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Small but Strong Lessons from Chemistry for Nanoscience[**]

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Somewhere between fashion and revolutionary substance, nanostructures have come to fill the popular, scientific, science fiction, and patent literature. The field is nicely interdisciplinary, with inputs to it in materials, techniques, and human expertise from chemistry, physics, and every branch of engineering. The level of hype is extraordinary, but the substance is great: the *meso* scale of the structure and dynamics of matter, so long neglected by chemistry, is being gradually filled in.

I entered the field too late (in age and inclination), too late to both relish the hype and, face it, to make a significant contribution. I am an outsider here, as I seem to be fated to be, as I was to organic, inorganic, and solid-state chemistry, to surface and high-pressure science. The outsider always faces trouble—he or she lacks the "tacit knowledge", as Michael Polanyi called it,[1] of a field—the little assumptions, constraints, and conventions that allow an insider to show in a lecture a sketchy slide with a but few technical words, and yet be sure that everyone in the audience understands. But the outsider may have one advantage, for he or she, in trying to make sense of what people in the field do, quite naturally makes connections to what is known elsewhere. It's not a matter of revealing the emperor's new clothes, it's an initially almost desperate attempt at linking to one's other experience to find something interesting to say. And not make a fool of oneself.

Knowledge is a wonderful construction, truly a house with many rooms.[2] Indeed, a contemporary hyperlinked house, where every new room turns out to be connected to every other one. There follow herein a few of the connections between chemistry and nanoscience I've made on entering research in the field. This is not a professional Review, but an informal reflection. So I am likely to have made egregious oversimplifications in what I say. And I say it in plain English and provocatively. *Angewandte Chemie* has kindly arranged for comments (anonymously or identified) to be sent to me so you can set me and the community straight.[3]

Most nanoparticles are not naked

It took me a while to realize that when people talked about CdSe nanosheets and clusters (just one personal entry point to nanostructure; I am very grateful to Taeghwan Hyeon for guiding me here) that what they really meant was such sheets and clusters stabilized by coordinating surfactants.

I should have known it, that naked, these nano-objects would be much too reactive for persistence. But I had never made nanoparticles, not even colloidal gold. So I missed the manipulations and reactants that made for one morphology and not another. Lacking the tacit knowledge of the field, I fell for the cartoons. Had I grown up with the original literature, I would have known that there is plenty there about the absolute necessity of ligands, not only for synthesis but for persistence.[4–7] We have a lot of information; there are direct NMR[8,9] and IR[10] spectroscopy studies of ligands bound to nanoparticles, enabling dynamic studies of ligands coming on and off.[11] Also people are finding creative chemical ways to strip ligands from nanocrystals surfaces.[12]

The reason for the qualifier "most" in the title of this section is of course that there are lots of kinetically persistent nano-objects in this universe. For a starter, most of the 70 million organic compounds made by us, namely the ones that form molecular crystals, are in that category. Some $(CH)_n$ and $(BH)_n^{q-}$ clusters, as well as transition-metal clusters bonded to carbonyl and cyclopentadienyl ligands, and the family of naked main-group clusters called Zintl ions (more of these later) are quite stable. But the nanoscience community, in its embrace of the cult of the new, prefers not to view "normal" molecules as nano-objects. To turn then to the bread and butter of the community, many fullerenes, nanotubes, and graphene are reasonably kinetically persistent on their own. As are exfoliated sheets from a variety of intrinsically layered materials, the MS_2 system (M a transition metal) being one example.

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One class of nano-objects I am uncertain about is that of the remarkable plasmonic nanostructures—metallic nanostructures of an impressive variety of architectures.[13–15] Whether grown from seeds or templated, they are made in the presence of various ligand/bases/reducing agents critical for their synthesis. Some, maybe a lot of these molecules must be on the surfaces of the plasmonic nanostructures. In fact, perhaps you need them for sensor or catalyst function. It's not clear that one should care to remove them completely.

Reactivity

In general, low-dimensionality nano-objects, with the exceptions listed above, are likely to be very reactive. Be they zero-dimensional (0D) clusters, or one-dimensional (1D) chains, or two-dimensional (2D) sheets, by cutting them out of a three-dimensional (3D) molecular solid, not by cutting along "dispersion force connections," but cutting bonds, we are doing great energetic violence to the molecule. The energetic driving force to restore the extended, covalently or ionically bonded structure is tremendous—in the age of easy computation every one of our students should find out for themselves just how much is gained by a ZnO line or sheet in reconstituting the three-dimensional solid.

We also create reactivity. If we cut a covalent solid such as silicon, we generate dangling bonds, one-electron radicals. If we cut a more ionic III–V (or in general an N-(VIII-N) compound),[16] we create acid and base reactivity, at the group III and group V element site, respectively.

How is a pristine nanostructure of the N-(VIII-N) type to respond to its energetic instability and kinetic reactivity?

Take zero on dimensionality

Before I try to answer that question, I had better face up to the trouble I have already gotten myself into just by writing of a) 0D, 1D, 2D, 3D, and b) cutting chemical bonds. Neither dimensionality nor chemical bonding are simple; I will restrain myself from tackling the latter, but will have much more to say herein about dimensionality. Because I have to, the idea is so foundational to nanoscience.

Most ambient-condition (of T and P) studies involve a common-sense definition of dimensionality, and depend on an unvoiced delineation of the object by not counting connections arising from dispersion forces or electrostatic multipole forces as bonds, with hydrogen bonds a contentious no-man's land.

The last sentence above begs for deconstruction—the separation of "real" chemical bonds from dispersion forces is questioned by adherents of the Quantum Theory of Atoms In Molecules (QTAIM).[17] And the statement assumes a structure, which in our day comes for molecules with more than 10 atoms at 0.01 Å resolution almost exclusively from X-ray or neutron diffraction. One interesting reflection for a chemist who has seen the over 700000 X-Ray structures in the Cambridge Structural Database and the approximately 150000 structures in the inorganic analogue (ICSD), is that structural information in nanoscience *rarely* comes from X-ray diffraction of single crystals.

