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An Overview and Exploration of Mathematical Approaches in Carbon Nanotubes and their Derivatives

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I. INTRODUCTION

Carbon nanotubes[1], nano-ribbons[2], graphene[3], fullerenes[4], polyacetalenes and their derivatives have obtained much attention recently due to their unique chemical, mechanical, thermal, optical, electronic and magnetic properties[5]. These carbon materials are lightweight and can support a large strain for their cross-section.Additionally, their ability to conduct electricity increases their potential and usefulness. Their ability to conduct electricity emerges from the π-π conjugation effect and alternating single and double bonds affecting the structure of the HOMO-LUMO levels.

Nanotechnology is:

1) the creation of useful materials, devices, and systems through the control of matter on the nanometer length-scale (so called nano-materials)
2) the exploitation of novel properties and phenomena developed at that scale

Nano-materials can be synthesized by top-down and bottom-up approaches. Each of these methods can include plasma etching, chemical vapor deposition (CVD), spin coating, Langmuir-Blodgett, electro-spinning, sol-gel, timber harvesting, molecular beam epitaxy, laser ablation, and ball milling techniques. The properties of materials produced by these processes may be characterized by SEM, TEM, Raman, FTIR, AFM, XPS, UPS, and SPM. Nano-materials can make specific use of quantum, wavelength-scale or sub-Planck length scale, interactions in 0D, 1D, 3D and 3D morphologies. In each of these geometries surface-area effects can tune the interactions.

Bottom-up approaches seek to shrink the size-scale of the fundamental building blocks of devices; essentially making smaller molecular components which execute similar functions as the larger-scale counterparts. Top-down approaches seek to alter the micro-fabrication methods directly and exhibit greater control of the nano-scale properties of materials. An example of a top-down approach is the use of photolithography or inkjet printing to create a transistor. An example of a bottom-up approach is molecular self-assembly through synthesis of complimentary chemical moieties.

When structures shrink to very small length scales, the associated surface area becomes very large. This surface area affect can alter the melting point of metals in small size scales. As the diameter of a nano-cluster, or equivalently the number of atoms in the cluster decreases, or the intermolecular spacing decreases[6], the melting point of the metal cluster can decrease. Furthermore, the scattered light observed by darkfield microscopy from illuminated nanoparticles can shift radically as a function of size. This has implications in the Lycurgus cup and stained glass windows in churches, wherein he transmitted and reflected light can vary significantly. The magnetic moment can also vary greatly with size[7]. The fraction of atoms at the surface increases greatly when the particle size enters into the 5 nm regime and surpasses the bulk atom fraction in the 2-3 nm regime[8]. More practically, these particles are finding their way into optoelectronic devices as a means to increase the out-coupling efficiency.

These small materials may provide a pathway to the single electron transistor (SET). A particularly interesting use of nanotechnology is the IBM advertisement made of xenon atoms[9]. One of the first people to draw attention to nanotechnology was Richard P. Feynman with his note "There's Plenty of Room at the Bottom".

Single-walled Carbon Nanotubes (SWCNTs)

Single-walled nanotubes can be characterized according to their m and n values, which designate specific relationships between lattice locations and electronic properties. When tuned properly, SWCNTs can carry high current densities on the order of 10^{13} A/m^2. SWCNT are widely known for their high van der Walls attraction forces; which are the molecular understanding for the Gecko's feet phenomena[10]. The Gecko's feet phenomena allows Geckos to climb on walls and ceilings but to the high surface area attraction between the molecules of the Gecko feet and the materials of the walls. It is this same property that is useful in the creation of dry adhesives

for use in outer space. Additionally, the carbon nanotube oscillators with a core tube of (9,0) and external tube of (18,0) can resonate in the gigahertz frequency regime offering for the opportunity for ultra-fast optical fibers and nano-antennae[11].

