Small is different: self-assembly and self-selection of size, shape and form in the nanoscale

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Finite materials systems with dimensions in the nanoscale range are often created through spontaneous, or directed, self-assembly, with self-selection of size (number of atoms), shape (spatial arrangement of the constituents), and form, that is thermodynamic phase (solid, liquid or gas), charge state, and degree of order (e.g., crystalline, disordered or amorphous). In a conversation in 1990 in Atlanta, Heinrich ('Heini') Rohrer (1933-2013) to whose memory this lecture is dedicated, termed this behavior in the nanoscale as "Nature's Way". In this lecture we discuss and demonstrate through computer-based first-principles quantum computations and simulations [1], often in conjunction with laboratory experiments, some of the key physical principles that underlie and govern the properties of materials at the nanoscale, exhibiting discrete quantized energy level spectra and specific structures and morphologies manifested in unique, non-scalable, size-dependent physical and chemical properties. These properties are often of emergent nature - that is, they are not commonly expected, or deduced, from knowledge learned at larger sizes. We focus on the following topics: (i) Formation, atomic arrangements, and properties of self-assembled metal nano-crystals protected by organic monolayers, whose structure and stability originate from superatomic electronic shell-closure (2); (ii) Size-dependence, structural fluxionality and dimensionality cross over in nanocatalysis (3), and (iii) Shape-transitions and electrocrystallization of liquid droplets brought about by applied electric fields (4).

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