Even if one did not know anything about dispersion forces, and did not have a hundred years of chemical tradition separating dispersion forces conceptually from chemical bonds, what one could do (if one has a structure) is to construct a histogram of separations of all atoms from a given atom, the discrete lattice equivalent of a radial distribution function for a liquid.

The structural two-dimensionality of graphite derives from just such a histogram—a given carbon atom in graphite has three nearest neighbors at 1.42 Å, six at 2.46, three at 2.84 within the layer, all less than the first interlayer separation of approximately 3.3 Å. The one-dimensionality of isotactic polyethylene similarly would give a more than twofold ratio between the first van der Waals contact and the shortest C–H and C–C distances in a chain. One could also look for a dimensionality criterion in reciprocal space, in the spacings of the first diffraction peaks of a crystal.

I will return twice to dimensionality, and try to distinguish structural from electronic aspects of its definition. Here I mention the first of many ambiguities about the definition, which is firmly rooted in the $P = 1$ atm world in which we move (bicycle tires, deep-sea diving, the Haber–Bosch process, and the surface of Mars extending our range, for sure). What is the dimensionality of a sample of, say, Xe? In a gas at 1 atm, 298 K, the Xe atoms are on the average around 37 Å apart. The gas sample is macroscopic, ergo 3D, but I think no one would disagree that it is effectively 0D, made up of weakly interacting atoms. In solid Xe at 5 K, the Xe–Xe distance in the fcc lattice is 4.34 Å.[18] The solid is characterized by a high van der Waals attraction between the element's atoms (witness its high melting point of 161 K), but I would say it is still effectively 0D. Next I get into real trouble: under compression, Xe is metallized, at around 130 GPa.[19] At this pressure the average Xe–Xe separation is 2.93 Å. And clearly the metal is 3D. So … at what Xe–Xe separation does 0D become 3D? I don't have an answer for you, except "You've asked a good question".

It is clear that a thick tome, or tomes are to be written on something as seemingly simple as dimensionality. Jay Siegel has appropriately scolded me for the impoverishing tone of a relegation of every molecule to zero dimensions. Of course, the local three-dimensionality of any non-planar molecule is essential—we would not have the loveliest intellectual framework that I know, that of organic stereochemistry, if those little beasts were not three dimensional. Michael O'Keeffe, a great geometer of chemical nature, reminds me to keep separate dimensionality and periodicity, commenting, "a one-dimensional rod (a 1-periodic structure) has rather boring symmetries. But a three-dimensional rod has rich symmetries.

There will be more to say on dimensionality, you can be sure. But let me return to the way a nano-object responds to its birth, in the unpromising condition of relative energetic instability and much enhanced reactivity.

Stabilization, on their own, and with a little help from their chemical friends

On their own, objects cut out of a preferred solid-state structure by severing covalent, ionic, or donor–acceptor bonds will try to heal themselves, so to speak. Experimentally, the response can be piece-wise probed (spectroscopically) in low-pressure vapor or in cold inert matrices. There is also much guidance to what ensues in the literature of high-vacuum surface science—I will return to this, in some detail, in subsequent Sections.

If the nano-object (be it particle, polymer, or film) is kinetically unstable, with sites of great acidity and/or basicity, then external molecules, bases and/or acids may stabilize it, may stabilize it by bonding to it, forming covalent or donor–acceptor bonds. Too great stabilization will inhibit growth; too little stabilization will not prevent collapse to the solid. The primary role of the ligands is to control the aggregation of the growing nanoparticle. That control is exercised dynamically, through ligands coming on and off. Both thermodynamic (Gibbs energies) and kinetic (activation energies) factors matter in the dynamics. If the ligand is a surfactant, with active hydrophilic and hydrophobic regions, these propensities can also play an important role in nanoparticle synthesis by controlling nucleation and growth. Just as in homogeneous-catalyst science, much depends on the exquisite tuning of ligands.

I will have more to say about what chemistry might teach us of the reactivity, acid–base character, and the structural changes to be expected of pristine and stabilized nano-objects. Here I want to justify my persistent use of the descriptor “ligand” rather than “surfactant”. The surfactant character of a ligand, with a typical hydrophilic and hydrophobic part, is certainly important in the kinetics of formation and in steric stabilization of the nanoparticle. But in focusing on the hydrophilic head group binding to the nanoparticle, the nomenclature obscures in some way the fact that most nano-objects, especially those formed from N-(VIII-N) compounds, contain sites of both Lewis base and acid functionality. Which seek acid and base partners, respectively.

The ligands that have made much semiconductor nanoscience possible are primarily Lewis bases. Receiving less attention, Lewis acids are also around, not the least of these being the proton transferred from hydronium ions if one is in aqueous media. Or the positive hydrogen bonded to oxygen in organic acids, if these are used as surfactants. There is also an important group of nanostructures, often catalytically active metal clusters, stabilized by the acidic $AlCl_3$.[20] Perhaps there is something to be gained from exploring more Lewis acid ligands.

A silicene interlude

We have graphene multilayers and the monolayer, and the intriguing physics of these. There is a growing literature out there of the Si analogue, silicene.[21] And that literature talks about silicene as if it were graphene. In part this is an attempt to live off graphene’s mystique, but part comes out of lack of knowledge of chemistry.[22] I don’t often say something categorical, but I will say that a pristine free-standing single layer sheet of silicene (or a Si nanotube) will not be made. Silicene exists and will be made only on a support of some sort, metal or semiconductor.

