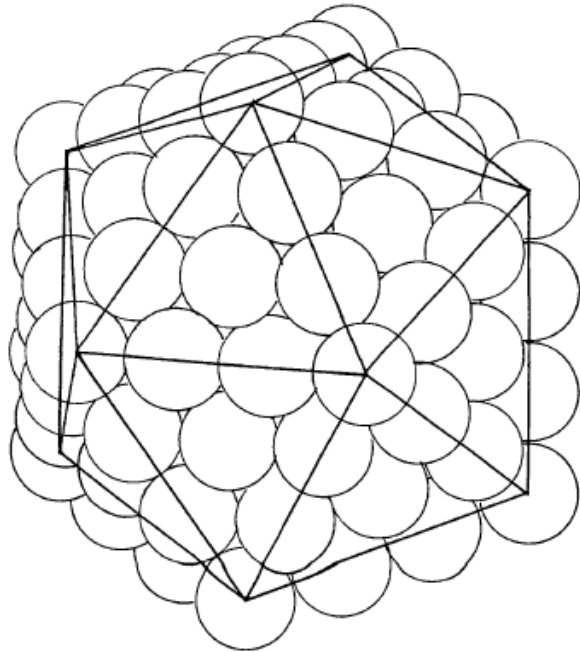
Evanescent x-ray scattering study of molten lead on Si. 5-fold local order is hard to directly observe in bulk liquids.

Observation of five-fold local symmetry in liquid lead, H. Reichert, O. Klein, H. Dosch, M. Denk, V. Honkimäki, T. Lippmann and G. Reiter, *Nature* **408** (2000) 839.

Figure 1 View of the dominant motif in the structure of bulk liquid lead and of interfacial liquid lead. **a**, Polytetrahedral arrangement predicted for close-packed monatomic liquids. **b**, Upper (pentagonal) half of the Pb icosahedron (**a**) captured by the potential landscape of the primitive Si(001) surface. **c**, Projection of the pentagonal structure onto four-fold coordinated sites of the Si(001) surface (lower pentagon, upper site position with minimum overlap of the projected electron density for rotation angle $\phi_n = 2\pi n/20$, where n is an integer; upper pentagon, hollow site with minimum overlap for $\phi_n = 2\pi(n+1/2)/20$; the overlap is denoted by η and shown in Fig. 3c as a function of the rotation ϕ of the pentagon).

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Mackay and Frank-Kasper polyhedra: Complex packings in intermetallics:



Third layer in an icosahedral packing of equal spheres.

A. L. Mackay, *Acta Crystallogr.* **15** (1962) 916.

Table 1. *The packing densities of icosahedral packings with increasing numbers of shells*

P_n is the density with a central sphere and
 P_n' without such a sphere

$$P_n = C_n/n^3 \times 6 \times 2.53615$$

$$P_n' = (C_n - 1)/(n - 0.04894)^3 \times 6 \times 2.53615.$$

Shell number	Number of spheres in shell	Contents C_n	P_n (density)	P_n'
0	1	—	—	—
1	12	3.5158	0.72585	0.60378
2	42	27.032	0.69760	0.72362
3	92	90.547	0.69237	0.71935
4	162	214.063	0.69053	0.71317
5	252	417.579	0.68969	0.70864
6	362	721.095	0.68923	0.70539
7	492	1144.611	0.68895	0.70299
8	642	1708.126	0.68877	0.70116
9	812	2431.642	0.68865	0.69971
10	1002	3335.158	0.68856	0.69856
∞	—	—	0.68818	0.68818