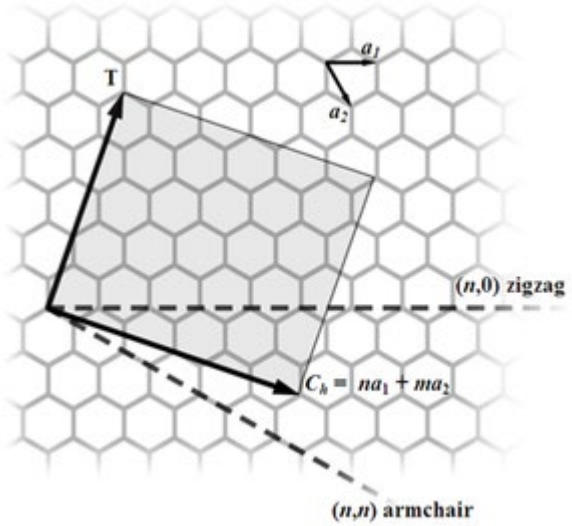

Figure 1: Source Liming Dai (CWRU) lecture notes

SWCNTs can be classified as armchair, zigzag or chiral. The constants m and n denote the maximum multiple of lattice basis vectors in orthogonal directions which the carbon nanotube fills the plane with. The diagonal from the origin site where the carbon nanotube basis starts to the (m,n) carbon creates the diagonal of the carbon nanotube. Therefore, the carbon nanotube diameter is given by: $d_t = \frac{c_h}{\pi} = \frac{\sqrt{3}a_{C-C}\sqrt{m^2+mn+n^2}}{\pi}$, where $a_{C\text{-}C}$ is the hybridized carbon-carbon bond length. The chirality and helicity can be interpreted from $\theta=\tan^{-1}(\frac{\sqrt{3}m}{m+2n})$ and is calculated for sample values of m and n:

		a=	0.246	nm
m	n	d (nm)	θ (rad)	
0	1	0.136	0.000	
1	1	0.235	0.524	
1	2	0.359	0.333	
1	3	0.489	0.243	
2	2	0.470	0.524	
2	3	0.591	0.409	
3	3	0.705	0.524	
3	4	0.825	0.441	
4	1	0.622	0.857	
4	2	0.718	0.714	

4	4	0.940	0.524
0	2	0.271	0.000
0	3	0.407	0.000
0	4	0.543	0.000
0	5	0.678	0.000
5	0	0.678	1.047
4	0	0.543	1.047
3	0	0.407	1.047
2	0	0.271	1.047
1	0	0.136	1.047

The respective (m,n) relationships are (m,m), (n,0) and (m≠n). A critical, classical criterion for metallic conductance is that (2n+m)=α*3, where α is an arbitrary positive constant. A metallic material is one which has no bandgap, a semiconductor has a small bandgap and an insulator has a large bandgap. The bandgap defines the energy 'distance' between the HOMO and the LUMO states.

The intrinsic Fermi level, the energy point at which the probability of picking an arbitrary state and it having an energy less than or equal to that value is .5, can be altered by doping. Doping with an n-dopant will increase the Fermi level and doping with a p-dopant will decrease the Fermi level[12].

One trend of importance for acetalenes is that increasing the molecular weight of a polymer increases the electron delocalization through both inductive and resonance effects. Therefore, the band gap of such longer polymers decreases.

Carbon nanotubes can be vertically or horizontally aligned. Furthermore, carbon nanotubes bay be multi-walled and can take on Russian doll or Swill roll morphologies. These may be differentiated between via TEM, although the Swiss roll has never been seen in TEM. The energy minimization tends to create a Russian doll structure due to a lack of dangling bonds[13].

The addition of cobalt allows for the creation of helical nanotubes wherein applied currents can create magnetic fields. Solenoid and torus-type NTs can therefore move small, magnetic nanoparticles. Chromium can cause extra curves in the CNTs because of its ability to form pentagonal lattices.

Derivatives may substitute parts of the carbon lattice for i) polymeric materials, which can support molecular self-assembly[14,15,16], andii) electron withdrawing/donating groups to shift the HOMO/LUMO/Fermi levels to be n-type or p-type. Specifically, changing m and n for single-walled carbon nanotubes (SWCNTs) can alter the charge mobility. The Kataura plot indicates the bandgap energy of a SWCNT as a function of the tube diameter[17]. The energy of the tube transition decreases with increases in the diameter. However, the system is not monatonic due to the role m and n play in altering the electrical properties.

A property that CNT exhibit which is unique to 1D solids is the van Hoffe singularity. These solids include points where the density of states (DOS) vs. energy (eV) plots have unusual patterns which are not seen in 3D structures[18,19].

