Structural, electronic, optical and vibrational properties of nanoscale carbons and nanowires: a colloquial review

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Structural, electronic, optical and vibrational properties of nanoscale carbons and nanowires: a colloquial review

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Abstract
This review addresses the field of nanoscience as viewed through the lens of the scientific career of Peter Eklund, thus with a special focus on nanocarbons and nanowires. Peter brought to his research an intense focus, imagination, tenacity, breadth and ingenuity rarely seen in modern science. His goal was to capture the essential physics of natural phenomena. This attitude also guides our writing: we focus on basic principles, without sacrificing accuracy, while hoping
to convey an enthusiasm for the science commensurate with Peter’s. The term ‘colloquial review’ is intended to capture this style of presentation.

The diverse phenomena of condensed matter physics involve electrons, phonons and the structures within which excitations reside. The ‘nano’ regime presents particularly interesting and challenging science. Finite size effects play a key role, exemplified by the discrete electronic and phonon spectra of C$_{60}$ and other fullerenes. The beauty of such molecules (as well as nanotubes and graphene) is reflected by the theoretical principles that govern their behavior. As to the challenge, ‘nano’ requires special care in materials preparation and treatment, since the surface-to-volume ratio is so high; they also often present difficulties of acquiring an experimental signal, since the samples can be quite small. All of the atoms participate in the various phenomena, without any genuinely ‘bulk’ properties. Peter was a master of overcoming such challenges.


As a material, graphite has come full circle. The 1970s renaissance in the science of graphite intercalation compounds paved the way for a later explosion in nanocarbon research by illuminating many beautiful fundamental phenomena, subsequently rediscovered in other forms of nanocarbon. In 1985, Smalley, Kroto, Curl, Heath and O’Brien discovered carbon cage molecules called fullerenes in the soot ablated from a rotating graphite target (Kroto et al 1985). Similarly, the vibrational properties of C$_{60}$—an icosahedral molecular form of carbon with the same sp$^2$ bonding geometry as graphene (Kroto et al 1985)—are tightly constrained by the high point group symmetry of this nanoscale system. All these systems ultimately relate to graphite, the bulk three-dimensional form of sp$^2$ carbon, whose properties have been well studied for over sixty years (Dresselhaus et al 1988).

The optical probes used to such great effect by Peter’s group mainly measured long-wavelength phonons, often in nanoscale carbon systems. Hence we review the long-wavelength vibrational properties of graphene, arguably the conceptual progenitor of this large material class. The two in-plane polarized optical phonons, one longitudinal (LO) and one transverse (TO), have identical frequencies, $\omega_{\text{LO}} = \omega_{\text{TO}} = 1590$ cm$^{-1}$ and consist of the two carbon atoms of a single unit cell vibrating against each other. The so-called ZO phonon at

**1. Phonons in nanomaterials: carbon nanotubes, C$_{60}$, graphene and semiconducting nanowires**

Phonons in systems with ordered, nanometer-scale structure demonstrate profound effects from both boundary conditions and the new spatial symmetries that are possible at very small length scales. For example, many of the properties of carbon nanotubes—a cylindrically confined, cylindrically symmetric form of carbon—can be derived from the vibrational properties of graphene, an extended two-dimensional form of carbon (Wallace 1947). Similarly, the vibrational properties of C$_{60}$—an icosahedral molecular form of carbon with the same sp$^2$ bonding geometry as graphene (Kroto et al 1985)—are tightly

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(Some figures in this article are in colour only in the electronic version)
865 cm\(^{-1}\) vibrates these two carbon atoms out of plane and out of phase. The three acoustic modes of graphene of course vanish in frequency at long wavelengths. The frequency of the longitudinal acoustic (LA) phonon varies as \(\omega = v_{\text{LA}} q\), where \(q\) is the wavevector and \(v_{\text{LA}} = 21 \, \text{km s}^{-1}\). The transverse acoustic (TA) phonon disperses as \(\omega = v_{\text{T}A} q\), with a slower sound speed of \(v_{\text{T}A} = 15 \, \text{km s}^{-1}\). Both of these values are much higher than those of typical solids, reflecting the strong covalent bonds of graphene. These two modes describe in-plane vibrations of the carbon atoms and their in-plane speeds are isotropic. Finally, an unusual flexure mode displays quadratic dispersion, \(\omega = vLq^2\), where \(L\) is the effective thickness of a layer of graphene. The precise value of \(L\) is somewhat arbitrary, since it is defined only in concert with \(v\), but one could take \(L \sim 0.1 \, \text{nm}\) for graphene. The other factor, \(v\), has units of velocity. These modes describe the out-of-plane motion of the carbon atoms for a wave that travels parallel to the plane. The flexure modes, sometimes called ZA, were observed in the first neutron scattering measurements of graphite phonons (Nicklow et al. 1972). Unlike for graphite, nearly all measurements of graphene have this layer lying on a substrate, and this substrate will affect the observed vibrational modes of graphene.

The long-wavelength phonons in a single-walled carbon nanotube (SWNT) are more interesting, in that they afford greater room for the effects of nanoscale geometry. The phonons of a single-walled nanotube depend on the wrapping indices \((n,m)\) of the nanotube; these describe the tube circumference in lattice coordinates (Dresselhaus and Eklund 2000). However, at long wavelength, many of the vibrations are independent of the wrapping indices and can be described by elasticity theory. Some early theories used zone folding to deduce the nanotube phonons from the known modes of a graphene sheet. Although zone folding of the scalar Schrödinger wave equation for electronic states works well, elasticity theory involves a vector wave equation, and zone folding gives poor results. Mahan (2002) derived the vibrations of a thin-walled hollow cylinder within elasticity theory and thereby predicted all of the long-wavelength low-frequency modes of the nanotube. Nanotube phonons have two quantum numbers: the wavevector \(q\) along the tube, and the angular momentum \(l\). The longitudinal acoustic (LA) phonon describes periodic elongation of the tube along the axis, with a frequency \(\omega = v_{\text{LA}} q\), an angular momentum \(l = 0\), and a speed \(v_{\text{LA}}\) identical to that in graphene. The transverse acoustic (TA) phonon exerts torsion, with a frequency \(\omega = v_{\text{T}A} q\), an angular momentum \(l = 0\), and a speed \(v_{\text{T}A}\) also essentially identical to that in graphene. The radial breathing mode (RBM), which was first described by Peter (Rao et al. 1997c), has no direct analog in graphene. Its speed is also \(v_{\text{LA}}\) and its angular momentum is \(l = 0\). He was also early to recognize the RBM as a resonant phenomenon (Pimenta et al. 1998a). The flexure modes retain their quadratic dispersion, but now the effective thickness \(L\) is the diameter of the nanotube. The angular momentum of flexural modes is \(l = 1\). Flexural modes are doubly degenerate, since they describe vibrations in the two-dimensional plane transverse to the tube axis. Since the electron states of a carbon nanotube also have an angular momentum, conservation of angular momentum constrains the electron–phonon scattering. Eklund was also early to distinguish the differences in behavior between semiconducting and metallic nanotubes from a spectroscopic standpoint (Pimenta et al. 1998b).