The reason for this is, of course, the well-known kinetic and energetic instability of Si–Si double bonds (or partial double bonds, as in silicene). π Bonding is worth very little at the Si–Si single, σ bond distances of approximately 2.35 Å. Si=Si bonds have to be protected sterically to be isolated.[23] They will latch on chemically to every piece of molecular dirt around. The graphite form of silicon is only a theoretical construct—there is nothing like the energetic balance of graphite and diamond structures for real Si. Two graphene layers condense to a bilayer held by dispersion forces, approximately 3.3 Å apart, with small exfoliation energy. On the other hand, two silicene layers are calculated to form Si–Si bonds between the layers (Si in general has no troubles with five-coordination); Figure 1 shows the computed equilibrium geometry of a free-standing bilayer.[24] If you provide more layers, the reaction to diamond structure Si is likely to be activation-less.

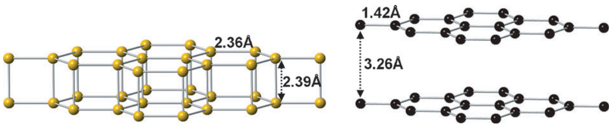

Figure 1. Left: the optimized structure of a two-layer silicene; right: the corresponding graphene bilayer. Both are in AA stacking.

Now SiH (silicane?) will have no problems. In silicon chemistry single bonds are favored. It’s just a matter of making it.

Zero-dimensional objects and charge stabilization

In the context of stability, chemistry has a lot to say about 0D nanostructures, or clusters of the elements or compounds. Most of these exist as such only in high vacuum, sailing down a mass-spectrometer vacuum chamber, or in an inert (usually noble gas) matrix at low temperatures. “Inert” depends on the species—you can study WH_6 in an Ar matrix at 4 K, you can’t study CH_3^+ in the same matrix—it reacts with Ar like a shot. The temperature delimits roughly the activation energy that could be surpassed; the concentration often matters. Much, much detailed information has been gained about metastable molecules in such conditions.[25] What is learned is often fascinating, and always instructive. But such metastable molecules will not make a practical catalyst.

To persist as a solid or in air, to be bottleable (a word that does not trip off the tongue lightly, but is plain English descriptive), to be viable at 1 atm and 293 K for a day, a molecule has to have activation energies of 15–20 $kcal\,mol^{-1}$ to dimerization and reaction with solvent. The majority of clusters are not viable in this sense. But there are exceptions, important to know.

Some neutral polyhedral hydrocarbons are stable, those without excessive strain, for example, dodecahedrane, $(CH)_{20}$, and cubane $(CH)_8$. We also have a few group 14 analogues of the hydrocarbons,[26] and the allotropes of phosphorus, some indeed clusters. There are also stable neutral clusters of transition metals, not naked but coordinated on the outside by three carbonyl groups or the electronically equivalent cyclopentadienyl (Cp, C_5H_5), exemplified by $[Co_4(CO)_{12}]$, $[Ir_6(CO)_{16}]$, $[Fe_5C(CO)_{15}]$, $[(CpRh)_3(CR)_2]$.[27] Some of these clusters are charged, and they share with stable polyhedral $(BH)_n^{2-}$ ions a magic electron count, typically described by the Wade–Mingos rules.[28] Magic electron counts also play an important role in the stability of metal clusters.[29] Of which we know a great deal experimentally, even if they are not bottleable.[30,31] One of the magic qualities of magic electron counts is how you can get at them from many seemingly different theoretical approaches…

For main-group elements in general, the same rules and their extensions suggest stability for certain naked main-group clusters with lone pairs on the outside, for example $[Ge_9]^{2-}$, $[Sn_9]^{4-}$, or $[Bi_9]^{5+}$.[32] These are called Zintl ions, in honor of Eduard Zintl, who recognized their potential. And who also has a fascinating group of main-group bonded, partially ionic structures named after him, the Zintl phases.[33,34] Zintl ions are sometimes negative, sometimes positive. In the solid state they are stabilized by strong ionic interactions with a counterion, such as K^+ for the anions. John Corbett's great achievement was to recognize that the anions could be solubilized, by sequestering the counterion, for instance in a [2.2.2]cryptand.[35] For the cations, superacids, and molten halides provide synthetic access.

Naked Zintl anions are moderately stable in solution; Coulomb repulsions play an important role in that stabilization. I know precious few naked *neutral* Zintl or Wade–Mingos polyhedra that survive in a bottle.[36]

Still another class of robust (and highly charged) nanosized clusters are the polyoxometalates,[37] combining M = W, Mo, V with a goodly number of oxygen atoms. A simpler[38] and a complex[39] structure in this series are shown in Figure 2.

The transition from discrete, viable molecular cluster to one inextricably embedded in a solid-state matrix is fascinating; the reader is directed to a perceptive discussion of this transition by Arndt Simon.[40]

The geometries of nanosheets

Two-dimensional nano-objects, single or multilayer, are the subject of much contemporary nanoscience. Except for graphene (BN as well, and other films formed from layered materials of the MS_2 type, M = transition metal) and other kinetically persistent carbon structures (nanotubes, fullerenes), these slabs have suffered in being cleaved out of a well-bonded three-dimensional material. Surface science has much to teach us about what will happen: first of all, such two-dimensional structures will readjust their geometry to heal themselves. The operative terms are relaxation and reconstruction.[41] The geometrical changes are pretty obvious from bonding considerations; they will often involve the strengthening of bonds at the surface of the nano-object, and, probably, weakened bonding of the surface layer to the subsurface one. Let me explain.

Suppose you take a very sharp knife to ethane and remove two hydrogen atoms. The remnant $H_2C–CH_2$ molecule knows what to do; it readjusts its geometry by becoming planar, forming a π bond, and decreasing the C–C distance from 1.54 to 1.34 A.

