EXPLORING MESOSCOPIA: THE BOLD NEW WORLD OF NANOSTRUCTURES

The revolutionary creation of new materials with controlled properties via nanostructuring is making possible a wide variety of technological advances.

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Interest in the physics of condensed matter at size scales larger than that of atoms but smaller than that of bulk solids—so-called mesoscopic physics—has grown rapidly over the past two decades, but it stems from much earlier beginnings in diverse disciplines. Indeed, nanostructured matter apparently had its genesis with the Big Bang. The structures of the earliest meteorites suggest that matter formed by the condensation of atoms into nanoscale clusters that then aggregated into larger masses under the action of gravity. Many examples of natural nanostructures can be found as well in biological systems from seashells to the human body.

However, the intentional and controlled human nanostructuring of matter did not begin until well into the second half of this century, after the *Physical Review* had already passed its 50th birthday. Many of the wide variety of threads that led to the creation of the new field of nanostructured materials have been woven into the prestigious fabric of the *Physical Review* throughout its recent history.

It is rather difficult to establish a date or distinguish any seminal event for the conception of the nanostructuring of condensed matter. As long ago as 1959, Richard Feynman at Caltech spoke in a prescient lecture to the American Physical Society about the creation of materials with new properties by the manipulation of matter on a small scale:[1]

> I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have.

The actual nanostructuring of condensed matter would wait some years. The interest in assembling materials from nanometer-sized "building blocks," whether layers

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or clusters, arose from the realization that by controlling the sizes of such atomic ensembles in the range of 1–100 nm one could begin to alter and prescribe the properties of the assembled nanostructured materials.

The theoretical formulation of quantum confinement by Ryogo Kubo[2] at Tokyo University in the early 1960s did much to launch this interest, although ultrafine particulates had long been synthesized and used for their unique properties. Following Kubo's work, researchers began to understand that ensembles of matter containing only tens to thousands of atoms could have structures and properties quite different from those of conventional materials on a coarser size scale, and work began in earnest around the world to investigate ultrafine particles and ultrathin films of matter. For example, it was found that even a cooperative phenomenon such as melting could be effected in small clusters of atoms at temperatures far below the melting point of the conventional solid.[3,4] (See figure 1.) The exploration of the physics of atomic ensembles in the mesoscopic size regime had begun. Researchers developed a variety of clever methods for the artificial nanostructuring of condensed matter (molecular-beam epitaxy, chemical vapor deposition and gas condensation, for example) and the high-resolution imaging of these structures (high-resolution electron microscopy and scanning tunneling microscopy, for example). The small but expanding world of "mesoscopia" would never be the same again.