Eklund and colleagues were the first to realize that the radial breathing mode is Raman active (Rao et al. 1997c), and that its frequency is inversely related to the radius \(R\) of a carbon nanotube: \(\omega_{\text{RBM}} = v_{\text{RBM}} / R\). Measuring the frequency by Raman spectroscopy and the radius by STM, they derived \(v_{\text{RBM}}\) experimentally. Mahan (2002) used elasticity theory to show that \(v_{\text{RBM}}\) is identical to the velocity of longitudinal phonons.

Some of the early theories of carbon nanotube phonons missed the flexure modes: all four long-wavelength modes in these treatments were acoustic, with \(\omega \propto q\). This error followed from a phonon dynamical matrix that lacked rotational symmetry. As noted by Born and von Karman in their first paper on phonons, the dynamical matrix must give zero for any rigid translation or rotation of the crystal. This condition on rigid rotations is usually lost in the periodic boundary conditions imposed on standard infinite three-dimensional crystals. But great care must be used to ensure that the dynamical matrix of lower-dimensional systems such as nanotubes has the required symmetries (Mahan and Jeon 2004).

In contrast to the relatively direct relationship between flat graphene and rolled nanotubes, the vibrational modes of a spherical C\(_{60}\) molecule, although derived ultimately from the same sp\(^2\) bonding, are profoundly affected by the high point group symmetry of this icosahedral molecule. An isolated C\(_{60}\) molecule has 180–6 = 174 intramolecular vibrational modes, but only 46 distinct mode frequencies survive the \(I_h\) symmetry (Dresselhaus et al. 1992). For weak intermolecular coupling (as in C\(_{60}\) films) the vibrational modes of the solid state resemble closely those of the free molecule. Group theory for an isolated molecule predicts that ten \((8H_u + 2A_g)\) modes are Raman active and four \((4F_u)\) are IR active (Dresselhaus et al. 1992). The remaining intramolecular modes are optically silent to first order.

Whereas nanotubes can be described as seamlessly wrapped graphene, semiconducting nanowires made of e.g. Si or GaP are best conceptualized as cylindrical sections through a parent three-dimensional bulk solid. As such, they suffer abrupt surface terminations that are absent in the essentially edgeless nanotube system. Hence new surface phonons appear, and the bulk-derived phonons experience confinement from the nanowire edges.

Raman spectroscopy is a powerful technique to study these phonons in nanostructures. The line-shape, peak position and peak width of Raman bands can shed light on crystalline quality, doping, secondary phases, impurities and crystalline disorder. We focus first on phonon confinement, surface optical phonons and stimulated Raman scattering in semiconducting nanowires, guided by significant contributions from Professor Eklund during his decade at Penn State. Later, we will discuss phonons in C\(_{60}\), another topic of great interest to Peter, and the extension to carbon systems that polymerize to themselves or
act as hosts for heteroatoms such as adsorbates, intercalants, and chemical functionalization.

Richter first proposed a phenomenological model to interpret Raman line-shapes in nanocrystals (Richter et al 1981). Campbell and Fauchet (Campbell and Fauchet 1986) extended it to describe cylindrical nanowires. We call it the RCF model. When a nanowire is narrower than the phonon mean free path, the RCF model fails. We extended it to describe cylindrical nanowires. We call it the extended RCF model. When a nanowire is narrower than the phonon mean free path, the RCF model fails. We extended it to describe cylindrical nanowires. We call it the extended RCF model.

\[ I_{NW}(\omega) = A \int_{0}^{\phi_{\text{max}}} \frac{|C(0,q_{\perp})|^2}{(\omega - \omega_{0}(q_{\perp}))^2 + \gamma^2} 2\pi q_{\perp} \, dq_{\perp} \] (1)

where \( C(0,q_{\perp}) \) is the Fourier coefficient of a Gaussian confinement function \( W(\alpha,D) = \exp[-(\alpha \cdot r/D)^2] \) in which \( \alpha \) is an adjustable parameter and \( q_{\perp} \) is the phonon wavevector perpendicular to the nanowire axis, extended to a continuum limit as a computational convenience. \( D \) is the diameter of the nanowire's crystalline core (not including any amorphous oxide coating).

The phonon dispersion relation \( \omega(q) \) is obtained from the bulk phonon dispersion as determined by e.g. neutron scattering (Nilsson and Nelín 1972). For Si nanowires (Adu 2004), the downshift of the phonons becoming significant (a downshift of \( \sim 2 \text{ cm}^{-1} \)) only below \( D = 10 \text{ nm} \), suggesting that a previously observed large downshift (10–20 cm\(^{-1}\)) of the first-order Raman peak in an ensemble of Si nanowires 10–20 nm in diameter arose from a phenomenon other than confinement (Li et al 1999, Wang et al 2000, Zhang et al 1998).

To acquire for variations in nanowire diameter within an ensemble specimen, Adu et al extended the RCF model by introducing a diameter distribution (Xiong et al 2003, Adu et al 2005), usually a log-normal distribution for nanowires grown by pulsed laser vaporization:

\[ I_{NW\text{D}}(\omega, \bar{D}) = \int_{0}^{\infty} F(D) I_{NW}(\omega, D) \, dD \] (2)

where \( F(D) \) describes the diameter distribution, \( I_{NW}(\omega, D) \) is the line-shape function for a nanowire of diameter \( D \) defined by equation (1), and \( \bar{D} \) is the most probable diameter obtained from the log-normal distribution. Figure 1 shows the Raman spectra of four nanowire samples with different diameters, excited at a low power (8 \( \mu \text{W} \text{ mm}^{-2} \)) to minimize laser-induced heating. Again, only below 10 nm diameter does the Raman band downshift and broaden asymmetrically as compared to bulk Si. The extended RCF model (solid lines) fits the experimental data very well (Adu 2004, Adu et al 2005). This measurement was the first clear demonstration of intrinsic confined phonon states probed by Raman scattering.