Let's take a look at a typical II–VI system, CdSe.[42] No matter which surface you cut out of a parent wurtzite lattice, you will expose some Cd and Se atoms. Viewed from an ionic viewpoint (Cd^{2+}, Se^{2-}), the surface will have one or more filled lone pairs at the Se, one or more empty orbitals at the Cd. If you don't give the surface a base or acid functionality to bind to (more of that in a moment) the surface atoms will look around for any bonding possibility. π Bonding between Cd and Se is available, maximized if the Cd and Se come closer together. Providing the bonding to the remaining atoms in the surface allows it; planarization (as for $CH_2{=}CH_2$) would induce inordinate strain. As we will see, there is another possible stabilizing distortion.

Let's look at a specific case, an unrelaxed (100) cut of CdSe as shown at left below in Figure 3. This surface exposes

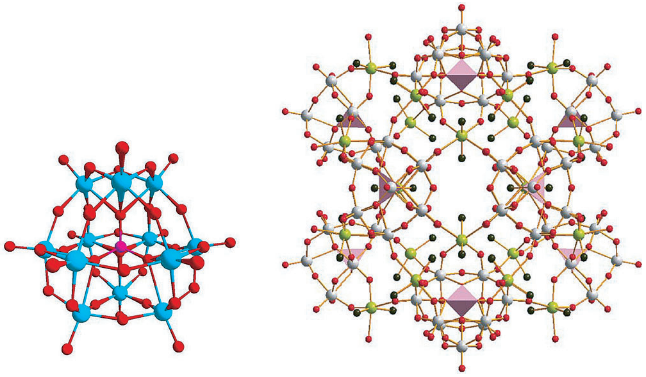

Figure 2. Two polyoxometalates. Left the phosphotungstate ion, the archetypical Keggin structure, $[PMo_{12}O_{40}]^{3-}$, Right: $[\{Sn(CH_3)_2(H_2O)\}_{24}\{Sn(CH_3)_2\}_{12}(A\text{-}PW_9O_{34})_{12}]^{36-}$. W gray, Sn green, O red, C black. PO_4 pieces are shown as pink tetrahedra.

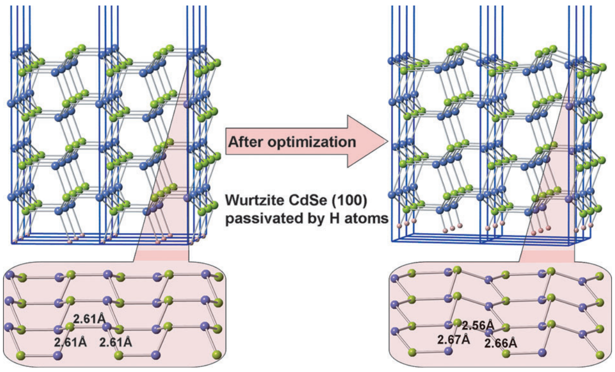

Figure 3. A two-dimensional four-layer slab cut out of a wurtzite CdSe lattice, passivated on its bottom side by hydrogen atoms and exposing the (100) surface. Se green, Cd blue; H pink.

pyramidal Cd and Se atoms, and a Cd–Se separation of 2.61 Å.

At right is the result of a quantum-mechanical exploration of the relaxation. Several structural features are apparent: The Cd–Se distance at the surface is shortened relative to the bulk, while the surface CdSe pair to subsurface bonds are elongated. And the surface CdSe pairs "buckle"—the Se becomes more pyramidal, the Cd "planarizes."[43]

The explanation of the decreased surface Cd–Se distance is in the aforementioned π bonding. The increased distance of the surface pair to the layer below is probably the outcome of a strain balance. But where does the buckling come from?

First of all, perhaps Si–Si is a better model for CdSe than C–C. This buckling, with little energy favoring it, occurs also in the well-known Si(100) surface reconstruction, one form of which is shown in Figure 4.[44] The energy favoring buckling over an unbuckled structure is only of the order of a few kcal/Si, but it is there.

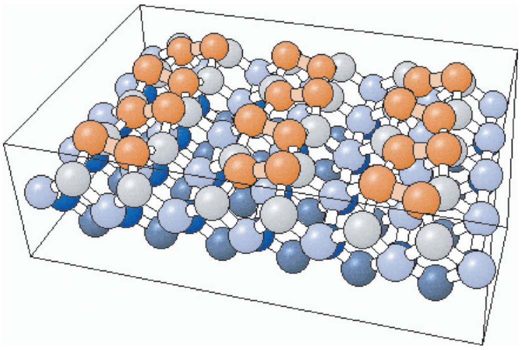

Figure 4. A (4×2) reconstruction of the Si(100) surface.[23] The orange Si atoms are those in the topmost layer, light blue the next layer below.

The buckling phenomenon is the working out of the preferred geometrics of the individual atoms/ions. Three-coordinate selenium compounds (e.g. the organic selenonium ions, $[SeR_3]^+$, and $[SeI_3]^+$) are pyramidal, with a well-understood high barrier to inversion. Three-coordinate Cd complexes are rare, but in calculations[45] they are planar. The π bonding (maximized in a planar $Se_2Cd–SeCd_2$ unit) is competing with strongly preferred pyramidalization at Se. A compromise emerges with buckling (pyramidalization at Se, planarization at Cd) and still some π bonding.

For an excellent account of CdSe surface relaxations with and without stabilizing surfactants, see the work of Manna et al.,[46] as well as the work of Rempel et al.,[47] and Kilina et al.[48]

As I mentioned above, the surface-science community has much to teach us about relaxation and reconstruction.[41] On metal surfaces, the more neighbors a surface atom maintains, the smaller the readjustment. On semiconductor surfaces, the changes observed are sometimes extensive—witness the dramatic 7 × 7 reconstruction of the Si(111) surface. Most of the time the changes are quite predictable—bonds form to relieve dangling orbitals, molecules turn on π bonding when they can.

A few final comments on 2D structures: Another place where two-dimensionality is prominent is in adsorbed monolayer and multilayer materials, from Langmuir–Blodgett films to chemisorbed (bonded) and physisorbed (dispersion force-connected) films, sputtered and nanofabricated films. The degree of homogeneity and control of thickness varies tremendously.

