

Quantum Dots : A New Regime In Science

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ABSTRACT

There are music instruments in which the excited waves are mostly inside a resonance body, for example in guitars or in organ pipes, but in others it is primarily the surface which is excited, such as in drums, where there are two-dimensional waves of the excited skin. In the same way there are not only volume waves the conduction electrons but also collective excitations of surface electrons. Breaking the crystal also breaks the local symmetry at the new surface. Atoms or molecules which previously occupied a site with a symmetry corresponding to their position in the bulk lattice are now found near the surface where the transitional periodicity stops at the surface, while it is still there towards the inside of the crystal.

1. INTRODUCTION

Nanotechnology and nanomaterials are expressions which have received enormous publicity in recent years. In general, nanotechnology is the word used for the manipulation of individual objects on an atomic or molecular scale or for nanostructures produced by lithographic techniques, while nanomaterials are nanoscale particles which can be produced by chemical synthesis and handled in masses. In both cases it is the special properties, different from those in the bulk, which causes the excitement.

Recognition of size effect started 1871 with William Thomson (knighted to Baron Kelvin of Large when he describes the size-dependence of the melting point of small particles or of pore-confined matter, a relation known as the Gibbs-Thomson equation. It combines the Clausius-Clapeyron equation for the temperature-pressure relation of phase transition equilibria with the Kelvin equation that describes the dependence of the vapour pressure of a small droplet on its radius.

Today there are many existing and planned applications which make use of nanosize effects intentionally. These range from catalysis over energy-related materials (solar cells, fuel cells, batteries, and hydrogen storage), nanomagnets and transistors (or other elements for electronics) to quantum dots where individual bits can be stored for quantum computing.

It turns out that size effects have two origins : they are either surface effects or quantum confinement effects. The surface effect reflects that the stabilization of an atom in a solid or liquid environment scales with the number of neighbours to which it can make bonds. The temperature of melting or of any other phase transition relates to this stabilization and therefore to the average number of neighbours. This leads to a smooth scaling law of transition temperature with particle radius or thickness of a layer or wire. The second effect applies only to conducting (metallic) or semiconducting materials.

2. SURFACE EFFECTS AND QUANTUM

CONFINEMENT EFFECTS

The dispersion f of a sample is defined as the fraction or percentage of atoms at a surface, relative to the total number of atoms in the sample. The surface area of a sphere, $A = 4\pi r^2$, divided by volume, $V = 4\pi r^3/3$, or in terms of diameter d , $6/d$. neglecting edge effects, the $F=A/V$ for large, thin plates of thickness d equals $1/d$, and also for long cylindrical wires $F=1/d$. thus, for anybody where a single narrow thickness d is defined the dispersion scales smoothly as $1/d$. this is the basis for the explanation of many observed properties which scale smoothly as $1/d$ or $1/r$, indicating that it is a surface effect.

The above scaling law extrapolates to infinity as d goes to Zero, which is unphysical. When the diameter of a specimen reaches the diameter of two atoms, every atom is directly exposed to the surface, and $F=1$. This is illustrated in figure for the example of cubic crystals with n atoms along an edge and a total number of $N=n^3$ atoms. The atoms are counted and F calculated as follows :

$$F = \frac{6n^2 - 12n + 8}{n^3} = \frac{6}{N^{1/3}} \left(1 - \frac{2}{N^{1/3}} + \frac{8}{6N^{2/3}} \right) \approx \frac{6}{N^{2/3}}$$

Electrons behave at the same time as particles and as waves. As waves they explore the entire space in which they are free to move. In clusters of noble gases they remain confined to the atoms, and in clusters of molecules like water or carbon dioxide they remain confined to these molecules. Noble gases or molecular clusters therefore do not show quantum size effects beyond the ones which they show in the isolated atoms or molecules. However, in semiconductors or metals the conduction electrons are free to move in the entire cluster or particle, and the electron waves adapt to the size of the particle in such a way that the nodes (this is where the amplitude of the oscillating wave is zero) of the waves are at the surface.

There are music instruments in which the excited waves are mostly inside a resonance body, for example in guitars or in organ pipes, but in others it is primarily the surface which is excited, such as in drums, where there are two-dimensional waves of the excited skin. In the same way there are not only volume waves the conduction electrons but also collective excitations of surface electrons.

Breaking the crystal also breaks the local symmetry at the new surface. Atoms or molecules which previously occupied a site with a symmetry corresponding to their position in the bulk lattice are now found near the surface where the translational periodicity stops at the surface, while it is still there towards the inside of the crystal.

Breaking the crystal also creates an imbalance of forces at the surface which calls for a new equilibrium. The dangling bonds of a fresh diamond surface want to be satisfied, and they achieve this by forming chemical bonds to molecules which are available in the environment. In humid air they will be terminated after a short time with surface hydroxyl groups. Many metals will form a thin oxide layer that lowers the surface energy. Both these effects occur by forming chemical bonds, a process that is called chemisorptions. Lower energy surfaces tend to further lower their energy by physisorption, i.e. by forming weaker adsorptive bonds. Such processes are extremely important in nanochemistry and serve to stabilize small particles by capping their surface but also to steer the morphology of crystallites of a given crystal structure to a wide variety of shapes. The basis of the latter process is the different adsorption strongly on a given surface essentially blocks this surface from growing. At other facets adsorption may be weak and dynamic, so that further atoms or molecules may be added whenever the adsorbate has left a surface site free for a moment.

3. THE AVERAGE COORDINATION NUMBER AND THE STABILITY OF A PARTICLE

In face-centered and hexagonal close packed cubic crystal structures an atom in the bulk is in direct contact with 12 neighbors, i.e. its coordination number is 12. A fragment of such a structure and the coordination number of several atoms at the surface is indicated. The highest value that is shown is 9 for an atom inside a surface layer of a (111) crystal face. It is readily seen that it is surrounded with six atoms of the same plane, and from below it is in contact with three further atoms. If one would place another layer on top this would give the atom three more direct neighbours and the full bulk coordination number of 12. An atom on the (110) surface has only four direct neighbours in the same plane, four more make contact from below, giving it a total of 8. Corner atoms have rather low coordination numbers.

To first order, if we neglect the interactions with the second and higher shells, each direct neighbour contributes with one bond to the binding energy or cohesive energy of an atom in the lattice. The total cohesive energy of a crystallite is the sum of all atomic contributions (without counting the interaction of a pair of atoms A – B and B – A twice). Obviously the smaller the crystallite the higher the dispersion and therefore the fraction of atoms with a lower coordination number, which results in a decrease of the average cohesive energy per atom. Plotted as a function of the number of atoms $N^{-1/3}$ this gives a linear scaling, showing convincingly that the origin is a surface effect.

The extrapolated coordination number for the bulk is 12, and the calculated cohesive energy per bond is 0.23 eV (experimental value : 0.25 eV, one-sixth of the bulk binding energy per atom). The large change in cohesive energy per atom is impressive. It is plausible that this will have consequences for the melting or sublimation temperature of a cluster.

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