NB: Single tetrahedron packs 0.78

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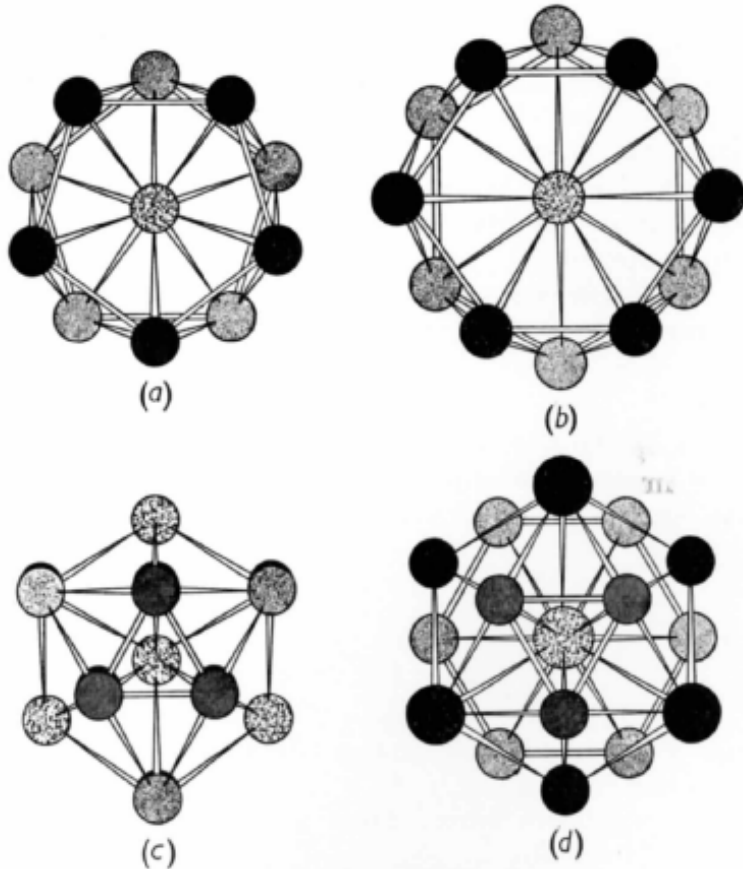


Fig. 1. The four 'normal coordination polyhedra' of complex alloy structures. For C.N. 12, two spheres above and below the central sphere, along the fivefold axis, are not shown. Similarly, two spheres above and below the central one of C.N. 14, along the sixfold axis are not shown. For C.N. 16 one sphere below the central one is not shown.
(a) Icosahedron, C.N. 12. (b) C.N. 14. (c) C.N. 15.
(d) C.N. 16.

Frank-Kasper polyhedra with CN = 12, 14, 15 and 16. These are common in many alloy phases. CN = 12 is an icosahedron.

The addition of extra atoms (for example, to CN = 12) can be considered similar to the introduction of disclinations.

F. C. Frank and J. S. Kasper, *Acta Crystallogr.* 11 (1958) 184; 12 (1959) 483.

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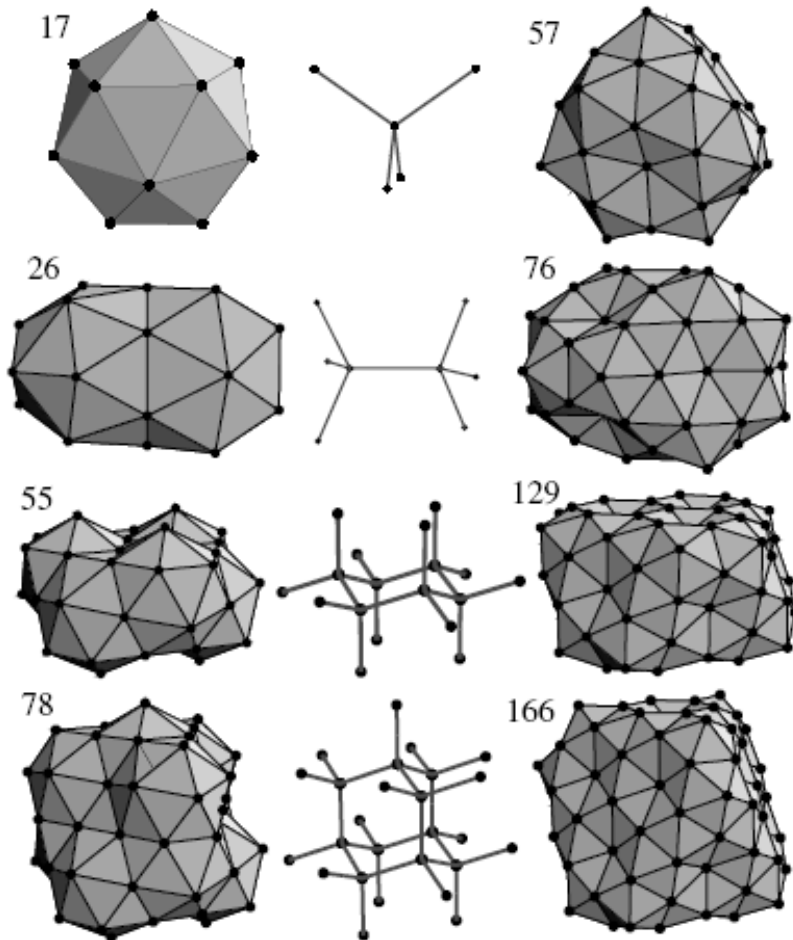


FIG. 3. Structures of some of the magic number clusters. On the right is the complete structure, in the middle the corresponding disclination network, and on the left the structure that is at the center of the cluster. All three have the same orientation.