In general I think there are few pristine thin (one or two layer-thick) two-dimensional films or slabs, little that is analogous to the zero-dimensional molecule at very low pressure or trapped in a neon matrix. Graphene and its analogous, as mentioned, are an exception. Arguing against me are the remarkably clean STM images one sees repeatedly in the literature. But these are not free-standing, but supported, by an inherent multilayer thickness of the same material, or a metal or oxide support underneath.

The depth of the surface layer is rarely discussed. There is however a literature on subsurface species, especial hydrides, their characterization, and the kinetics of their emergence from the solid.[49]

The geometries and reactivities of stabilized nanostructures

The initially exposed surface of nanostructures cut out of covalently or ionically bonded solids is highly reactive—in the CdSe case at hand it has a superb Lewis acid in Cd's low-lying empty orbitals, and equally good Lewis base character in those Se lone pairs. That reactivity is only partially quenched by whatever surface healing takes place—the relaxed surface is likely to remain a seat of reactivity.

It is easy to predict roughly, not exactly, what the structural and reactivity consequences will be. The coordinating base and acid will heal to some extent the damage done to the initial structure by cutting it out of the solid. So if we are talking about a CdSe nanofilm, with the reconstruction shown above, when you add a layer of NH_3 (bases, bonding at Cd) one gets the geometry shown in Figure 5.

Note the return of the surface Cd–Se distance to more or less its value in the bulk. The flattening at Cd is, of, course reduced, while pyramidalization at Se is retained. If we now add a further Lewis acid, modeled in this case by the slightly

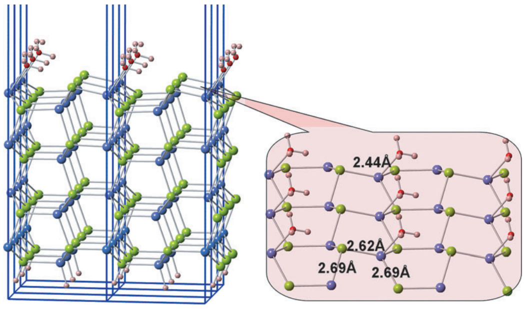

Figure 5. Optimized geometry for NH_3 adsorption on a passivated four-layer slab model of the CdSe(100) surface. Se green, Cd blue, H pink, N red.

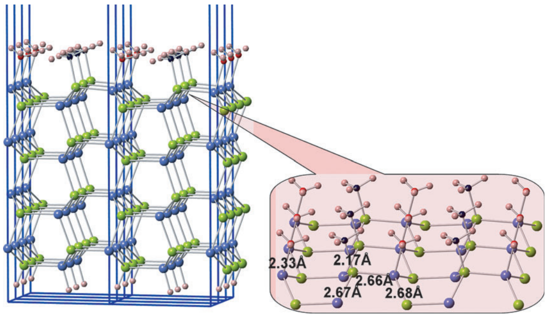

Figure 6. Optimized geometry for NH_3 and BH_3 adsorption on a four-layer slab model for the CdSe(100) surface passivated by H atoms. Se green, Cd blue, H pink, B black, N red.

unrealistic (from the point of view of a practical reagent) borane, BH_3, one obtains the geometry shown in Figure 6.

The added bases and acids essentially restore the bulk structure, substituting for the internal acid–base bonding that characterizes the solid. That this happens is not a universally held view.[50] It will be noticed that the Cd–Se distances at the surface are distended; perhaps this is a sign of repulsive NH_3–BH_3 interactions in this model.

We are beginning to get information on still another way by which nanocrystals stabilize themselves, by depletion of one ion at the surface. So PbSe nanocrystals have been shown by the Hens group to have a coating of Pb.[51]

The stabilized surface will be less reactive, a tautology of course, for it has been stabilized, hasn't it?

A bridge

Remarkably, quite stable crystals of base-stabilized semiconductor nanostructures, 1D and 2D, have been synthesized by Jing Li and co-workers.[52] So the geometric consequences of stabilization may now be seen from their structures and spectra. A picture of one of them is shown in Figure 7. Some of the 2D structures (not those shown herein) are linked up chemically in 3D ways (e.g. by alkyldiamines); nature is not going to stop playing dimensionality games with us.

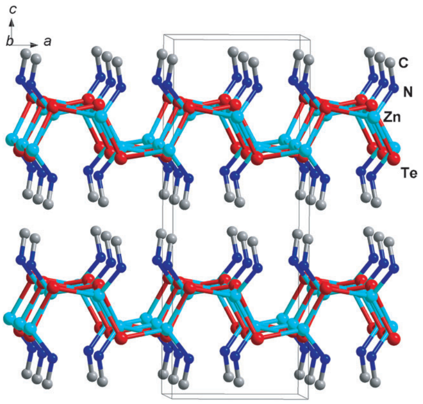

Figure 7. A view of the crystal structure of 2D [ZnTe(methylamine)]. Cd light blue, Se red, N dark blue, C gray.

Zero-dimensions again

What will be the response of naked clusters to their instability? They will relax and reconstruct, to a varying degree, depending on the strength of the remaining bonds, the nearby magic electron counts, and the ionicity of the structure.