A flux-dependent change in line-shape and peak position, first observed by the Eklund group (Adu et al 2006a, 2006b, Gupta et al 2003a) complicates the analysis. Since the phonon frequency and lifetime are temperature dependent, a more accurate temperature-dependent RCF line-shape can be written as (Adu et al 2006a):

\[ I_{NW}(\omega) = \int_{0}^{\phi_{\text{max}}} \frac{|C(q_{\perp})|^2}{[\omega - \omega_{0}(q_{\perp}, T(z))]^2 + \Gamma(T(z))/2} 2\pi q_{\perp} \, dq_{\perp} \] (3)

where \( T(z) \) gives the temperature variation arising from laser heating. \( T(z) \) can be modeled by assuming the temperature increase above ambient due to laser heating follows the same Gaussian profile as the laser beam (Adu et al 2006a). Both \( \Gamma(T) \) and \( \omega_{0}(T) \) incorporate anharmonic interactions and thermal expansion. For narrow nanowires (\( D < 10 \text{ nm} \)), Raman band asymmetry results from both phonon confinement and inhomogeneous laser heating, while laser inhomogeneous heating dominates the line-shape of wider wires, supporting the claim of Piscanec et al (2003). A similar approach has been applied to Ge nanowires (Jalilian et al 2006).

Modes localized to surfaces or interfaces that propagate along the interface (Sernelius 2001) are particularly tractable for well-ordered surfaces with translational symmetry (Cardona and Güntherodt 2000). These surface phonons can become Raman active if the translational symmetry along the surface is broken through surface roughness, construction of a grating along the surface, or by probing the evanescent wave using a prism with an attenuated total reflection geometry (Falge et al 1974). In a dielectric continuum model for surface optical phonons in a nanowire, the lattice vibration associated with a polar material polarizes a medium with a dielectric function \( \epsilon(\omega) \) (Strossci and Dutta 2001). Solving the electrostatic equations yields the dispersion relation \( \omega_{SO}(q) \) for a surface optical mode in an infinitely long cylindrical nanowire. In the limit \( q \gg \omega/c \), the dispersion of the surface optical (SO) mode can be written as (Gupta et al 2003b):

\[ \omega_{SO}^2 = \omega_{TO}^2 + \frac{\omega_0^2}{\epsilon_{\infty} + \epsilon_m f(x)} \] (4)
where $x = qR$, $\omega_p$ is the screened ion plasma frequency given by $\omega_p^2 = \omega_{LO}^2 + \omega_{TO}^2/\epsilon_\infty$ where $\omega_{LO}$ is the LO frequency at the zone center, $R$ is the wire radius and $f(x)$ is obtained from the eigenvalue equation for the polarization (Gupta et al. 2003b).

**Figure 2.** Surface optical (SO) phonon dispersion of cylindrical GaP nanowires from equation (4). The horizontal dashed line gives the schematic experimental frequency of the SO phonon. The wavelength of the surface potential that breaks the symmetry can then be obtained from the vertical dashed line. Adapted from Gupta et al. (2003b).

Figure 2 plots the calculated surface optical phonon frequency $\omega_{SO}$ versus $qR$ for gallium phosphide nanowires in air (Gupta et al. 2003b). The surface optical phonon evolves between the bulk LO and TO frequencies. A horizontal line represents the nanowire surface optical frequency observed by Raman scattering. The corresponding wavevector $q$ — the wavenumber of the axial potential that breaks translation symmetry and hence activates this phonon — is obtained from the vertical dashed arrow. Figure 3 shows the Raman spectra of GaP nanowires carried out in three different dielectric media, revealing TO, LO and SO bands, the surface optical (SO) Raman band downshifts as $\epsilon_m$ increases, consistent with the model of equation (4).

The surface optical phonon dispersion for a nanowire of rectangular cross-section is more complicated, as there is no analytical solution to the eigenvalue problem (Xiong et al. 2004). Nevertheless, the microscopic mechanism is similar to that for cylindrical GaP nanowires.

What breaks the translational symmetry of the surface potential? Diameter modulation along the nanowire axis provides one such mechanism. Such variations have been seen in transmission electron microscopy for cylindrical GaP nanowires (Gupta et al. 2003b, Xiong et al. 2006b) and ZnS nanowires of rectangular cross-section (Xiong et al. 2004). This diameter modulation is consistent with observations on micron-sized Si whiskers grown by VLS in the 1970s, where it was ascribed to a growth instability (Givargizov 1973). Recently, a similar diameter variation in Si nanowires has been observed (Ross et al. 2005). The activation of nanowire surface optical phonons in Raman spectra suggests that such diameter modulations are important for the physical properties of nanowires.

Polarization-dependent Raman scattering from individual semiconducting nanowires also reveals an antenna effect (Chen et al. 2008, Xiong et al. 2006a). Even more interesting is how the polarized Raman response depends on the nanowire length. Nanowires with cleaved end facets behave as Fabry–Perot resonators which can support optically pumped lasing (Johnson et al. 2002). Recently, such cavity modes have also been seen in Raman scattering (Wu et al. 2009). Figure 4 shows the integrated Raman Stokes intensity of the TO phonon versus laser power for a series of GaP nanowires between 200 nm and 3.3 μm long, all cut from the same parent nanowire by a focused ion beam. In nanowires longer than 2 μm, the Raman intensity is approximately linear in the laser power up to 1 mW, which is characteristic of spontaneous Raman scattering, while higher laser powers induce significant heating. Nanowires shorter than 1.1 μm exhibit spontaneous Raman emission ($I_{TO} \propto P$) at low laser power, but show a strong nonlinear behavior $I_{TO} \propto P^n$ above a threshold power, where the exponent $n$ grows rapidly with decreasing length, reaching $n \sim 4.3$ for the 270 nm long nanowire. The threshold power decreases as the length decreases. This nonlinearity is a signature of stimulated Raman scattering. The low threshold power (0.1–0.5 mW) indicates that the GaP nanowire cavity has a very high quality factor $Q \sim 15,000$, perhaps ascribable to whispering gallery modes similar to those seen in spherical microcavities (Spillane et al. 2002). Peter’s discovery of stimulated Raman scattering in a single nanowire cavity shows promise for low threshold nanowire Raman laser (Wu et al. 2009).

Raman scattering can also shed light on the dopant distributions in nanowires (Imamura et al. 2008) and zone folding in twinned nanowires (Lopez et al. 2009). Outstanding puzzles remain. For example, radial breathing modes in silicon nanowires have been predicted (Thonhauser and Mahan 2005, Peelaers et al. 2009), but not yet observed experimentally.

**Figure 3.** Raman spectra of GaP nanowires collected in air (bottom) dichloromethane (middle) and aniline (top). Solid squares are the data and the thin lines are from a Lorentzian line-shape analysis. Adapted from Gupta et al. (2003b).
2. Pristine carbon nanostructures: polymerization and photophysics of C$_{60}$

Peter was fascinated by the high symmetry of the C$_{60}$ molecule and his initial studies focused on understanding its vibrational properties (Eklund et al. 1995b). His group sublimed high-purity C$_{60}$ micro-crystalline powders in an inert atmosphere to prepare thin films of C$_{60}$ on silicon and quartz substrates. In a thin film, C$_{60}$ molecules assemble into a face centered cubic (fcc) lattice. The weak intermolecular interaction (Pacheco and Ramalho 1997) and nearly spherical molecular shape allow C$_{60}$ to spin rapidly about its lattice positions above 260 K (Heiney et al. 1991b).

