Chirality controls nanotube growth

Roadblocks to sustainability
A cerium and aluminum alloy
Anti-malaria drug design
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Dislocation theory of chirality-controlled nanotube growth

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The periodic makeup of carbon nanotubes suggests that their formation should obey the principles established for crystals. Nevertheless, this important connection remained elusive for decades and no theoretical regularities in the rates and product type distribution have been found. Here we contend that any nanotube can be viewed as having a screw dislocation along the axis. Consequently, its growth rate is shown to be proportional to the Burgers vector of such dislocation and therefore to the chiral angle of the tube. This is corroborated by the ab initio energy calculations, and agrees surprisingly well with diverse experimental measurements, which shows that the revealed kinetic mechanism and the deduced predictions are remarkably robust across the broad base of factual data.

\textbf{Synthesis of carbon nanotubes (CNTs), traditionally referred to as “growth” due to their drawn-out crystal morphology, has been a great challenge for experiment and theory. They are produced in a seemingly random distribution of diameters and chiral symmetry, often specified by the angle \(\theta\) between the circumference and the zigzag motif of atoms. Despite tremendous efforts (1–4), the growth mechanism remains unclear in significant details. Theory has been discussed mainly at the 2 distinct scales, continuum-phenomenological vapor-liquid-solid (VLS) model (5) and atomistic simulations (6–14). Here we invoke the concepts established for macroscopic crystals and transfer this to a nanotube viewing as having an axial screw dislocation. Following this logic further, we show that the growth rate must be proportional to the magnitude of the Burgers vector of such dislocation and is ultimately proportional to the chiral angle of the tube.

Despite its molecular size and round shape, a CNT possesses the attributes of an ideal crystal, as well as possible deviations in the form of defects (15). The notion of edge dislocation (5/7 defect) was first applied to CNTs in the context of mechanical relaxation and turned out rather useful, leading to an understanding of yield and superplasticity (16, 17). In the following, we invoke another fundamental dislocation type, the screw dislocation, and explore its utility in understanding CNT growth.

\textbf{Results and Discussion}

Our initial plan is to follow Frank’s seminal work (18). It resolved the problem of crystal growth kinetics, where nucleating every next crystal plane on top of a previously completed one would encounter a significant barrier. Frank suggested that a screw dislocation provides a non-barrier path for the sequential accretion of material along the spiral ladder of a crystal lattice, so that the growing facet never becomes a complete low-index plane.

In this regard, the armchair and zigzag tubes are special; each of these achiral types represent a stack of complete atomic rings, so that the circular end-edge is entirely uniform (Fig. 1\textsuperscript{A} illustrates the zigzag case), similar to a low-index crystal plane. Any chiral tube can be viewed as a basic zigzag, but with a “defect”—a running through the center-hollow screw dislocation of a Burgers vector \(\mathbf{b}\) (Fig. 1\textsuperscript{B–D}) (19). (The reason to choose the zigzag tube rather than armchair as a basic one will become clear later.) In a gedanken experiment, one dissects the wall of a zigzag tube axially (Fig. 1\textsuperscript{B}) and then reseals the cut after sliding its sides by a vector \(\mathbf{b} = \mathbf{b}_\parallel + \mathbf{b}_\perp\). Consequently, the tube end-edge gains a kink-step of height \(b_\parallel\) (or equivalently, a few smaller kinks). By inspection (\textit{SI Text} and Fig. S1), we see that a CNT with conventional indices (n, m) corresponds to a purely zigzag \((n + m/2, 0)\) with an axial screw dislocation “defect” of Burgers vector \(\mathbf{b}_\parallel = m(-\frac{1}{2}, 1)\), for an odd m, a purely zigzag tube \((n + m/2 + \frac{1}{2}, 0)\) and additionally a small edge component \(b_\perp = -\frac{1}{2}\) (Fig. S1); accordingly, its circular end-rim has m kinks.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Fig1.png}
\caption{An axial screw dislocation in the CNT. An achiral zigzag (n, 0) tube (A) can be viewed as a perfect crystal, and transformed into a chiral one by cutting, shifting by a Burgers vector \(\mathbf{b}\) (red arrows in B–D), and resealing a tube-cylinder (E). The chiral (n, 1) in (C) and (n, 2) in (D) tubes contain the axial screw dislocations with a single and double value of \(b_\parallel\), accordingly; the correspond-
\end{figure}