Fullerenes

Fullerenes are similar to SWCNTs in their conjugated π-bonded structure except that their ends are not typically left open. Instead, the lattice is completed with a curved carbon surface and no opening remains. This leads to a completely closed structure. For these closed structures, Euler's theorem applies. Truncated icosahedra and Euler's theorem for polyhedral:

$$f + v = e + 2$$

$f = p + h$

$2e = 5p + 6h$

$3v = 5p + 6h$

$\frac{p}{2} = f + v - e = 6$implies p=12

This allows for the calculation of the smallest fullerenes and the number of pentagonal and hexagonal faces for each case. Additionally, the number of carbons and diameters for specific n,m systems are given by:

m	n	N	d (nm)
0	1	20	0.678
1	1	60	2.034
1	2	140	4.747
1	3	260	8.816
2	2	240	8.138
2	3	380	12.885
3	3	540	18.310
3	4	740	25.091
4	1	420	14.241
4	2	560	18.988
4	4	960	32.550
0	2	80	2.713
0	3	180	6.103
0	4	320	10.850
0	5	500	16.953
5	0	500	16.953
4	0	320	10.850
3	0	180	6.103
2	0	80	2.713
1	0	20	0.678
5	5	1500	50.860
6	6	2160	73.239

The coordinates of graphene carbon atoms are shown for different systemsand are calculated via the following equations:

a= 0.246 nm

xn= mn*a

yn= n*mn*a*tan(theta)

m	n	x (nm)	theta (rad)	y (nm)
0	0	0	0.00	0.00
1	0	0.246	1.05	0.00
2	0	0.492	1.05	0.00
3	0	0.738	1.05	0.00
4	0	0.984	1.05	0.00
5	0	1.23	1.05	0.00
6	0	1.476	1.05	0.00
1	1	0.246	0.52	0.14
1	2	0.246	0.33	0.17
1	3	0.246	0.24	0.18
1	4	0.246	0.19	0.19
1	5	0.246	0.16	0.19
1	6	0.246	0.13	0.20
2	1	0.492	0.71	0.43
2	2	0.492	0.52	0.57
2	3	0.492	0.41	0.64
2	4	0.492	0.33	0.68
2	5	0.492	0.28	0.71
2	6	0.492	0.24	0.73
3	1	0.738	0.80	0.77

Some interesting applications for graphene are as electronic audio speakers[20], ultracapacitors[21], transistors[22], quantum dots[23].

It is known that C60 can be a strong oxidizing agent, and that atoms or ions such as oxygen and iodine can be implanted into its structure[24]. Perhaps larger molecules such as sugars can be implanted into appropriately-sized fullerenes and through modification of the fullerene to incorporate a polymeric structure which can be tuned to open and trigger molecular or pharma-molecular drug release based upon pH, salinity, temperature, or irradiation-dependent effects.

Polymers may be branched or linear, flexible or rigid, lightly or heavily cross-linked, cyclical, dridri-grafted, interpenetrating, starred, and polyrotaxaned networks[25].Each one of these characteristics alters key molecular properties with implications in pharmaceutical, medical, surfactant, fracking and other industries.

Snell's Law and Bragg Diffraction

Snell's law denotes the change in the angle with respect to surface normal that a light ray experiences when traveling from a medium with refractive index, n_1, into a second medium with refractive index, n_2. The law goes that $n_1 \mathrm{Sin}[\theta_1] = n_2 \mathrm{Sin}[\theta_2]$.

Bragg's law denotes the angle at which maximum constructive interference from a crystal lattice of scattering sites, and is given by the formula: $2 * d * \mathrm{Sin}[\theta\ ] = \alpha * \lambda$; where d is the distance between the scattering sites (the isotropic lattice constant), θ is the angle that the constructive interference occurs at, α is any positive integer, and λ is the wavelength of the light scattered.Assuming that the electromagnetic source, often a laser, and the scattering sites are in a different refractive index media, the angle will be shifted by Snell's law. The following formula will correct for this phenomenon and calculate the wavelength of maximum constructive interference at a specific angle and internal and external refractive index:$2 * d * \frac{n_1}{n_2} \mathrm{Sin}[\theta_1] = \alpha * \lambda$.

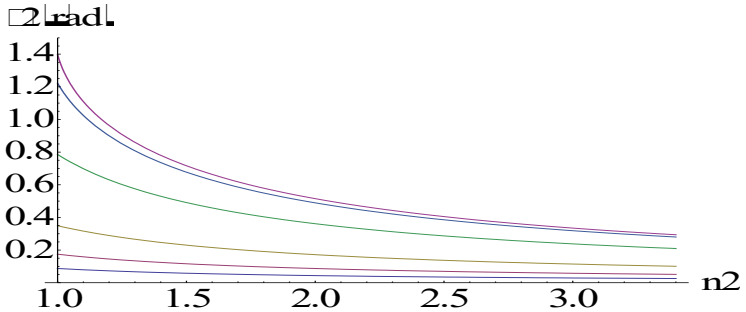

Figure 2: The angle of incidence with respect to surface normal in medium 2 for a ray at theta 1 in air (medium 1**).**