Figure 5 show the first Raman spectra of C$_{60}$ films reported by the Eklund group (a), (b), compared to another early C$_{60}$ film Raman spectrum (c) which differed significantly from that reported by Peter. When using an Ar ion laser at 488 or 514 nm to excite the Raman spectra, the most prominent peak occurs at either 1458 or 1469 cm$^{-1}$. Different results were obtained if the experiments were carried out in air or oxygen, as opposed to vacuum or an inert atmosphere. Through meticulous studies, the Eklund group traced this diversity of results to two photochemical transformations which alter the structure of pristine solid C$_{60}$ while leaving the fullerene shells largely intact: photopolymerization of C$_{60}$ and photo-enhanced diffusion of O$_2$ into interstitial voids in the fullerene lattice. In the former case, covalent carbon–carbon bonds interlink fullerene molecules (Rao et al. 1993b). In the latter case, O$_2$ molecules under the action of UV/visible light exhibit enhanced diffusion into the lattice (Rao et al. 1993a, Eloi et al. 1993).

The vibrations of C$_{60}$ in the solid state are very similar to those of the isolated molecule, comprising 46 distinct

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**Figure 4.** TO Raman band intensity dependence on length and laser power. Panel (a) gives a linear plot of the integrated TO band intensity versus laser power for seven nanowires of different lengths. For wires shorter than about one micron, nonlinearity is observed. Panel (b) is a log–log plot for the data shown in (a). Stimulated Raman scattering is seen for wires shorter than 1 μm. The threshold depends on nanowire length. Adapted from Wu et al. (2009).

**Figure 5.** Normalized Raman spectra of C$_{60}$ films on Si(100) taken under different environmental conditions and laser power densities $\Phi$: (a) in 1 atm of He and $\Phi = 5$ W cm$^{-2}$, (b) in 1 atm of O$_2$ and $\Phi = 75$ W cm$^{-2}$, and (c) in 1 atm of He and $\Phi = 75$ W cm$^{-2}$. The inset shows the XRD scan of the C$_{60}$ film that produced the Raman spectrum of (a). Adapted from Zhou et al. (1992).
frequencies of which ten are Raman active, eight with H₂ symmetry and two with A₂ symmetry. The two A₂ modes appear at 493 and 1469 cm⁻¹ in figure 5(a); these are called A₂(1) and A₂(2). The early literature disagreed on the frequency of A₂(2). This high-frequency tangential mode involves the symmetric, simultaneous contraction of all 12 pentagonal rings in the molecule. Using a low laser power density of 5 W cm⁻² on an oxygen-free sample, the Eklund group reported a polarized mode at 1469 cm⁻¹ and assigned it to the A₂(2) pentagonal pinch mode (Zhou et al. 1992). Raman measurements performed in the presence of air or O₂, as in figures 5(b) and 6, encounter O₂ molecules physisorbed in the octahedral interstices in the fcc C₆₀ lattice. Initially, these guest molecules produce almost no measurable change in the Raman spectrum relative to that observed in pristine, oxygen-free C₆₀ films (figure 5(a)). However, in the continued presence of UV/visible light this interstitial O₂ eventually oxidizes the fullerene shell at which point changes in the Raman and IR spectra can be detected (Rao et al. 1993a).

A line at 1458 cm⁻¹ (also sometimes seen at 1460 cm⁻¹, as in figure 5) that was incorrectly assigned in early research to the A₂(2) mode in oxygen-free C₆₀ films was shown later by the Eklund group to be only ∼80% (i.e., not 100%) polarized (Eklund et al. 1992), and therefore not the A₂(2) mode. The Eklund group demonstrated that the 1458 cm⁻¹ line is instead a clear signature of solid C₆₀ in the phototransformed, polymeric state (Rao et al. 1993b). A well-known photochemical 2 + 2 cycloaddition was proposed as the mechanism of covalent attachment between C₆₀ molecules. If carbon–carbon double bonds on two adjacent molecules are oriented parallel to one another and separated by less than ∼4.2 Å, then photochemical assistance can break these double bonds and produce a four-membered ring, as in the left panel of figure 7 (Venkatesan and Ramanurthy 1991).

The simplest example of 2 + 2 cycloaddition is the dimerization of ethylene (C₂H₄) to cyclobutane (C₄H₈), shown in figure 7(a). Two C₆₀ molecules can dimerize by a similar mechanism, as shown in figure 7(b). Solid C₆₀ satisfies the general topochemical requirement for 2 + 2 cycloaddition, since each C₆₀ molecule contains 30 double bonds tangential to the ball surface, and the double bonds on adjacent molecules can be separated by as little as 3.5 Å in pristine solid C₆₀ (HeineyJ. Phys.: Condens. Matter 22 (2010) 334201 et al. 1991b). In this photochemical mechanism, an incident photon prepares one molecule in the lowest excited triplet state T₁. This molecule then reacts with an adjacent molecule that is in the singlet ground state S₀. Three photophysical properties of C₆₀ lead to a significant optically pumped population of the T₁ state: efficient dipole-allowed transitions (above ∼2.3 eV) from the ground state to excited singlet states (Wang et al. 1992), nearly 100% efficient intersystem crossing of the excited molecule into T₁ (Hung and Grabowski 1991), and a long T₁ lifetime of ∼40 ps (Arbogast et al. 1991). If air or O₂ is present, the lifetime of the first excited triplet state of C₆₀ is significantly reduced (Hung and Grabowski 1991) and the photopolymerization is quenched.

This phototransformation mechanism was confirmed in the Eklund group through time evolution studies of the A₂(2) mode in oxygen-free films under increasing exposure to a high

Figure 6. The Eklund group exercised extreme caution in the thin film preparation of C₆₀ to uncover the role of oxygen in the observed Raman data. A thin film deposition apparatus was installed inside a He glove box, and sample transfer procedures from the glove box to spectrometers were developed to facilitate complete exclusion of oxygen from the C₆₀ film during all stages of sample preparation and Raman measurements. Pictured from left to right are Rao, Wang, Professor Eklund, Ren (behind), Wang and Zhou. Photo circa 1993.