In some as yet partially published work, we have looked in a comparative way at the equilibrium geometries of clusters cut out of a covalent network (the group 14 structures, a partially ionic yet primarily covalent or donor–acceptor bonded structure (CdSe), and a very ionic solid (NaCl). The damage done to a silicon cluster is extreme—one to three Si–Si bonds cut. The reconstruction is major, and the resulting structures, studied by many theoreticians, bear little resemblance to a piece of the solid.[53] Moreover, for any size cluster there appear to be several shallow energy minima close to each other in energy. Is the cluster in a kind of liquid state?[54]

For CdSe nanocrystals, the smaller the cluster, the more structural rearrangement takes place.[55,56] As the crystal size increases, the reconstruction is more on the outside of the cluster; the inside approaches the bulk structure. Nothing remarkable in this—the nanocrystals becomes a small crystal, and develops a surface. There appear to be exceptions to this, stable clusters with well-defined size, departing dramatically from pieces of the solid, such as $(CdSe)_{34}$.[57]

For NaCl, the preferred cluster geometries differ little from those of the solid.[58–60] An exception appears to be a "maximally exposed" $(NaCl)_{16}$, that begins as an $(NaCl)_4$ cube capped six times on its faces. The energetics of the clusters adheres beautifully to a screened Madelung energy expression. While the clusters remember their solid parentage,[61] the distances follow the healing scenario—thus while the Na^+–Cl^- separation is 2.81 Å in rocksalt, it is (experimentally!) 2.36 Å (r_e) in molecular NaCl.[62]

I do not have the time here to explore the fascinating question of the cluster size at which packing in noble gas and metal clusters transforms from initial icosahedral order to translational symmetry and close packing.[63] And at what cluster size does an aggregate of atoms of a transition-metal element become a metal? One should not expect an answer that fits all sizes—it may be the critical size is one for cohesive energy, another for conductivity.

What is the driving force for relaxation and reconstruction, for these sometimes major transformations of clusters from their bulk fragment structure? To use the language of physics: the imperative is to get as many states and electrons out of the Fermi-level region and to lower energy. Or, in the lingo of chemistry: form as many bonds as you can.

Dimensionality: two case studies

Dimensionality is one of those words whose meaning everyone knows yet which are difficult to define. This is hardly a reason to dispense with the word; the reader familiar with my ideas knows that I accept, even relish, the utility of imprecise expression in advancing reliable knowledge.[64] Let me enter the discussion with two personal case studies, which connect up a number of ideas above, and which bring into focus questions of dimensionality.

1) Xiao-Dong Wen in my group did some calculations on carbon nanotubes under pressure, and found that at a certain pressure they might undergo concerted Diels–Alder reaction zipping up into a 3D lattice. The calculations were 3D, with periodic boundary conditions, but we created an effectively 2D array by the usual maneuver of adopting one large lattice spacing.

We then thought could we try to effect the reaction, with the help of Zhongwu Wang at Cornell. So we looked for real carbon nanotubes that might align themselves for compression. The first revelation (to an outsider, not to person in the field) was that there is no crystal structure of a nanotube. Yet we know a lot, really a lot about them. There is no crystal structure because there is no macroscopic crystal of any, and there is no macroscopic crystal because carbon nanotubes are not monodisperse—nanotubes are inherently made in a range of lengths (even when their diameter and helicity can be controlled). We looked for the research group that could give us the most monodisperse nanotubes; it is that of Mark Hersam at Northwestern. With the help of Sang-Yong Ju, Xiao-Dong Wen and Zhongwu Wang compressed these nanotubes. With ambiguous results, which is why you haven't seen a paper. We haven't given up.

Green and Hersam's state-of-the-art separations began with a commercially purchased sample that contained a mélange of approximately 45 different chirality nanotube types, having diameters of approximately 0.7–1.1 nm. The group was able to separate out the chiral (6,5) nanotubes from this mixture, with great selectivity in chirality and diameter (ca. 0.76 nm). The average length of the nanotubes was 860 nm, with substantial dispersion.[65] Putting aside the dispersion in length, one could ask whether one of these nanotubes is a 0D or 1D object. Given their length, it makes all the sense to call them 1D. If they were shorter, one might also wonder what is the effect of termination of the tube on its electronic properties.

2) In another study,[66] we looked theoretically at a neutral 1D infinite Pb chain excised from a 3D Au_2P_2Pb structure synthesized by Eschen and Jeitschko[67] (see Figure 8). The Au and P bonding relationships pointed to Au^{+I} and P^{-I} formal oxidation states, and thus a zero-valent Pb. With a Pb–Pb distance of about 3.20 Å, shorter than in metallic lead. A -Pb-Pb-Pb-Pb- chain; now that's pretty interesting.[68,69]

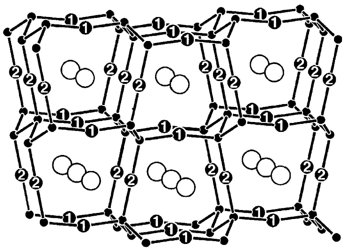

Figure 8. The Structure of Au_2P_2Pb. The open circles are the Pb atoms, the numbered dark spheres Au, the small dark spheres P.

To our surprise (we were naïve), the Pb chain extracted—in the computer—from the 3D solid did not stay linear. It kinked. And when we allowed it to check out more complex structures, it went into helices, as shown in Figure 9. When I say "it went" I mean that the energy spontaneously was lowered by that distortion. We were surprised, but the molecule was trying to teach us a lesson. It wanted to be an fcc 3D structure, that's what lead "wants". We were forcing it to be 1D, but allowing it the freedom of putting more and more atoms in the one-dimensional unit cell. Of course it chose the more "three-dimensional-like" unit cell that gave more and more atoms more nearest neighbors. The simplest 1D line didn't stand a chance.

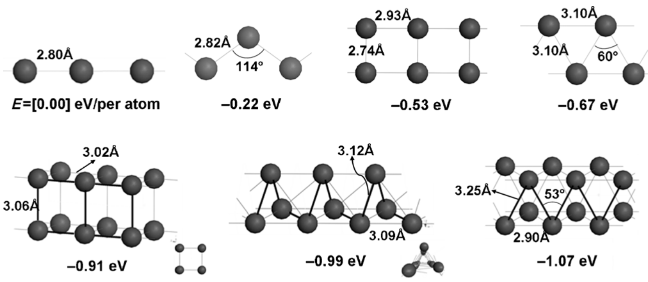

Figure 9. The relative energies of some 1D lead-atom polymers.