Multilayers, clusters, nanophase materials

Among the various nanostructures, multilayered materials have had the longest history; they have already seen applications to semiconductor devices, strained-layer superlattices and magnetic multilayers.[5] The first of these applications was investigated as early as the 1970s, when Leo Esaki and his coworkers at IBM postulated and demonstrated the possibility of nanostructuring multilayered quantum heterostructures using newly developed
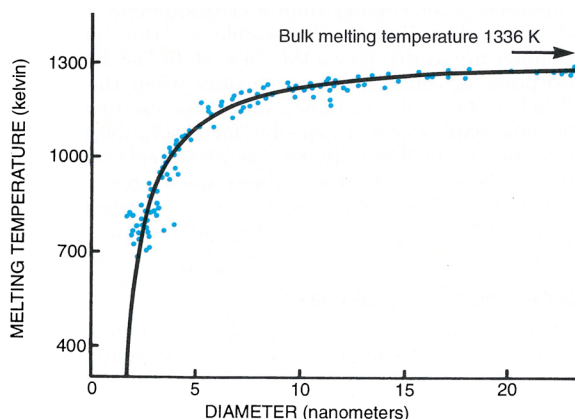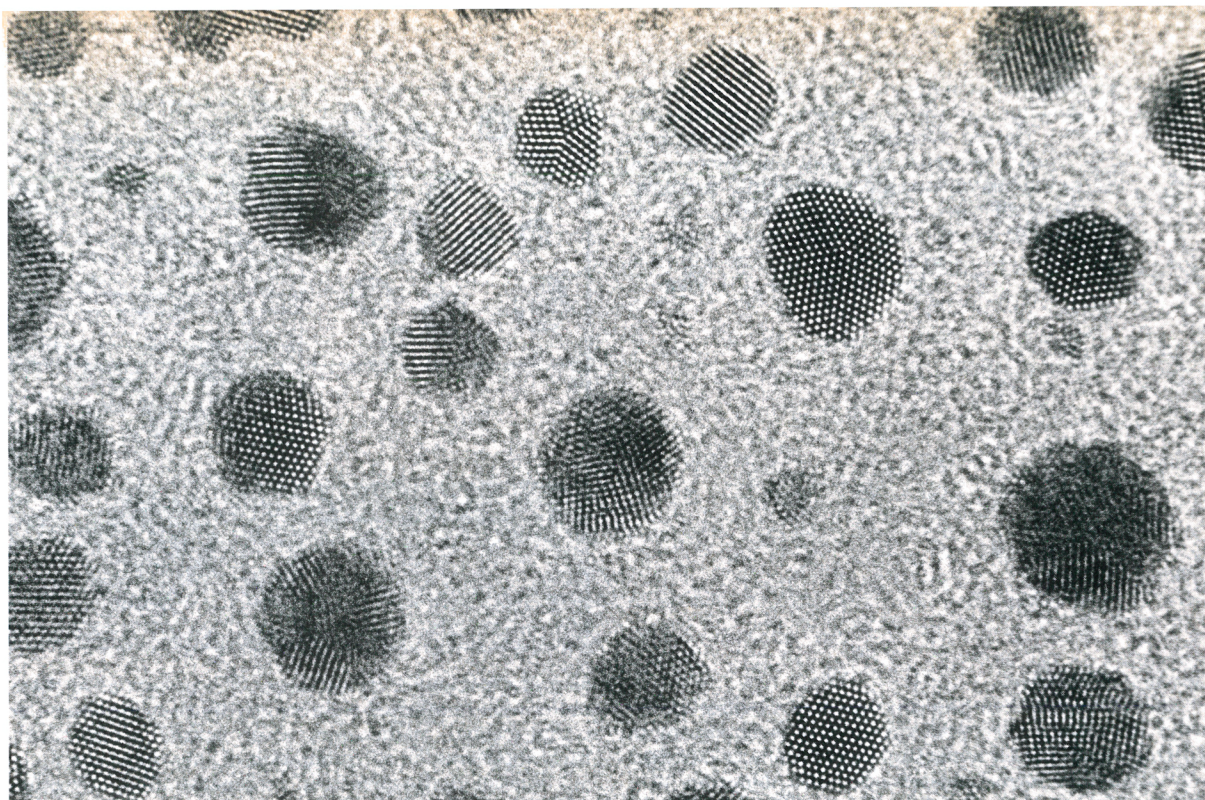
Gold clusters and the size dependence of their melting temperature. The spacing of atomic planes in the high-resolution electron micrograph above is about 0.2 nm. The melting temperature (left) was determined by electron diffraction. (Image courtesy of Marc Flüeli and Philippe-André Buffat; graph adapted from ref. 3.) **Figure 1**

methods for growing thin semiconducting films.

The evident technological potential of these new devices in the burgeoning electronics and computer industries helped to drive the rapid advances in that exciting new field. By using the low-dimensional quantum states in these multilayers, it became possible for the first time to engineer a variety of electronic and photonic devices, such as high-speed field-effect transistors and high-efficiency lasers. More recently, nanostructuring of multilayers has allowed creation of a variety of nonlinear optoelectronic devices, such as lasers and light-emitting diodes. Informative articles in these and closely related areas have recently appeared in these pages. (See the February 1990 special issue of PHYSICS TODAY on nanoscale and ultrafast devices; the articles by Leroy L. Chang and Esaki and by L. M. Falicov, October 1992, pages 36 and 46, respectively; and the June 1993 special issue on optics of nanostructures.)

Research on clusters in the 1970s included both experimental studies and theoretical calculations of their atomic and electronic structures.[6] However, it was really not until after the advent of beams of atom clusters with selected sizes that one could critically explore the physics and chemistry of these confined ensembles. Since then, research on isolated clusters of atoms has rapidly expanded, and understanding of their potential, particularly as constituents of new materials, has increased.[7]

The synthesis of materials by consolidation of small clusters was first suggested in the early 1980s by Herbert Gleiter at the University of the Saarland in Germany and was applied initially to metals[8] and then to nanophase ceramics.[9] (Nanophase materials are modulated over nanometer length scales in three dimensions.) Most recently, a variety of carbon-based fullerenes have also been assembled into materials with much potential interest.[10] The field of cluster-assembled nanophase materials has grown rapidly during the last several years, as has that of nanostructured multilayers. In addition to effects of confinement, interfaces play an important and sometimes dominant role in these two