Giant Magneto-resistance (GMR)

Ferromagnetic, antiferromagnetic and ferromagnetic interactions dominate below a certain critical temperature and exhibit correlated spins which are material dependent. The correlated spins create domains of longer range ordering within the magnetic material's structure[26]. This can lead to unique patterns in the magnetization, degree of spin alignment, of the material in an applied magnetic field. The GMR allows small changes in the applied electric field to create large differences in the magnetization of the system[27]. This property is widely and commercially utilized in hard disks[28].

Single Electron Transistor (SET)

The transistor, discovered at Bell laboratories in 1947[29]revolutionized information technology and created the computer revolution. Intel cofounder Gordon E. Moore, observed that "the number of transistors that may be placed on an integrated circuit is doubled approximately every two years"[30]. The single electron transistor is hypothesized to have the most power and space efficient of device designs achievable. In order to create a single electron transistor the thermal fluctuations caused by statistical energy availability must be suppressed. Therefore, e^2/C must be much greater than k_BT. At room temperature, C is approximately 10^{-18} F. This implies that the quantum dot size must be on the order of magnitude of 1 nm. The fabrication of particles in such a size-scale is extraordinarily difficult and, therefore, the solution appears to be to operate SETs at low temperatures.

Learning from the best: Important Lessons in Scientific Endeavors

It is imperative to understand the major leaps in understanding that have occurred in science and engineering such that one i) knows the bounds of knowledge and begin to look for room to close the gaps left in conceptualizations, ii) knows the relative value of our own work in the grand scheme of all knowledge, and iii) strives to emulate the types of thinking which have led to breakthroughs. It is at the boundaries of our knowledge that there is the most to be gained through experimental and theoretical work. Some people which have created particularly large leaps in scientific advancement are: Novoselov and Geim; Tomonaga, Schwinger and Feynman; Curl, Kroto, Smalley; Heeger, MacDiarmid, and Shirakawa; Shockley, Bardeen and Brattain; Bardeen, Cooper and Schrieffer; Fert, Grunberg; Ruska, Binnig and Rowler; Chu, Cohen-Tannoudji and Phillips, Fenn and Tonaka.

Several morals can be deduced when considering the Nobel laureates' stories as fables. Some of these are: "work hard and it will pay off", "the Nobel prize can be won in as little as ten days work", "you could miss very important discoveries if you do not look at the data very closely." This is what happened to Exxon Mobil. Scientists at this company had discovered C60 bit did not properly attribute the peak. "Introducing people who don't know each other can pay off", "Take a simple idea and follow it through to the end", "You can win the Nobel prize very young like Jophsen did", "It can take two years working day and night to verify a single result from your colleagues."

Emerging Ideas

Several opportunities for new studies include the determination of the equivalent resistance of a C-C or a C=C in a SWNT as a Norton equivalent circuit and Thevenin equivalent circuit. This type of study would involve writing an equivalent resistance/capacitance of these two elements, and deriving the equivalent resistance using simplification steps and Kirchoff's laws. The equivalent circuit resistance/capacitance would depend on them and n and metallic properties of a given SWN. The derived expressions could be fit to the experimentally measured IV curves.

Computing the maximum volume inside fullerene and associated chemical derivatives. This would assist in estimating which molecules fir inside of these structures. The specific volume would depend on the volume of a cylinder with diameter d_t as derived previously, plus a contribution from a partial ellipsoid endcaps.

Furthermore, mathematical models are capable of evaluating the theoretical maximum length before a horizontally-aligned SWCNT could no longer support itself. This would involve resolving the Bernoullicantilever beam equation which is a 3rd order or coupled 4th and 2nd order PDE[31,32].

II. CONCLUSIONS

Nanotechnology offers new, unique control over matter which provides for materials with unique chemical, mechanical, thermal, optical, electrical and magnetic properties. It is clear that the field of nanotechnology is expanding exponentially and that continued experimentation and exploration of the novel materials and their properties will yield great benefit to society-at-large. Nanotechnology will allow for scientists and engineers to apply new experimental and theoretical techniques to solve common problems in the fields of electronics, medical, pharmaceutical, lighting and display technologies. Due to the commercial and academic interests of these processes and materials, nanotechnology, related materials and processes will be of great interest for some time.

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