Figure 7. The 2 + 2 cycloaddition reaction between parallel carbon double bonds on adjacent molecules is shown schematically in (a) of the left panel, while (b) shows a C₆₀ dimer produced by the same reaction. The right panel shows: (a) a bimolecular photochemical reaction in which a C₆₀ monomer in the excited triplet state M reacts with a monomer in the ground state M to form a dimer D and (b) a schematic energy level diagram for the C₆₀ monomer, showing the principal levels involved. The kᵢ are the respective rate constants and the other symbols are described in the text. Adapted from Eklund et al. (1995c).
laser flux (Wang et al 1993). A narrow line at 1469 cm\(^{-1}\) is initially observed, indicating that the film is pristine \(C_{60}\). With increasing photon dose, a broader peak appears at 1458 cm\(^{-1}\) and grows at the expense of the 1469 cm\(^{-1}\) line. This characteristic evolution is the Raman signature of photopolymerization in solid \(C_{60}\) (Rao et al 1993b).

Additional evidence for the photopolymerized phase includes the observation that a pristine \(C_{60}\) film is readily soluble in organic solvents such as toluene, whereas photopolymerized \(C_{60}\) is not. In addition, the laser desorption mass spectrum of pristine \(C_{60}\) shows the presence of \((C_{60})_n\) clusters with \(n < 4\); these clusters are identified with cross-linked \(C_{60}\) molecules induced by the desorption laser itself. Laser desorption mass spectra of a phototransformed \(C_{60}\) film show more than 20 clear peaks; these are identified with large clusters of fullerene molecules such as \((C_{60})_{20}\). Furthermore, the number of the first-order Raman and IR intramolecular vibrational modes increases in the phototransformed phase, as in figure 5(c), due to the reduction in symmetry below \(I_h\). Finally, a new low-frequency Raman-active mode appears at \(\sim 118\) cm\(^{-1}\) in the phototransformed phase, one which has been identified with an interball mode (Wang et al 1994, Rao et al 1993b).

Theoretical studies of \(C_{60}\) dimerization have taken several approaches, including generalized tight-binding molecular dynamics (Menon et al 1994), modified neglect of differential overlap and tight-binding methods (Strout et al 1993), and local-orbital-based first principle molecular dynamics (Adams et al 1994). All of these studies indicate that \(2 + 2\) cycloaddition yields the most stable dimer geometry. Two years after the report of photopolymerized \(C_{60}\), other research groups showed that polymerization can also be induced in solid \(C_{60}\) through simultaneous application of high temperature and high pressure, yielding the one, two and three-dimensional polymerized structures depicted in figure 8 (Iwasa et al 1994, Nuñez-Regueiro et al 1995).

Raman spectroscopy has become an indispensable characterization tool in carbon science. The Eklund group played a pivotal role in advancing our understanding of all forms of carbon, ranging from the graphite intercalation compounds in the 1970s (described below), through the fullerene studies described above, to carbon nanotubes in the past decade and graphene in the present era (Bandow et al 1998, Dresselhaus and Eklund 2000, Eklund et al 1995a, Gupta et al 2006, Pimenta et al 1998a, 1998b, Rao et al 1998, 1997b). Eklund was also interested in the molecular spectra of \(C_{60}\) in terms of the very large number of harmonics and combination modes (more than 200) observed in the IR and Raman spectra, a phenomenon essentially unique to fullerenes. His group did the pioneering work in this research area, as described in his book (Dresselhaus et al 1996).

3. Carbon nanostructures with heteroatoms: physical adsorption, intercalation, and chemical functionalization

The structure and properties of graphite and other carbon polymorphs can be greatly modified by adding atoms or molecules to the all-carbon host (Fischer et al 2000). Closed-shell atomic or molecular species generally interact weakly with the carbon sheet, leading to a diverse range of physical adsorption phenomena focused upon the dynamics and phase behavior of the adsorbates themselves. Open-shell species with weak ionization potentials or strong electron affinities, such as the alkali metals, alkaline metals, or sulfuric acid, experience stronger charge-transfer interactions with an \(sp^2\) carbon sheet. Hence, these species can dilate the space between weakly bound carbon layers and thereby infiltrate the carbon host, whether graphite (Dresselhaus and Dresselhaus 1981, 2002), solid \(C_{60}\) (Murphy et al 1992), carbon nanotubes (Lee et al 1997, Rao et al 1997a) or even one-dimensional carbon polymers such as polyacetylene, \((CH)_x\) (Heiney et al 1991a). Finally, species such as hydrogen or fluorine can covalently bind to carbon, changing the hybridization from \(sp^2\) to \(sp^3\), with profound effects on the electronic and structural properties.

Adsorption onto graphitic materials has played an important role historically in surface science, including Peter’s own elegant investigations using transport measurements to elucidate the physical adsorption of cyclic hydrocarbons with varying degrees of aromaticity onto graphene and nanotubes (Sumanasekera et al 2002) and his careful studies on the interaction of hydrogen with nanoscale carbons, which provided some of the critical clarifying measurements on the physics of these systems (Williams et al 2002, Narehood et al 2002, Pradhan et al 2002). Fundamental questions include the nature of the adsorption potential, as influenced by the unusual electronic properties of nanotubes and graphene (Castro Neto et al 2009) and the various adsorbate phenomena, such as unusual phases and transitions between them. Potential applications are diverse, including gas separations, storage and sensing (Romero et al 2005, Sholl and Johnson 2006, Cole et al 1981). To understand physical adsorption onto nanotubes and graphene, it helps to recall a previous generation’s experience with adsorption onto graphite. Single-surface experiments are challenging due to the low surface-to-volume ratio. For physical adsorption, scanning tunneling microscopy is generally not useful, except for the most strongly bound gases like Xe (Weiss and Eigler 1992). Fortunately, exfoliated
graphite has a high surface area (>20 m² g⁻¹) with uniform, extended honeycomb facets. As such, gas can imbibe within a macroscopic porous sample, yet experience an adsorption environment nearly identical to that on a flat surface. Weak binding to a surface in physical adsorption also implies small kinetic barriers, hence the adsorbate mobility is high and the heat of adsorption is small, so equilibration is rapid. Therefore experiments can determine both the film coverage \( N \) (by subtracting the number of gas atoms from the total number of atoms) and the chemical potential \( \mu_{\text{film}} \) of the adsorbed film, since it equals \( \mu_{\text{vapor}} \). For an ideal monatomic gas, \( \mu_{\text{film}}(N, T) = \mu_{\text{vapor}} = \beta^{-1} \ln(n\lambda^3) \), where \( \lambda = (2\pi R^2/m)^{1/2} \) is the thermal de Broglie wavelength, \( m \) is the atomic mass, \( n = P\beta \) is the coexisting vapor density at pressure \( P \), and \( \beta^{-1} = k_B T \). In principle, one thermodynamic measurement (an adsorption isotherm) could determine all of the thermodynamic properties of the adsorbed gas. In practice, however, \( P \) is immeasurably small at low \( T \). Fortunately, one can measure another thermodynamic function, the specific heat of the graphite is small and can be subtracted. Since the temperature integral of specific heat \( C \) can merge data from the two thermodynamic techniques using a Maxwell relation, \( (\partial S/\partial N)_T = (\partial \mu_{\text{film}}/\partial T)_N \). Complementing these thermodynamic measurements are x-ray and neutron scattering probes, NMR, Raman spectroscopy and other experimental studies. Electron diffraction and and neutron reflectivity also provide useful structural information on a single exposed surface of graphite or graphene. These various methods have been reviewed extensively (Dash et al 1994, Zeppenfeld 2001, Bruch et al 2007a, 2007b).

