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Preface

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1 The story behind the Nanotube Rush

Nanotubes have evolved into one of the most intensively studied materials and are held responsible for co-triggering the Nanotechnology Revolution. Why? This preface attempts to provide a brief answer to "why" and "how" nanotubes have kept amazing both Scientists and Engineers over the past decades.

Even though nanotubes have been identified as contiguous hollow tubes in the core structure of carbon fibers in the 1970's [1], their popularity rose drastically following their observation on the cathode of a carbon arc used to produce fullerenes [2], the starting point of the Nanotube Rush era. Nanotubes, especially those of carbon, excite both fundamental scientists and engineers interested in applications due to the unique combination of their properties.

First of all, these molecular systems are nanometer-sized in diameter, but up to centimeters long, yielding an unprecedented length/diameter aspect ratio exceeding 10^7. Carbon nanotubes can be thought of as narrow strips of graphene [3] rolled up into seamless tubes. They form spontaneously and efficiently under well-defined conditions either as single-wall nanotubes (SWNTs) or nested multi-wall nanotubes (MWNTs). Contiguous carbon nanotubes exhibit a high degree of atomic-scale perfection. This fact, along with their close relationship with graphene, makes nanotubes chemically inert. Same as graphene under tension, nanotubes are two orders of magnitude stronger than steel at 1/6th of the weight. The melting point of nanotubes of about 4,000 K in "ideal" vacuum [4], close to that of graphite, exceeds that of any metal. Depending on the atomic structure of nanotubes, including diameter, single-wall nanotubes act as ballistic conductors of electrons or show semiconducting behavior. Carbon nanotubes seem to be also excellent conductors of heat, expected to exceed the record thermal conductivity of isotopically pure diamond. Moreover, similar to the related graphite, carbon nanotubes appear to be bio-compatible in many environments.

2 Nanotube applications guiding the way

Due to the amazing combination of their properties, nanotubes appear ideal for a wide range of current or future applications. Their high mechanical strength, combined with high electrical/thermal conductivity, allows the formation of strong, transparent, yet electrically and thermally conductive composites – including electromagnetic shielding of cables and conductive coatings of aircraft components – at relatively low loading levels of very few weight percent. Nanotubes can also be spun into yarns with toughness competing with Kevlar. Nanotube yarns can be knotted, plied, braided and woven into conductive fabrics that remain tough even under ultraviolet radiation.

Due to the large aspect ratio, as near other "sharp" objects, the electric field is locally enhanced by two orders of magnitude close to the tip of nanotubes, thus significantly enhancing their field electron emission properties. Since – unlike other cold cathodes – nanotubes have a high melting point and maintain their high aspect ratio over time, they have a future as successors of electron guns in cathode ray-tube (CRT) displays with a significant advantage: nanotube arrays attached to a substrate make bright, ultra-flat displays, with each pixel lit by the current from several gated nanotubes beneath it.

Due to their long electron mean free path, single-wall carbon nanotubes are ballistic conductors of electrons or holes, which makes them appealing as building blocks of future molecular electronics circuits. Carbon nanotube-based field-effect transistors surpass in all the relevant criteria current silicon-based devices at a small fraction of the size. Carbon nanotubes are also likely to play a key role in future electronics applications, including spintronics and quantum computing.

Nanotubes have found a large-scale application as an additive to the graphite component of Li-ion batteries. Forming an elastic filler, they absorb the slack and prevent reorientation of graphite crystallites during their expansion/contraction associated with the intercalation/deintercalation of Li ions, thus increasing energy delivery and the number of useful charge/discharge cycles. High conductivity combined with a high surface-to-volume ratio opens an application of nanotube assemblies as electrodes in super-capacitors and fuel cells. Unusual arrangements of conductive and insulating nanotube yarns may yield electronic fabrics with supercapacitor functionality.

Under various conditions, nanotube arrays appear to be bio-compatible with human tissue. The combination of their nanometer-size diameter, well-defined cylindrical shape, and lack of chemical reactivity offer promises for the use of nanotubes as efficient templates for the proliferation of neurons. With carbon nanotubes as additive to nylon micro-catheters used in surgery, the occurrence of thrombus formation appears to be efficiently suppressed.

Even though no longer at the forefront of potential applications, reversible hydrogen storage is likely to benefit from the light weight and large accessible surface area of nanotubes and related sp^2 bonded carbon nanostructures. Reproducible measurements suggest the capability of carbon nanotubes to store up to 2% (weight) molecular hydrogen at room temperature.

3 Nanotubes as a test ground of fundamental science

Even though it was the applications of nanotubes that have grabbed most of the media limelight, nanotubes themselves offer a unique possibility to explore fundamental properties of quasi one-dimensional (1D) conductors and semiconductors. For one, any phase transition – including onset of superconductivity or magnetic ordering – should be suppressed in strictly one-dimensional systems. Furthermore, free carriers in one-dimensional conductors have been postulated to behave as a Luttinger liquid rather than being subject to the Fermi-Dirac statistics. The screening behavior of these 1D systems modifies the optical properties of nanotubes significantly. An important example is the large binding energy of excitons that, in semiconducting nanotubes, is two orders of magnitude larger than in 3D semiconductors and thus comparable to the band gap.