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A graphene (or tube) edge must be docked to a step on the catalyst surface, to avoid its “arch-bridge” warping caused by the curvature. A catalyst mitigates the dangling bond instability and propensity to closure through the formation of pentagons and hexagons, but higher kinetic behavior: there is not much energy needed to restart each atomic ring, and in growth it behaves like a chiral tube.

The kinks at the end-rim of a chiral tube serve as “cozy corners” (18, 21) for the new atoms docking, while the growth rate is, as a result, a clear picture of growth emerges for an arbitrary (n, m) tube. With properties similar to the Frank’s dislocation-assisted crystal growth (18), such a tube should readily accept new carbon (as Fig. S1B illustrates, an “ultimate chiral” tube with θ = 30°). A zigzag tube must wait for fluctuative re-initiation after each atomic ring is complete. The ratio of their growth rates can be roughly estimated as 

\[ \frac{G^*_{1200}}{G^*_{300}} \sim 10^{-4} \text{ to } 10^{-6} \] 

Thus the carbon deposition rate depends on the chiral angle and tube diameter d as

\[ K \sim k_{\text{deposition}} \sin(\theta) \]

The small left box in the schematics corresponds to the views (A) and (D) in the direction normal to the surface
where the approximation \( \sin(\theta) \approx \theta \) is accurate to 4% for the range of interest, \( 0 \leq \theta \leq \pi/6 \). Upon arriving at this remarkably simple relationship—predicting the amount of CNTs to be proportional to their respective chiral angles—one is compelled to seek its confirmation in experimental data.

Eq. 1 predicts a greater length of nearly armchair tubes relative to rather short and slower growing zigzag. To characterize the tube distribution experimentally it is necessary to unbundle the ropes by sonication (24–29), in the process breaking the tubes into smaller fragments. Because of the fragmentation, greater length translates into a greater number of fragments, i.e., larger abundance.

Before carrying out comparisons with the experimental literature, it is important to recall the basic limitations of the model. Regarding the feedstock decomposition, carbon diffusion across the catalyst to the tube, and its attachment to the end-edge, we assumed the last stage to be limiting. In other words, the microscopic rate constant \( k_s \) is small, although we do not investigate here the exact atomistic mechanism or the activation barrier of this last step. The demonstrated dominance of kink-attachment (no initiation needed) relative to the zigzag-edge (high \( G^*_{ZZ} \)) is valid in not-too-hot CVD, but the rate difference may weaken at 3,000–4,000 K of arc-discharge or laser ablation: with the factor of \( \exp[-(G^*_{ZZ} - G^*_{AC})(kT)] \sim 10^{-1} \)–1–2 only, the zigzag edge can grow at a comparable rate, making the trend of Eq. 1 less pronounced. Last but not the least, experimental characterization of CNTs by type is usually preceded by additional processing as noted above, which may somewhat alter the distribution of species relative to the as-grown raw material.

With these caveats, Eq. 1 predicts a greater abundance of nearly armchair tubes compared to small amounts or no zigzag. After considering common CNT growth methods, such as various CVD [high pressure carbon monoxide HiPco (24), cobalt-molybdenum catalyzed CoMoCat (25), cobalt-catalyzed on MCM-41 template Co-MCM-41 (26), and ACCVD using alcohol as feedstock (27)], arc discharge (28), and laser ablation (29), we present a composite plot of the chiral angle distribution in Fig. 3. To our surprise, the data from such disparate sources overall follows Eq. 1 well, with HiPco, ACCVD, and arc discharge (28) data fitting Eq. 1 quantitatively, and the CoMoCat data also in good qualitative agreement. Beyond the mere abundance of large chiral angle CNTs, for the HiPco product, data also in good qualitative agreement. Beyond the mere

Fig. 3. The distribution of CNT product as a function of chiral angle \( \theta \). Experimental data of CoMoCat (25), HiPco (24), arc discharge (28), and ACCVD (27), are extracted from literature. The present model and Eq. 1 predict \( N \propto (\theta) \), which yields 11%, 33%, and 56% for the presented intervals (black-gray), to be compared with experimental data (colored).