Nanostructured materials. The schematic drawings show the four types of nanostructured materials, classified according to integral modulation dimensionality, from zero in **a** to three in **d**. **a:** Clusters of any aspect ratio from 1 to infinity. **b:** Multilayers. **c:** Ultrafine-grained overlayers, coatings or buried layers. **d:** Nanophase materials. Intermediate cases can also exist. (Adapted from ref. 11.) **Figure 2**
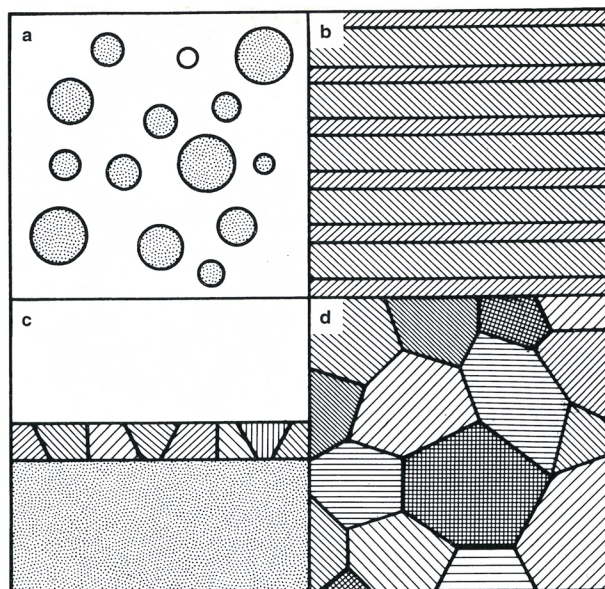
classes of material.

Knowledge of how the physical and chemical properties of clusters vary with cluster size is important to both our fundamental understanding of condensed matter and our ability to use cluster-assembled materials in a variety of technological applications. The manner in which the structures and properties of collections of condensed atoms in a single cluster vary with cluster size, from atomic or molecular behavior to bulk solid-state behavior, is a touchstone in the development of realistic theoretical models for condensed matter. (See the article by Marvin L. Cohen and Walter D. Knight in PHYSICS TODAY, December 1990, page 42.) Such variation has an impact on our understanding of the forces acting among atoms, the structures of collections of atoms, electronic effects caused by spatial confinement of delocalized valence electrons ("quantum size effects") and cooperative atomic phenomena such as lattice vibrations or melting ("many body" phenomena).

It is becoming increasingly clear that one can synthesize nanophase materials assembled from atom clusters with a wide variety of unique or improved optical, electronic, magnetic, mechanical and chemical properties with attendant potentially useful technological applications. This possibility is creating a new revolution in our ability to engineer condensed matter for the needs of society. In this respect, these materials are following in the footsteps of the nanostructured multilayered semiconducting materials that have had such a profound impact in electronics and computers.

Nanophase materials are closely related to nanostructured multilayers in that they are basically the three-dimensional analogs of those one-dimensionally modulated structures. The creation and development of these two types of materials have followed somewhat parallel paths separated by more than a decade, but it is becoming ever more apparent that they, along with clusters and their two-dimensionally modulated analogs—nanostructured coatings, overlayers and buried layers—form a logical set of nanostructured materials.[11] (See figure 2). All of these materials are modulated over nanometer length scales in zero to three dimensions, are spatially confined below 100 nm in at least one of these dimensions and have a significant percentage (greater than 1%) of their atoms associated with interfaces such

as grain boundaries or surfaces. The properties of these materials are affected significantly by their structural or compositional modulation, their spatial confinement, their interfaces or a combination of these parameters.

Spatial confinement can in general affect any property when the size of the atomic ensemble becomes comparable to or smaller than a critical length scale for the mechanism that is responsible for that property. Examples are as diverse as the "blue shifts" of the optical absorption in semiconducting clusters when their sizes fall below the 5–50-nm Bohr radii of the excitonic (electron–hole pair) states responsible for absorption and the strengthening of normally soft metals when their grain sizes fall below about 50 nm, where the sources of dislocations (the defects responsible for easy deformation) become difficult to activate under conventional applied stresses.

Some recent successes

During the past several years the physics, chemistry and materials research communities have made exciting progress in characterizing and understanding nanostructured materials, including individual atom clusters, cluster-assembled nanophase materials and multilayers. Since confinement affects magazine articles as well as materials, I will describe only a few of the many notable examples.