I see in these entry points to the field the complexity of structural dimensionality. The limits of any definition are apparent, not that I want a "precise" one—chemistry is not mathematics. But could we gain something from looking at dimensionality in another way?

Electronic dimensionality

Dimensionality is not only structural. Electronic dimensionality can be defined in terms of anisotropies of various electronic properties. But these can ultimately be traced back to the band structure and density of states (DOS) of any material, and it is on features of these that I would like to focus.

How to distinguish a structure of lower dimensionality in a complex material? I suggest that one focus on the bandwidth developed, relative to the spacing of the bands. Supposing you separate the units in any solid to infinity—and in the process do not take molecules apart to atoms in a molecular solid; if you expand a benzene crystal, keep benzene molecules; separate graphite to graphenes. If you do this, then the bands will narrow. Running the process now in the opposite direction, from infinite separation of the subunits to the equilibrium crystal, the bands will broaden. I would define a material as being of lower dimensionality (0D for molecular crystals, 1D for organic or inorganic polymers, 2D for layered, slippery structures) if the band-width developed in such an aggregation is, say, less than or equal to 0.1 eV.

This number is arbitrary; I've chosen it to be around 10% of the typical spacing of the levels in a molecule, arising from intramolecular interaction. To put it another way, the dimensionality might be defined by the ratio of *inter* to *intra*molecular/ionic overlaps, and I mean quantum-mechanical overlap integrals. If that ratio is small, the dimensionality is lowered.

Let me now describe dimension by dimension some special features.[70]

0D: As laid out above, great separations of atoms or groups of atoms from other atoms lead to narrow bands, for it is orbital overlap that gives dispersion of bands.[71] There may be other reasons for small band widths, for instance low crystal symmetry and many avoided crossings, but if all the valence bands are narrow, this is an indicator of electronic zero-dimensionality.

Are the molecules in a molecular crystal (say benzene) 0D or 3D? I would say they are 0D; the electronic criterion I just discussed most prominent in my mind. How about a hydrogen-bonded crystal, say of acetic acid? I would still call it 0D, but there is a wide range of opinion on this. It could be that it is useful to think of a hydrogen-bonded crystal as electronically 0D, but structurally 3D.

1D: Polymeric structures with all localized bonds (e.g. polyethylene) will be characterized by all narrow bands. If the polymer has some delocalized electrons, for example, π bands, as in polyacetylene, these may be wide. But the density of states (DOS) of all the bands in one-dimensional systems has a characteristic shape—large values of the DOS (van Hove singularities) at the top and bottom of each band.

2D: The electronic signature of two-dimensional delocalized lattices is a sharp "square" onset of some bands in the DOS.

3D: The variety of three-dimensional bands and resultant DOS curves is immense, with narrow and wide bands, and much overlap of bands at different points in the Brillouin zone. One characteristic of the vast majority of three-dimensional structures, but especially prominent in metallic ones, is a parabolic onset (at the bottom of the valence band) of the density of states.

Quantum confinement, the most striking expression of the *nano* in nano-objects, has a marked dependence on dimensionality. This is not a new story;[72] for a lovely experimental demonstration, see the work of Yu et al.[73]

In general structural and electronic dimensionalities go hand in hand. Very ionic crystals—take NaCl—are an interesting and well-understood exception where one has low dispersion bands, but a structurally three-dimensional crystal. Some of the most intriguing cases are metallic crystals in which structural and electronic dimensionality diverge—for instance, a structure that is three-dimensional by the interatomic separation criterion, but where there are two-dimensional, layer-like features in the electronic structure.[74]

Dirt matters, dirt doesn't matter

The ends of nanotubes, the edge of graphene or MoS_2 ribbons, the molecules on the faces of a plasmonic nanostructure—these seem not to bother much experimentalists or theorists in the nanostructure community. For the most part, we don't have good analytical techniques for finding out what the termination is, chemically. So the literature in general forgets about it, sweeping the dirt under the rug, so to speak. Renaming it as "adventitious coadsorbates" seems to help. There are exceptions—we really know a lot about the termination of silicon surfaces.[75] And precisely terminated (by hydrogen atoms) graphene nanoribbons have been made.[76]

But dirt is chemical, and there is no way in the world that dangling C atoms at the edges of graphene, or undercoordinated Mo ions in MoS_2 ribbons are going to remain that way in the real world. These "defects" are prime sites of reactivity. And the nanotube or nanoribbon is not sitting in a vacuum, it is in the midst of a chemical soup of varying complexity in which that tube was synthesized, that ribbon was excised. The surgery was not done by a Maxwell demon with his little knife—it was done by chemical reactions. Terminations and defects are chemical hot spots—they will react, they will be dirtied, chemically. As one finds for surfaces moving from high vacuum to ambient P and T reaction conditions in a catalytic reactor, so for the edges of 0D and 1D nano-objects—just about everything can go on the surface, at the ends. Hydroxide termination is popular, as is hydrogen (these from water), sulfide and SR groups are likely to bind strongly.[77,78]

Termination, even if unseen in microscopic detail, can be utilized. A clever use of "dirt", of a special kind, may be seen in the work of the Nuckols group, who etch with an oxygen plasma a gap in a nanotube, and then graft chemically a bridge between the presumed carboxylic acid groups at the cut edge.[79]

Does termination matter? Yes and no. My equivocating answer is based on some chemical analogies. We have much experience on substituent effects on structure (all those structures in the Cambridge Structural Database). For normal saturated or unsaturated molecules—think of a polyethylene or polyene (polyacetylene) oligomer, $CH_3(CH_2)_nCH_3$ or $CH_3(HC{=}CH)_nCH_3$—substituent effects of even a very strong σ or π donor or acceptor die off very quickly, my observation is that within 0.01 Å the bond distances two or three single or double bonds in from the end are the same as in an unsubstituted molecule. I think (without computational support as yet) there is something special about an odd-C-number π-electron system, essentially a polyenyl radical, in that it will propagate the effect of a π-interacting substituent further.