Polytetrahedral clusters, J. P. K. Doye and D. J. Wales, *Phys. Rev. Lett.* 86 (2001) 5719.

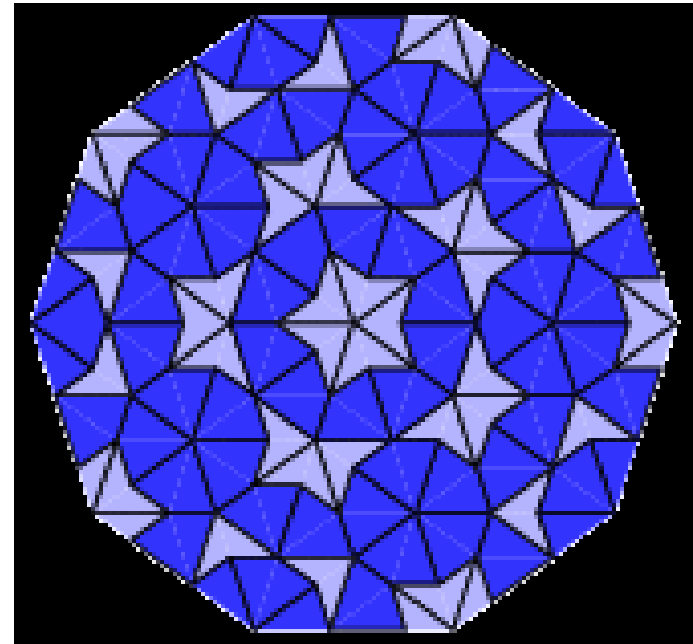
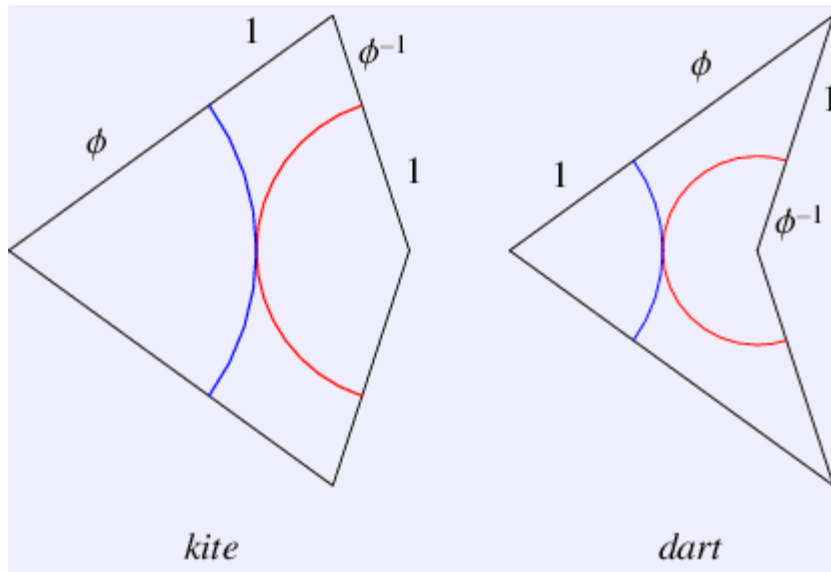
The authors used a potential that favors polytetrahedral packing and found that the disclination networks of stable clusters look like stable hydrocarbons.

The cluster on the top left (17 atoms) has one atom in the center of a CN=16 F-K polyhedron. The CN=16 F-K polyhedron is generated from an icosahedron by introducing 4 disclinations and so on ...