Studies of films on graphite yield a wide variety of monolayer phase diagrams, depending on the commensuration, i.e. the degree of mismatch between the graphite hexagons and the natural lattice constant of the adsorbate, which is controlled mainly by the Lennard-Jones diameter \( \sigma \). At low film coverage, one obtains a quasi-2D periodic potential with atomic band structure effects (Cole et al 1981). At higher coverage, a sub-monolayer film undergoes one or more two-dimensional phase transitions. For weakly corrugated potentials (e.g. Ar or CH₄), the phase diagram resembles that of an ideal 2D system. A 2D condensation transition occurs at moderate temperatures, typically about one-half of the 3D value. The measured critical exponent of the coexistence curve (Kim and Chan 1984) agrees nearly perfectly with the value \( \beta_c = 1/8 \) predicted by the 2D Ising model, one of the most fundamental measurements in surface science. At lower temperature, even a small corrugation affects the commensurate solid, whose 2D lattice exhibits orientational epitaxy, a temperature-dependent rotation of the film relative to the graphite substrate, which terminates in a distinct transition with Bragg diffraction spots evolving into liquid-like structure factor (Shrimpton et al 1988, D’amico et al 1990). For the quantum fluids, the corrugation gaps the long-wavelength phonon spectrum by ~0.94 meV (Lauter et al 1992) and forces a high-temperature transition to a \( \sqrt{3} \times \sqrt{3}R30^\circ \) commensurate phase at \( T_{\text{order}} \sim 3 \) K for helium isotopes and ~20 K for hydrogen isotopes. This transition displays the 2D critical exponents of the three-state Potts model (Schick et al 1977).

Adsorbed films on graphene have only recently begun to be explored. Physical adsorption on graphene would appear straightforward because the key difference, compared to graphite, is a presumably small shift of the adsorption potential (Gordillo and Boronat 2009). From a qualitative point of view, we therefore expect physically adsorbed films on graphene to be similar to those on semi-infinite graphite. In contrast, many novel phenomena result from the reduced dimensionality of atoms adsorbed onto or inside carbon nanotubes (Calbi et al 2001a). Taking the adsorption potential \( U(\rho) \) to be cylindrically symmetric, the solutions of the single-particle Schrödinger equation assume the form:

\[
\Psi_{n,v,k}(\rho, \theta, z) = \Phi_{n,v}(\rho) \exp[i(v\theta + kz)].
\]

The longitudinal wavevector \( k = p_z/h \) with \( p_z \) the momentum along the tube axis. The rotational quantum number \( \nu \approx \pm 1, \pm 2, \ldots \) corresponds to angular momentum \( L_\theta = \nu h \). To a good approximation (Stan and Cole 1998), the energy is a sum of radial, rotational and longitudinal contributions:

\[
E_{n,v,k} = E_{n,v} + p_z^2/(2m) \approx E_{n,0} + L_\theta^2/(2m(\rho)\nu^2) + p_z^2/(2m).
\]

Here, \( \langle \rho \rangle \) is the mean distance of the gas atom from the tube axis. The subscript \( n = 1, 2, 3 \ldots \) labels the nth solution of the radial Schrödinger equation for a specified \( \nu \), with eigenvalue \( E_{n,\nu} \). If the tube is narrow, then the spacing between radial energy levels is large, so that only the ground state \( n = 1, \nu = 0 \) is excited at low temperature and the lowest energy excitations are axial with a quasi-continuous spectrum: a one-dimensional gas. Even when collisions become important, this system remains essentially a quasi-1D fluid. The rotational degree of freedom is excited at \( T_{\text{rot}} \sim k_B T/(\nu\hbar)^2 \), which is a few Kelvin for He or H₂ and smaller for a heavier particle. For temperatures slightly above \( T_{\text{rot}} \) the system manifests two degrees of freedom, \( z \) and \( \theta \), and therefore acts as a 2D gas: \( C/(Nk_B) = 1 \). This dimensional crossover has been explored in detail for quantum fluids inside narrow nanotubes (Gatica et al 2000).

Classical gases within nanotubes do not exhibit low-temperature transverse or angular delocalization due to zero-point motion, so the molecules localize in the region of minimum potential. The ratio of the molecular size \( \sigma \) to the nanotube radius \( R \) defines two limiting cases. The limit \( \sigma \leq R \) is exemplified by the peapod geometry, wherein \( C_{60} \) molecules are imbedded within a narrow nanotube in single file along the tube axis (Smith et al 1998). This remarkable situation is simple to model if one considers only the translational degree of freedom along the tube axis, in which case one obtains an analytical expression for the 1D equation of state (Gürsey 1950). However, this model’s application to the \( C_{60} \) peapods requires further approximations: only nearest-neighbor interactions and negligible transverse motion or diffusive friction (i.e. the nanotube simply constrains the \( C_{60} \) molecules to a line). Also, the molecules are implicitly assumed to be freely rotating, insofar as rotational coupling is ignored. At room temperature and above, all of these
assumptions should be accurate (Calbi et al. 2003). In the other limiting classical case, $\sigma \ll R$, low-coverage adsorption occurs close to the nanotube wall, at the adsorption potential minimum. When the density of molecules increases to the point that their mutual repulsion dominates the substrate attraction, subsequent molecules are obliged to adsorb in a less attractive region, near the center of the pore. Such a capillary condensation transition is familiar from porous media (Gatica and Cole 2005).

Although few experiments have studied adsorption within individual nanotubes (Böttner et al. 2009), many experiments have investigated adsorption onto bundles of nanotubes (Calbi et al. 2008, Johnson and Cole 2008, Migone 2008). One key finding is the importance of heterogeneity in the bundle packing. Intersitial adsorption occurs primarily in the wider channels, as determined by the distribution of nanotube radii and the kinetics of bundle formation. Very strong adsorption occurs in the V-shaped grooves between nanotubes along the outside surface of the bundle. This space is occupied at the lowest pressures, followed by monolayer formation on the rest of the bundle surface, then adsorption in a second-layer groove defined by the intersection between semicircular monolayer films on adjacent tubes. Experiments are in semi-quantitative agreement with calculations based on semi-empirical adsorption potentials that are derived from adsorption on graphite (Calbi et al. 2001b, Talapatra et al. 2002).

