ML.24-B MAPPING CHARGE DEFORMATION DENSITIES.

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Suppose we had an ideal set of X-ray diffraction data, unsurpassed in accuracy and resolution. How would we proceed to a reliable deformation density map? We can choose Fourier or least-squares methods.

Among the drawbacks of Fourier methods: we need unbiased atomic parameters, *e.g.* from neutron diffraction (expensive, often imprecise, frequently discordant with the X-ray results) or from high-order X-ray refinement (with what value of s_{min}?); severe background noise, getting much worse with higher resolution; unsuitable for non-centrosymmetric structures; yield only dynamically smeared densities.

Least-squares methods overcome all these disabilities in exchange for one crucial uncertainty — is our model valid (*e.g.* multipole expansion, convolution approximation)? If so, we have a clean static deformation map, with estimated standard deviations, suitable for rigorous interpretation. If not, we may have garbage.

Several tests are available. We expect $\langle \Delta F \rangle \sim 0$ and $\langle w\Delta^2 \rangle \sim 1$ uniformly in different parts of reciprocal space and in different F ranges. The residual difference density should show only random noise (What is that?). The total density should nowhere be negative. Vibration amplitudes of bonded atoms should be equal along the bond. The same model should pass all these tests consistently with different structures of similar type and accuracy. Finally, we can compare our experimental deformation density with an accurate theoretical map.

Such comparisons are rare. Few molecules large enough to crystallize readily are small enough for high-quality calculations. So we compromise; assume transferability and compare the experimental density in a large molecule with the theoretical density of a smaller fragment.

ML.25-A CRYSTALS, MOLECULES AND CHEMISTS.

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The last decade has seen a quiet revolution in the amount and accuracy of information provided by single crystal X-ray analysis of small molecules. In 1980 over 10 times as many "accurate" (R<5%) structures were published than in 1970. Even without analysis of charge density or thermal motion these structures probably represent as high a concentration of useful information as provided by any other chemical technique. Yet the use of it by chemists has been limited, due in part, perhaps, to the traditional 'difficulty in understanding crystallography'.

The Cambridge File of structural data is unique in providing chemists with a vast array of crystal and molecular geometry for organic and organometallic molecules. It is comprehensive, with perhaps 1 million checked atomic positions from ca. 30 000 published structures, and easy to use. We understand only a small fraction of the information in any one crystal structure, but systematic analysis of the data is beginning to reveal quantitative patterns. In particular the chemist can view synoptically features of hundreds of related molecules or crystals. Three such examples are:
-Small differences (say 0.01 Å or 0.3°) in geometry between related molecules can be measured reliably. These can be used to test models of bonding; thus the precise geometry of cyclopropane rings depends on the nature and orientation of conjugating substituents. Studies on aromatic compounds can easily provide quantitative substituent parameters which may have advantages over those normally derived from rate or equilibrium data.
-The approach of 'chemical reaction pathways' where many similar structures are compared has great potential in studying low energy processes, particularly conformational changes. When a large amount of structural data are available for simple molecular fragments we can deduce a considerable amount about their potential energy surfaces.
-Although our understanding of crystal structures is very imperfect a huge amount of information on intermolecular geometry can be retrieved from the Data File. Frequently geometrical motifs can be seen which represent favoured arrangements for packing and can be taken to correspond to attractive intermolecular forces.

The Data File provides a valuable 'museum' of crystal structures which may be useful to chemists seeking a particular arrangement of atoms, for instance in solid state reactions, crystal engineering, solid state spectroscopy etc. As our understanding and design of molecular crystals improves, the solid state could play an increasing role in chemistry.

ML.25-B RECENT DEVELOPMENTS IN CRYSTAL GROWTH SCIENCE.

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The results of many authors will be reviewed in four categories.

I. NUCLEATION

1. In the bulk of pure metals (Ga) supercooling to 50% of the melting temperature is reached. Nuclei have unstable structures and are several Å in diameter.
2. On surfaces, the condensate either continues the substrate lattice or forms 2D or 3D nuclei, depending on wetting conditions. Quasi-liquid adsorption layers on the vapour-solid interface are possible.
3. Monolayer coverage changes condensate-substrate interaction and thus condensation kinetics.
4. Classical nucleation rate formulae work for nuclei of both macroscopic and atomic sizes.
5. UV light induces surface charges and provokes faster nucleation by the "2D Wilson chamber" mechanism.

II. VAPOUR GROWTH - CHEMICAL VAPOUR DEPOSITION (CVD)

1. Dense adsorption monolayers rather than the rare ones are predicted to be an intermediate phase in CVD of Si, GaAs, InAs.
2. Surface electric field due to adatom-substrate electronegativities difference may drastically (up to factors of two) decrease bond strength in admolecules.
3. Dipole-dipole attraction in adlayer (InCl on InAs(111)As) may cause its 2D condensation.
4. Adlayer composition and chemical reactions on steps and surface govern the growth rate and its anisotropy.

III. SOLUTION GROWTH

1. Electrocrystallization of dislocation-free Ag proceeds by 2D nucleation at theoretically predicted high (≈40%) supersaturations.

2. In-situ X-ray topography allows one to directly observe the growth on single dislocations and by 2D nucleation on dislocation-free ADP crystals.
3. Low supersaturations (≈1%) are needed for 2D nucleation on ADP (110).
4. Growth rate fluctuations occur during growth via 2D nucleation, probably due to impurities, reflecting fluctuations of nucleation events.

IV. MELT GROWTH. CREATIONS OF DEFECTS

1. Capture of impurities occurs via statistical selection of species by kinks and steps and via diffusion through the interface. Capture anisotropy often reflects difference in equilibrium impurity concentration in the interface atomic nets. In solution growth, impurity concentration dependence on growth step orientation was observed.
2. Macroscopic particles are trapped due to instability of particle-interface thin film of melt or solution.
3. Macrodislocation density is determined by thermal and concentration stresses, while microloops of dislocations are due to decomposition of solid solutions (in melt-grown Si).