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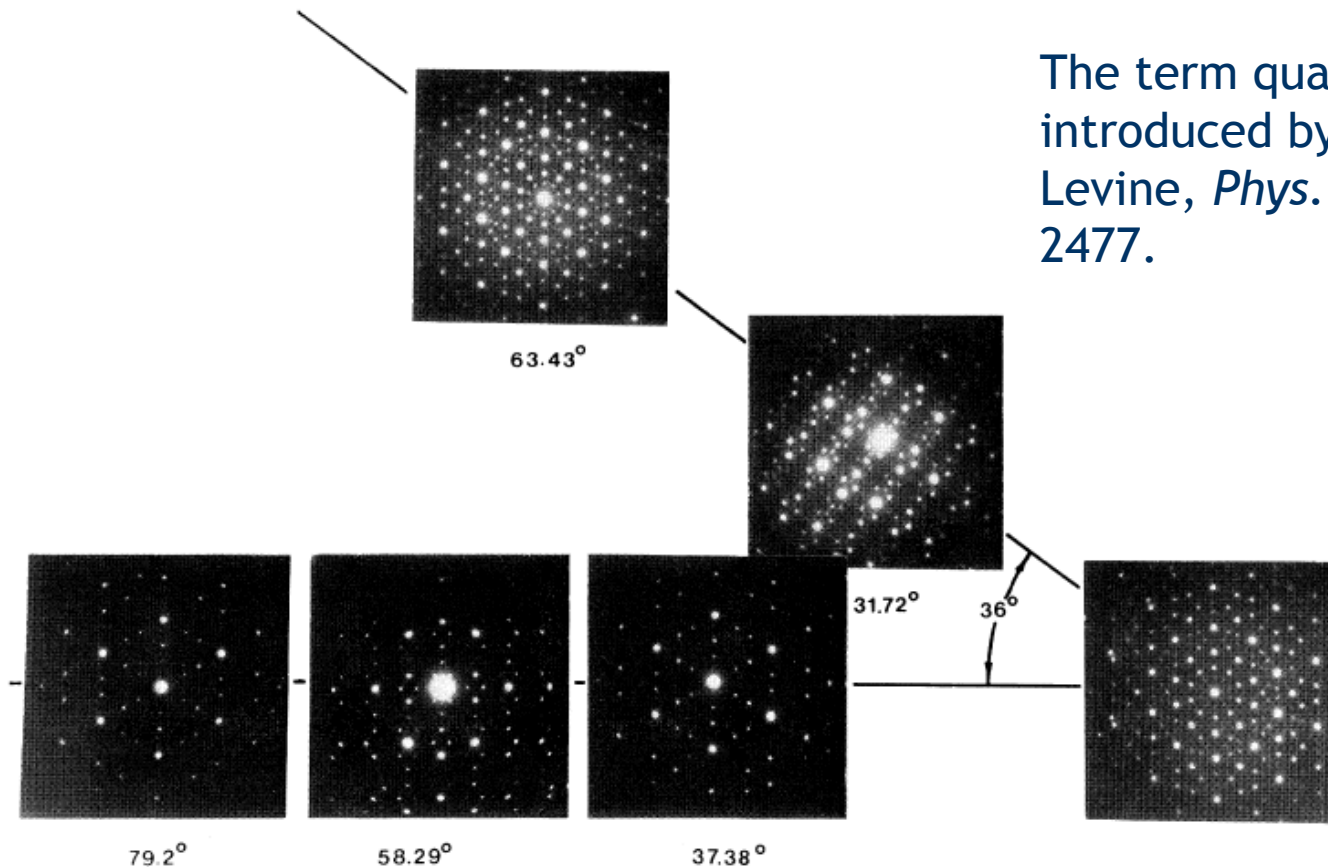
Quasicrystals:

The Penrose tiling of darts and kites:



No translational periodicity (no unit cell) but sharp Bragg diffraction peaks (Alan Mackay, Birkbeck College, London).

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The term quasicrystal was introduced by Steinhardt and Levine, *Phys. Rev. Lett.* **53** (1984) 2477.

FIG. 2. Selected-area electron diffraction patterns taken from a single grain of the icosahedral phase. Rotations match those in Fig. 1.

Al-14% Mn. Metallic phase with long range orientational order and no translational symmetry, D. Schechtman, I. Blech, D. Gratias and J. W. Cahn, *Phys. Rev. Lett.* **53** (1984) 1951.

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The connection: D. R. Nelson and F. Spaepen, *Polytetrahedral order in condensed matter*, Solid State Physics (San Diego, CA: Academic Press) **42** (1989) 1-90. The question is how does one accommodate tetrahedral motifs in condensed phases: In liquids, the disclination network is dynamic and disordered; in metallic glasses, it is static and disordered; in quasicrystals, it looks like a Penrose tiling; in intermetallics such as the F-K phases, the disclination network is crystalline. Also D. R. Nelson, *Phys. Rev. Lett.* **50** (1983) 982.