ATOMIC STRUCTURE OF COILED CARBON NANOTUBES

Amand A. Lucas

Physics Department
Facultés Universitaires Notre-Dame de la Paix
B5000 Namur, Belgium

INTRODUCTION

Following the Fullerene discoveries [1], carbon nanotubes were first observed [2] as a byproduct of the arc-discharge synthesis of C60 [3]. Now monolayer and multilayer nanotubes can be prepared by several methods [4]-[9]. In particular the CCVD (catalysed chemical vapor decomposition) method used to grow carbon microfilaments [7] has been successfully adapted to reduce the diameter of the filaments to the nanometer size range [8]. In the work of Ivanov et al [9], a Co-silica catalyst was used to decompose acetylene in various experimental conditions which could be optimized to obtain a fairly narrow distribution of outer diameters of 15-20 nm. Post annealing in H_2 resulted in nanotubes being rid of most of their amorphous carbon coating [9], leaving well graphitized nanofilaments suitable for detailed studies with high resolution transmission electron microscopy (TEM) and diffraction (TED) [10].

COILED NANOTUBES

Among the most interesting morphologies observed in TEM [9], [10], coiled nanotubes occured in up to 10 % abundance. These nanostructures are similar to the coiled microfilaments observed previously and studied e.g. in ref.[11]. The quality of the graphitization was such that a novel textural characteristic of the coils could be revealed for the first time, namely that the coiling does not take place continuously but in a stepwise manner. This is immediately understood by refering to Fig.1 which shows a model of a coiled wire wound on a cylinder of either circular or polygonal cross sections. The nanotubes are made of a regular succession of pieces of straight cylindrical tubes somehow linked together at the sharp bends, as in Fig.1b. This polygonized structure was revealed by direct high-resolution TEM and confirmed by selected area TED [9], [10]. The reader is refered to these published works for details on the observational evidences. Kinetic arguments have been advanced in ref.[12] to explain the possible growth mechanism of such structures.

ATOMIC STRUCTURE

High-resolution TEM [9] shows that the lattice fringes of the individual cylindrical graphene sheets remain continuous through the successive bends of the coil. Another important piece of evidence obtained from TEM and TED was that there are about a dozen bends per coil turn. Hence the bend angle, projected onto the plane normal to the coil axis, must be around 30°. Graphite is so stiff for inplane deformations that it is inconceivable that such sharp bends could be realized by a continuous elastic deformation of an initially straight tube. Besides, the deformed tube would not be stable under removal of the elastic stress. It appears that some plastic deformation at each bend must have been introduced during the growth process. Grain boundaries could be excluded by the lack of TEM evidence and their incompatibility with the cylindrical geometry. Hints as to the nature of the defects responsible for the sharp knee-like bends are provided by previous experimental TEM data on conical terminations of nanotubes [13] and by pioneering theoretical works on tubule connections [14] and on the stability of hypothetical carbon tori [15]. The crucial remark is that the apex at the convex side of a knee is a parabolic point (two positive curvatures) while at the concave side, the apex is a hyperbolic or saddle point (one positive and one negative curvatures). From the Fullerene structures, one knows that to produce positive curvatures in the honeycomb lattice requires pentagonal ring defects while saddle points are introduced by means of a heptagonal ring. Such defects are obtained by removing or inserting 60° wedges into the hexagonal network. On this basis, the atomic structure which is proposed for a single bend of a coiled tube is schematically illustrated in Fig.2. Following Dunlap's construction [14], one considers joining two pieces of straight circular tubes (which can be achiral or chiral) by starting from their pressed or planar projection onto the honeycomb lattice. In such projections, the two pieces make an angle of 30° (Fig.2a). By introducing a pair of diametrically opposed 5-7 ring defects at the knee, it is then possible to inflate the knee into a continuous bend while maintaining all interatomic sp2 bonds close to their natural 1.4 Å value (Fig. 2b). Model building [10] as well as force-field calculations [16] indicate that upon inflation the bend angle θ growths towards an equilibrium value close to 40° rather than 30°. Tube diameters and chiralities can be chosen to build up in this way coaxial, multilayer coils satisfying the graphite 3.4 Å c-spacing. Efforts at determining the exact experimental knee angles from TEM-TED pictures are underway.

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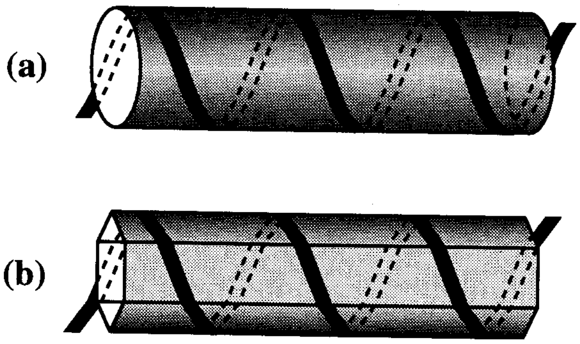

Fig. 1 : Continuous (a) versus polygonized (b) coil

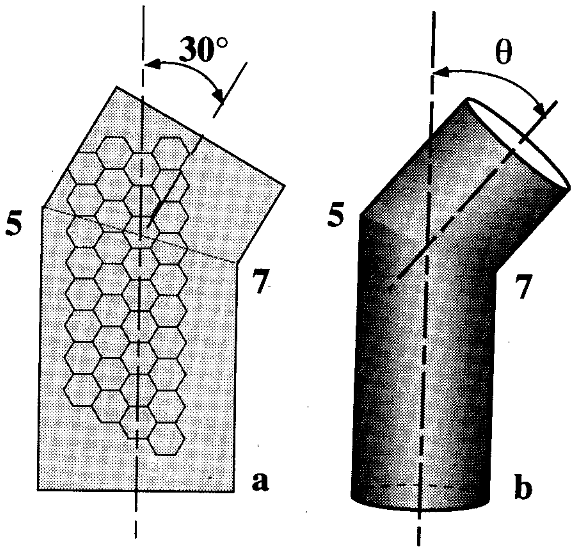

Fig. 2 : Pressed (a) vs inflated (b) tube bend.