Recent adsorption experiments from the Cobden-Vilches group at the University of Washington measure adsorption on the outside of a single carbon nanotube, achieved by measuring the resonant frequency shift of a vibrating nanotube in equilibrium with a gas (Wang et al. 2010). Figure 9 displays one such data set. These low-temperature adsorption isotherms exhibit two near-discontinuities. The larger jump is attributed to a transition from a gas to a commensurate phase, shown schematically in figure 9, analogous to that of Kr on planar graphite below 130 K (Fain et al. 1980). The smaller jump at higher coverage is interpreted as a transition to an incommensurate solid. The flat region between the jumps may reflect a reentrant fluid phase conjectured to occur for krypton on graphite (Specht et al. 1987). These data, one of the first studies of nano-matter on a single cylindrical surface, raise numerous fundamental questions about adsorbate structure and dynamics and their effect on electronic transport.

One general point needs to be addressed: since single-nanotube adsorption is a one-dimensional problem, no phase transition in the strict thermodynamic sense is possible. The apparent discontinuities in simulations and experiments must be rounded close to a nominal transition pressure. Numerical studies suggest that this rounding covers an exceedingly narrow pressure interval for the systems discussed here (Swift et al. 1993, Trasca et al. 2004). One interesting question, yet to be explored, is how the fluctuations near these quasi-transitions are revealed through electron transport or scattering. Density fluctuations will nearly diverge according to the general relation $\langle \Delta N^2 \rangle = \langle \partial N / \partial \ln P \rangle_T$, derived from equation (5). One anticipates behavior analogous to critical opalescence or the critical scattering of electrons at the Curie point of a ferromagnet.

Beyond this weakly bound physical adsorption regime, a wide class of other ‘adsorbates’ interact more strongly with carbon, but still preserve the sp2 bonding geometry of the carbon host. Since these species interact strongly enough to infiltrate between the layers of the bulk graphite lattice, they are no longer normal adsorbates, but genuine dopants, with substantial charge transfer to the host carbon lattice. In fact, the so-called graphite intercalation compounds motivated Peter’s initial contact with several contributors to this festschrift. Intercalation occurs when the charge-transfer dopants form their own ordered sublattice, the most dramatic example being the ordered stacking sequence of $N$ graphene layers alternating with one or more intercalant layers in one-dimensional superlattices, a so-called ‘stage $N$’ graphite intercalation compound.

Guest–host charge transfer is a common feature of all the carbon-based intercalation compounds. Although the literature from the 1960s calls these materials ionic salts, they were actually good metals. Graphite intercalation compounds display textbook signatures of the nearly free electron model: temperature-dependent in-plane resistivity following Matthiessen’s rule with weak electron–phonon interactions, a temperature-independent Pauli spin susceptibility with minimal Stoner enhancement, a Drude-like reflectivity spectra without complications from overlapping inter-band transitions, and a linear specific heat coefficient whose magnitude is consistent with other measures of the density of states at the Fermi energy (Claye et al. 2000). All of the forms of alkali-doped carbon depicted in figure 10 constitute synthetic metals with conduction by delocalized $\pi$ electrons or (in conducting polymers) solitons. The $\pi$-derived states are broadly dispersive along the direction of conjugation and weakly dispersive along interlayer, intermolecular or inter-tube directions.

Peter was the most important contributor to the Raman spectroscopy of graphite intercalation compounds. Raman spectroscopy turned out to be a very important tool for studying these systems, largely because of his excellent pioneering work. Early graphite intercalation research offered the
possibility of studying individual graphene layers separated from each other by layers of the intercalant; hence it was a very early example of a nanostructure. In certain compounds one could separately study the Raman spectra of the carbon layer and the intercalant layer, because the relevant modes occurred at different frequencies. In stage 1 compounds, an intercalant layer separates each graphene layer from the others. In stage 2 compounds, each graphene layer has a graphene neighbor to one side and an intercalant layer to the other. Compositions of stage \( n > 2 \) have two types of graphene constituents: two layers like those in stage 2 compounds and the remainder with only graphene neighbors. Peter measured the frequencies, intensities and line-shapes of the Raman features due to the graphitic host material and the intercalant, studying the perturbations of each upon the other as a function of intercalant species and staging. In this way he obtained great insights into intercalation. Peter performed inspirational work on staging in \( \text{H}_2\text{SO}_4 \) intercalation compounds where he monitored both the electrochemistry and the Raman spectra \textit{in situ} as staging proceeded (Chan \textit{et al} 1987a, Sumanasekera \textit{et al} 1999). He did complementary pioneering work on acceptor compounds in the bromine intercalant system, where he could study the spectra of both sp\(^2\) carbon and bromine (Eklund \textit{et al} 1978, Chen \textit{et al} 2003). This work was seminal to the field, advancing both materials physics and Raman spectroscopy in highly novel ways.

Superlattices in graphite intercalation compounds (Safran and Hamann 1979, Dahn \textit{et al} 1982) and doped polymers (Ma \textit{et al} 1988) arise from competition between anisotropic dopant–dopant and dopant–host interactions, as modulated by temperature-dependent entropic contributions, the dopant chemical potential \( \mu \), and the pressure \( P \). Staging is only stable when the effective in-plane dopant–dopant interaction is attractive while the effective out-of-plane dopant–dopant interaction is repulsive. In intercalated graphite at low temperatures, the in-plane attraction between intercalants dominates. Hence, an interlayer gallery is fully occupied by intercalants at a spacing consistent with their mutual hard-core repulsion and the strength of potential energy corrugations imposed by the honeycomb lattice. This interlayer filling occurs in a sequence of stages with increasing dopant concentration, including multiphase coexistence over most of the range of \( \mu \). Near saturation doping, the system attains stage 1 plus random vacancies. At sufficiently high temperature, each two-dimensional layer of intercalants melts and the system becomes a dilute, stage-1 lattice gas, with the intercalants distributed randomly.