Our approach comprised the methods of dislocation theory and the basic notions of nucleation; when we needed to evaluate and compare the energies of certain atomic configurations, we performed the computations with the density functional theory.

The self-consistent DFT calculations were performed to determine the kink formation energy. We used the general gradient approximation (GGA), with the PW91 functional (30), ultra-soft pseudopotential and plane wave basis set. All of the calculations were done with the VASP, Vienna Ab initio Simulation Package (31). The default cutoff energy of 286.74 eV and the convergence stop criteria as the force tolerance \( f_{\text{max}} < 0.01 \) eV/Å were used. Due to the large unit cell size, only one k-point (Gamma point) was used in the calculation, while additional careful testing is described below.

The (111) metal surface, with or without metal steps, was modeled within the periodic boundary conditions (PBC), with the unit cell 1.4757 nm \( \times \) 1.4757 nm (to attach the zigzag carbon strip/ribbon) or 12.297 nm \( \times \) 17.34 nm (to attach the armchair carbon strip). Along the z-direction perpendicular to the slab surface, the slab was separated by 1.5 nm during the calculation. The metal surface was modeled by a single atomic slab due to the large number of atoms in the unit cell size (80–110 atoms per cell, Figs. 52 and 53). During the relaxation, the metal coordinate perpendicular to the metal slab was fixed to avoid unreasonable movement in the z-direction. For the surface with the step, 2 extra metal lines were placed on the slab to produce a step configuration (Fig. 53). The graphene strip with an armchair or zigzag edge was attached to the transition metal surface (Fe, Co, and Ni) and fully relaxed by the conjugate gradient (CG) method. For the stepped metal surface, the strip was positioned exactly between the 2 steps. Without a metal step, the graphene strip tends to form an arch-bridge shape, as shown in Fig. 52. The high curvature and large strain in the ribbon mean that it is not suitable for modeling the kink.

To model the kink formation more realistically, and to mimic the experimental observation and recent theoretical studies (14, 22, 23, 32), the armchair or zigzag strip was attached between the 2 metal steps. In this case, although simplicity, it apparently grasps the central features of real processes and must map the way to control CNT chirality during growth—a great challenge in today’s nanotube research. If in some implementations, the length of the CNT correlates with the chirality, it possibly provides length as an easier approach to selection. Besides the practical implications, we believe that bridging the nanotube growth and structure on one hand, and the dislocation views in classical crystal growth on the other, should stimulate advances in theory and practice in this important field.
of each kink was calculated as,

$$E_{kink} = (E_2 - E_1)/4,$$

where $E_1$ and $E_2$ are energies of the perfectly straight strip and the strip with the kinks, respectively.

To support the validity of the used constrained (in the normal z-direction) metal monolayer model and the single $k = 0$ (Gamma-point) calculations, we performed additional computations for 1 case of Ni-metal. Table S1 shows the calculation results based on an unconstrained double metal layer with the Gamma-point (0,0,0) only or with $2 \times 2 \times 1$ k-points. Because of the great expense of these calculations, only the C-Ni system was studied and only the zigzag case structures were calculated with $2 \times 2 \times 1$ k-points. As shown in Table S1, both the absolute energies and the energy difference found with single $k$-point and $2 \times 2 \times 1$ $k$-points agree with each other very well. Similar to the constrained monolayer calculation, the fully-relaxed double layer model shows that the nucleation barrier on an armchair edge is negligible (0.03 eV, similar to 0.04 eV calculated with the z-frozen monolayer model) and the nucleation barrier on a zigzag edge (1.36 eV, similar to the 1.54 eV based on the monolayer model) remains significantly larger than the thermal activation energy $k_BT$.

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