The structures of individual atom clusters are difficult to characterize, owing to the very small size scale involved. Direct observation methods, such as electron microscopy, are useful in probing the structures of clusters larger than about 2 nm that contain hundreds of atoms or more. Methods with greater resolution, such as field-ion or scanning tunneling microscopy, which might be used to observe smaller clusters, suffer from the need for the clusters to be placed on a substrate that may alter their structure.

However, experiments have successfully characterized the structures of isolated small clusters containing tens of atoms by using their chemical activity as a probe. As atoms are individually added to a cluster, the ability of the cluster to react chemically with surrounding gas molecules changes, depending on the particular atomic structure of its surface. Stephen Riley and his coworkers at Argonne National Laboratory[12] have used this selective

Nickel cluster. The model shows how a 55-atom icosahedral cluster could absorb 44 hydrogen atoms (green and blue) and how an H_2O molecule (oxygen in dark blue) would preferentially bind to a 56th nickel atom (orange) located outside the icosahedral shell. Experimentally, Ni_{55} binds 44 hydrogen atoms, and Ni_{56} exhibits dramatically enhanced binding of H_2O, supporting this structural assignment. (Adapted from ref. 12.) **Figure 3**
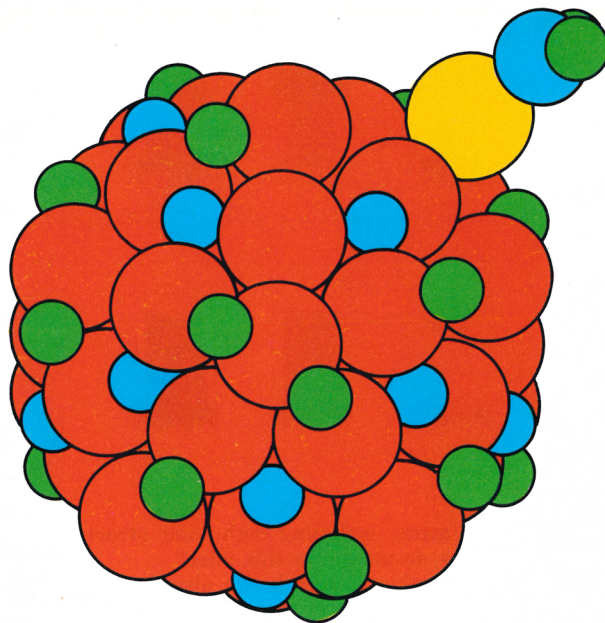
chemical reactivity with ammonia or water molecules to characterize the atomic structures of clusters containing fewer than about 200 atoms of either of the transition metals nickel or cobalt. (See figure 3.) They find that the structure changes with the addition of metal atoms, though not in a monotonic fashion, and it changes differently for the two metals. The atoms are arranged in an icosahedral structure for some size ranges and in more closely packed structures typical of bulk metals at other sizes. The propensity for forming the icosahedral structure is greater in the nickel clusters, consistent with the decrease in d-electron bonding in nickel relative to cobalt.

The optical properties of noninteracting assemblages of small semiconductor clusters are exciting from both the scientific and technological points of view. Louis Brus and his colleagues at AT&T Bell Laboratories[13] have synthesized cadmium selenide clusters containing hundreds to thousands of atoms over a range of average diameters in the nanometer regime. These clusters are chemically capped to yield very narrow size distributions and to prevent them from interacting with one another when assembled in liquid or solid media. As a result, the optical properties of the assembled clusters are essentially the same as those of the individual clusters.

In such a small CdSe cluster, the loosely bound valence electrons are confined in space more than they would be in a material of conventional size. They therefore absorb light in a different frequency range. Indeed, the frequencies of light absorbed depend directly upon the degree of such quantum confinement and hence on the cluster size. Thus assemblages of CdSe clusters of different sizes can appear to have different colors across the full spectrum of visible light. (See figure 4.) Not only do such quantum size effects in clusters provide a basis for verifying our understanding of the electronic structure of condensed matter, but they may also provide for engineered optical properties that will find useful applications in optical and computing devices.

The assembly of larger atom clusters into bulk nanophase materials can also have dramatic effects upon their properties. In this case, the clusters interact fully with one another, yet the effects of cluster size are still very important. Clusters of metals or ceramics in the size range of 5–25 nm have been consolidated to form ultrafine-grained polycrystals that have mechanical properties remarkably different from and frequently better than those of their conventional coarse-grained counterparts.