Edges and surfaces, if clean, certainly lead to special physics, with potentially striking experimental consequences. The transport-limiting surface traps in dye-sensitized TiO_2 nanoparticles are one example.[80,81] Another one is provided by the physics of topological insulators, materials that look from their bulk structure to be insulators, but have "protected" conducting states at their termination.[82,83]

The ambiguity of my response to the question above derives from the fact that some of the properties of nano-objects depend on the surrounding ligands, adventitious or designed. And some do not. Stability (kinetic, energetic) certainly is a function of termination. Other properties, often electronic ones—quantum confinement, plasmon oscillations—may be an inherent attribute of the nano-object. For those properties, perhaps there is no reason worry about how the nanostructure is terminated.

See below for a special problem that theory has with ends.

What you can trust about theory?

It is clear that quantum-mechanical modeling of molecules and extended structures has become easy to do. Much too easy, I would say. Not because I don't trust the results of calculations, and not because I know too well how much improper treatment of electron correlation can affect a chemical outcome—relative energies in particular, but also equilibrium geometries. What worries me more (and just what you would expect from me …) is that the calculations are done in a way blindly, with no calibration on related chemistry, no controlling checks with chemical intuition. When this gets combined with a *perceived* valuation of hype—I put it this way because in fact the granting agencies that support our research and the various prize or award-granting committees of the community know oh so well what is real achievement and what is hype—the net result is that a lot of silliness get published.

In the long run this is OK; the experimentalists are never fooled by theoretical excesses. And those of us who know chemistry, anyway teach our students how to tell senseless results from those that touch upon reality, or push through to real understanding and prediction.

There is a special problem that theory has with unterminated structures—ribbons cut off on the sides, polymers lacking ends. If passivation is not chosen as a strategy, then the radical lobes of the unterminated carbon atoms, or under-coordinated transition metals, will generate states that are roughly in the middle energetically, above filled levels, below empty levels in a typical molecule that has a substantial gap between filled and unfilled levels. If such levels—states, the physicists call them—are not identified as "intruder" states, not really real, but arising from the artifact of termination, they may be mistaken for real states in the band gap, important electronically. And if electrons are placed in them, there is no end to the trouble one can get into. These band gap states are, of course, the origin of the reactivity of the terminated but not passivated point, line, or plane. But they have little to do with the fundamental electronic structure of the material.

To return to the question posed in the heading of this section, my answer on a nice day is "*caveat emptor*" (buyer beware). And on a bad day, "Not much". Particularly suspect (to me) in the current literature are calculations tinged by chemical and physical unrealism. In this category I would place numerous claims to be able to tune band gaps by creating bizarre (to me) physical defects and chemical decorations of nanoribbons and graphenes. Or claims of ambient condition stability for hypothetical clusters without the simplest probe of computing barriers to dimerization or reaction with acids or bases.

Very reasonable to me are computations that can be calibrated by comparison to experiment at some stage. I think calculations of preferred chemisorption sites and surface reconstructions of 0D clusters and 2D surfaces are reliable. Reaction pathways are also a place where good theory can be immensely informative. It goes without saying that theory is really of value when it is used to perform numerical experiments that capture a trend. Not numbers, but a trend.

One essential place where theory really has a hard time is in dealing with amorphous matter. Aside from the natural prejudice for simplicity, people really want translational periodicity in their calculations, for then the quantum mechanical problem reduces to one of the size of the unit cell. But the real world refuses to abide by our prejudices. And it is often an aperiodic, maximally defect-ridden, amorphous world, where emergent function is found in matter that it is as far from periodic as possible. Debra Rolison documents and captures this ornery tendency of the real world in an aptly titled article, "*Catalytic Nanoarchitectures—the Importance of Nothing and the Unimportance of Periodicity*".[84]

Molecular dynamics, whether done with empirical potentials or quantum mechanics, guzzling down whatever computer resources we make available to it, at least pushes us to consider the realities of an entropic universe. A real challenge to the quantum mechanical community is to come up with ways of calculating the electronic structure of amorphous systems.[85]

Small lessons

I hope that these reflections have been more than an exhibition of my ignorance of the field. The synthetic achievements of nanoscience are incredible—who could have imagined such fine control of mesoscale structure! The fine tuning of color, magnetism, and catalytic activity[86] by nanostructural detail is truly impressive. And the field is so interdisciplinary—it forces its practitioners to step outside, step across.

The ideas I have discussed are pretty simple (or perhaps I have made them simpler than they should be). And these ideas are part of the general knowledge of the community. That the instability attendant upon severance of strong bonds in nano-object formation should have strong consequences on structure and reactivity is obvious. As is the fact that we should pay attention to the lessons of surface science on relaxation and reconstruction, with bond breaking and reformation an essential part of the way we think about these processes. It makes sense that the reactivity of nano-objects, as well as strategies for their stabilization, can be understood with simple acid and base ideas. Frontier orbital arguments, my stock in trade, are just another (very useful) way to approach questions of reactivity. The ambiguities lurking in our facile attribution of dimensionality, the deeper real questions about dimensionality in materials that I have posed—these are not original to me; they occur to anyone pondering nano-objects.

There is little original in what I say, but perhaps there is some value in seeing what is known in another light.

Simple chemistry, be it of Si–Si multiple bonds, of Se and Cd in their compounds, of Zintl phases and [$Co_4(CO)_{12}$], of the geometrical peculiarities of a Si(100) surface reconstruction, clearly speaks to the new, nano world. What we have learned in chemistry, beautiful knowledge, gained without waiting for microscopes to let us physically see down in there, of course applies to nano-objects. It's one world.

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