4 Problem solution by hand-in-hand collaboration between Experiment and Theory

Many initial problems have been solved since the beginning of the Nanotube Rush era. Intensive collaboration between Theory and Experiment, especially in the field of single-wall nanotubes, became the key to rapid progress, which continues until the present. Among the many examples, observed inconsistencies in nanotube conductivity measurements were reconciled by learning, how to make good contacts reproducibly. Also, superconducting behavior in nanotubes has only been observed, after good contacts between nanotubes and leads have been established. Still, many problems remain and await solution, including the controlled production of carbon nanotubes with a well-defined atomic structure, which is a critical parameter in deciding, whether a particular SWNT is metallic or semiconducting, and whether it will perform to required specifications.

The entire arsenal of experimental and theoretical techniques that had been developed to characterize low-dimensional systems, ranging from nanoparticles to surfaces, has been applied to nanotubes. Nanotube metrology has matured to a well-established field affecting not only quality control, but also providing guidance regarding the likely behavior of particular samples. On the experimental side, most direct information about the morphology of individual single- and multi-wall tubes, including diameter and interlayer spacing, has been provided by high-resolution transmission electron microscopy. Raman spectroscopy has proven especially valuable in providing information about the fraction of graphitic carbon in the sample and determining the distribution of nanotube diameters by analyzing the diameter-dependent radial breathing mode. Photoluminescence spectra offer a powerful way to determine the chirality distribution among semiconducting nanotubes. These methods are often combined with Scanning Probe Microscopy and other spectroscopic techniques to characterize nanotube samples in terms of uniformity, purity, chemical modifications, and defects.

Theoretical techniques used to investigate the relative stability and mechanical properties of nanotubes range from continuum elasticity theory to bond-order potentials. Since the electronic structure in carbon nanotubes is dominated by $2p\pi$ electronic states, the single $pp\pi$ band Hückel model has proven very useful in understanding the electronic structure and quantum transport in nanotubes. *Ab initio* density functional theory (DFT) calculations, or their parameterized tight-binding counterparts, are the methods of choice to determine the electronic structure and stability of pristine and functionalized nanotubes and related structures in the electronic ground state. Description of excited-state dynamics of nanotubes requires calculations beyond DFT, including combinations of time-dependent DFT with molecular dynamics, GW calculations of electronic spectra, and the Bethe-Salpeter equation to describe excitonic states.

5 Future of Carbon Nanotubes

In the first decade of the 21st century, almost two decades after the onset of the Nanotube Rush, the Nanotube field is as vital as ever. The rate of publications and patent applications in the field of nanotubes is continuously increasing. Whereas the stream of breakthrough discoveries has been holding on until the present, other outstanding problems, identified in this book, still await solution. Cross-fertilization with emerging related fields, such as graphene, will likely accelerate progress by providing insight from a different viewpoint. The continuing vitality of the nanotube field is unusual, when compared to other research areas that initially appeared at least as appealing, including the field of Fullerenes and High-Temperature superconductivity. Reasons for the unexpected evolution of the field in the recent past may bear hints about the future.

One feature that sets the field of nanotubes apart from other similarly appealing areas is the wide field of promising applications, ranging from molecular electronics and quantum computing to materials science and medicine. Fundamental interest in the properties of this unusual material, combined with an apparently unlimited potential for applications, have sparked off international, interdisciplinary collaborations on a previously unprecedented scale and demonstrated the benefits of such collaborations.

The intense need for communication among the disciplines established sections dedicated to Nanotube Science at many conferences in different fields. The Internet offers web sites dedicated to Nanotubes, linking the scientific Nanotube community together and providing advice to the interested novice. Conferences dedicated to nanotubes, including the NT series initiated by the NT99 workshop in 1999, attract hundreds of scientists every year to new venues and new countries. With their vision to provide access to information for all at minimum cost and to foster scientific collaboration between different disciplines and cultures around the globe, nanotube conferences fulfill several worthy missions at the same time. Very appealing appears their educational mission, namely to give young aspiring scientists a fair chance to discuss with their senior colleagues. The inspiration coming from days of intense information exchange, where age differences are swept away in the heat of the discussion, is likely to fuel the nanotube field for many more years to come.

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References

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2. S. Iijima, Nature **354**, 56 (1991).
3. Graphitic carbon is a layered structre. Graphene is a monolayer of graphite.
4. Computer simulations suggest that the melting temperature of nanotubes should lie close to ≈4,000 K, observed in high-purity graphite. The observed reduction of the melting point to above 3,000 K has been linked to defects and residual oxygen under experimental conditions.