For example, nanophase copper and palladium assembled from clusters with diameters in the range of 5–7 nm can have hardness and yield-strength values up to 500% greater than those of the conventionally produced metal.[14] This increased strength arises from the increased difficulty of creating and moving dislocations in the spatially confined grains of nanophase metals.

In ceramics, on the other hand, which are normally difficult to deform and hence very brittle, cluster assembly yields a different benefit. One can render ceramics ductile[15] (capable of easier deformation) by synthesizing them from clusters with sizes below about 15 nm. This ductility results from the increased ease with which the ultrafine grains created by the clusters can slide by one another in a process called grain-boundary sliding. This increased ease of sliding is enabled by the short diffusion distances in these materials that are required for the necessary local healing of incipient cracks that could otherwise form during this grain-over-grain sliding process.

It is very early in the application of these new materials, but both the increased ductility exhibited by nanophase ceramics and the increased strength observed in cluster-assembled metals should find use in a wide variety of future technological applications, including small machine parts for which wear or corrosion resistance is an important design criterion.

In magnetic multilayers, such as those formed by alternating layers of ferromagnetic iron and chromium, it is possible[16] to nanostructure the system so that its electrical resistance decreases by up to a factor of 2 through the application of a magnetic field of 2 tesla. Such a large effect, called giant magnetoresistance, occurs when the magnetic moments of the neighboring alternating layers of Fe and Cr are arranged in an antiparallel fashion; then the application of the magnetic field overcomes the antiferromagnetic coupling and aligns the layers into a condition of parallel ferromagnetic ordering, strongly reducing the electron scattering in the system. It is important to control the nature of the interfaces
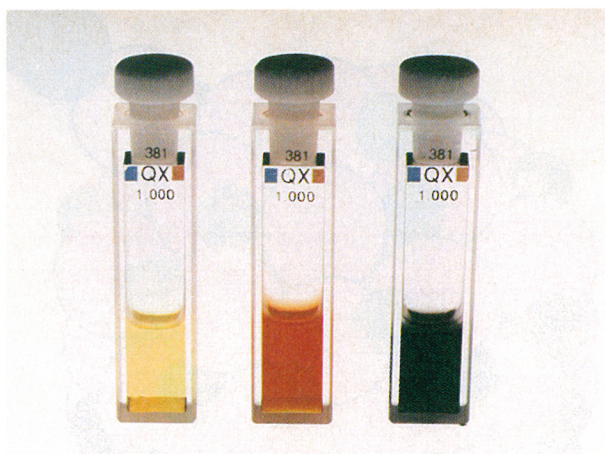
Colors indicating varying degrees of quantum confinement.[13] The cuvettes contain phenyl-capped CdSe crystallites of differing sizes dissolved in 4-ethylpyridine. Left: Clusters of 1.2–1.5 nm diameter and 3.0 eV bandgap. Center: 3.0–3.5 nm diameter, 2.3 eV bandgap. Right: Bulk material, 1.8 eV bandgap. **Figure 4**

between the layers, including both their structure and their chemistry, to maximize this effect.

Magnetoresistive materials are already used in the magnetic recording industry as read heads owing to their low noise and good signal handling capabilities. One can expect nanostructured materials to have a significant impact in this area as researchers develop new materials with stable giant magnetoresistance at room temperature that can operate at low magnetic fields around 10^{-3} tesla. The exciting recent discoveries that nanostructured materials other than multilayers (such as magnetic cobalt clusters embedded in a nonmagnetic matrix of copper or silver, or magnetic plate-like NiFe deposits embedded in silver) also exhibit giant magnetoresistance should hasten the advent of their useful application.[17]

The future

Research published in the *Physical Review* and elsewhere over the past several years indicates that there are tremendous opportunities for synthesizing nanostructured materials with new architectures. This synthesis can be done from atomic or molecular precursors via the assembly of atom layers and clusters and by a myriad of other techniques now becoming available, such as nanoscale lithography and biological templating. The keys to the future of nanostructured materials, however, are our ability to continue to improve the properties of materials by artificially structuring them on nanometer length scales and our ability to develop the methods for producing these materials in commercially viable quantities. Based on what we have learned to date about mesoscopic physics and on the successes secured by the entry of nanostructured devices into industry, it appears that the future holds great promise for nanostructured materials.

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