What is the source of the effective attraction between intercalants within the same gallery? The effect is counter-intuitive, since charge-transfer dopants should repel each other through direct Coulomb interactions. At low dopant concentration, the layers of the carbon host deform elastically around well separated intercalant ions, creating elastic dipoles (Safran and Hamann 1979) whose magnitude and decay length depend on the strain gradient (see figure 11). Crucially, nearby dipoles in the same interlayer gallery attract each other, since this minimizes the total elastic deformation of the host. Elastically stiff hosts such as the TiS\(_2\), which is composed of thick, covalently bonded, S–Ti–S trilayers, support only weak strain dipoles that decay slowly with distance from the intercalant ion. Consequently, the elastically mediated dopant–dopant attraction in transition metal dichalcogenides is weak, and the only stable intercalated structure is stage 1 with random in-plane site occupancy. In contrast, the
Molecular $C_{60}$ solid in the fcc structure offers tetrahedral and octahedral interstitial sites suitable for intercalation (Murphy et al 1992). Solid $C_{60}$ is readily $n$-doped via reduction by alkali or alkaline earth metals, but apparently cannot be $p$-doped since oxidizing acids destroy the molecule. Doping solid $C_{60}$ with alkali metals $M = K$, Rb and Cs generates a series of well-defined crystallographic phases $M_xC_{60}$, where $x = 1, 3, 4$ and 6. At low concentration, alkali ions preferentially occupy the larger octahedral sites up to 1:1 alkali:$C_{60}$ stoichiometry, accompanied by slight lattice contraction due to ionic interactions, because even $Cs^+$ is too small for hard sphere repulsion to be a factor. Approaching $M_3C_{60}$, the smaller tetrahedral sites, two per molecule, begin to fill. The system either phase separates or behaves as a lattice gas depending on the intercalant (including alkaline earth alloys). Beyond $M_4C_{60}$ the host lattice transforms to tetrahedral, which accommodates four intercalants per fullerene since the latter are no longer close-packed. Finally, bct gives way to body-centered cubic at intercalants per fullerene since the latter are no longer close-packed. At $x = 3$ (Hebard 1992). Very narrow conduction bands produce the high density of states at the Fermi level favorable to superconductivity (Gunnarsson 2004). Careful consideration of Jahn–Teller distortions, exciton binding, and electron–electron correlation is required to reconcile the high $T_c$ (up to at least 33 K) with a BCS-like pairing mechanism.

Lattice gas behavior of the intercalant is not observed beyond the fcc limit, but a continuously variable doping per fullerene, in principle from 0 to 12 electrons, can be realized with mixed alkali/alkaline earth site occupancy. This feature was exploited to settle a controversy about the physical origin of fulleride superconductivity (Yildirim et al 1996). Recent reports of superconductivity above 11 K in $CaC_6$ (Emery et al 2008) may stimulate a re-examination of non-Fermi liquid behavior in doped carbon hosts.

The Eklund group prepared $M_xC_{60}$ samples using the glove box of figure 6, and discovered several interesting effects through Raman analysis (Eklund et al 1995b). The $A_g(2)$ mode frequency is sensitive to doping—downshifting by $\sim 6$ cm$^{-1}$ for each electron transferred to the ball—and can be used to monitor the diffusion of the alkali during intercalation. This mode softening due to charge transfer is roughly 70% as large as that observed in graphite intercalation compounds. In contrast to the $A_g(2)$ mode, the $A_g(1)$ radial breathing mode at 493 cm$^{-1}$ in $C_{60}$, seen in figure 5(a), hardens by $\sim 7$ cm$^{-1}$ upon doping to $M_xC_{60}$. Apparently a competing effect overwhelms the carbon–carbon bond elongation that is associated with charge transfer. Theoretical calculations indicate that an electrostatic interaction arising from the charged $C_{60}$ ball is partly responsible for the observed upshift (Jishi and Dresselhaus 1992).

What about ordered bundles of single-wall carbon nanotubes, also called ropes (Thess et al 1996)? Since cylinders are, crudely speaking, stiffer than sheets, the elastic deformation dipole in the tubes surrounding an intercalant in a nanotube bundle should be weaker than in graphite. Although rigid rotations about tube axes may yield local commensurability between adjacent tubes, the weakness of the interlayer corrugation and the incompatibility between $(n - m) \mod 3 \neq 0$ tubes and the 3-fold symmetry of the two-dimensional bundle lattice frustrates long-range order. In addition, the large separation between the centers of adjacent nanotubes should result in a weak interaction between hypothetical parallel chains of intercalants. One suspects that intercalated nanotube bundles are unlikely to show staging, instead favoring lattice gas behavior with random filling. Guest–host charge transfer and the resulting Madelung energy should then govern the phase stability, rather than the elastically mediated dopant–dopant interactions of graphite intercalation compounds.

Direct determination of doped nanotube structures is hindered by the difficulty of obtaining well-ordered host lattices of single-walled nanotubes with monodisperse diameter (Thess et al 1996). X-ray diffraction of bundles doped to saturation by $K$, $Rb$ and $Cs$ (Duclaux et al 2003) shows a shift in the first-order $(1, 0)$ peak—a characteristic of the 2D triangular bundle lattice—to lower wavevector, a shift that increases with atomic number of the alkali (see figure 12). This shift suggests a dilation of bundles which remain crystalline upon doping. However, the starting material in this experiment results from high-temperature annealing, which is known to increase the average tube diameter, since small-diameter tubes are less thermally stable than large-diameter ones. Thus, the small shift of the $(1, 0)$ peak between pristine and saturation-doped materials may correspond not to lattice dilation, but to a change in the average diameter of the constituent tubes. Curiously, the compositions determined by weight uptake correspond to one alkali atom per eight carbons, the same as the...
Figure 13. In situ powder x-ray profiles measured at fixed cell potentials during Li insertion (left, bottom to top) and de-insertion (right, bottom to top). As Li insertion progresses, the first-order rope peak at \( q = 4\pi \sin \theta / \lambda = 0.43 \, \text{Å}^{-1} \) decreases in intensity without shifting or broadening. Crystalline ropes are restored after de-insertion only after washing followed by a high-temperature anneal. Adapted from Claye et al (2000).

saturated stage-1 phase of graphite intercalation compounds. This correspondence suggests that electrostatics governs the stability of these compounds. Despite a relatively high concentration of inserted alkali atoms, the observed diffraction patterns do not exhibit new lattice symmetries and do not correspond to the ordered structures proposed by simulations (Gao et al 1998, Fischer et al 2000).

In situ experiments exploiting electrochemical control, where the sample serves as a working electrode, can accommodate measurement of x-ray diffraction, Raman scattering, reflectivity, resistivity and Pauli susceptibility (via conduction electron spin resonance) during charge/discharge cycles. In addition, a plot of cell potential versus dopant concentration can reveal general features of the phase diagram, such as staging transitions and coexistence regimes. Eklund recognized the beauty of this approach, exploiting it to perform in situ neutron diffraction during staging transitions of sulfuric acid in graphite (Chan et al 1987b). Much later, Peter measured resonant Raman scattering in p-doped nanotubes while electrochemically tuning the Fermi energy (Claye et al 2000).

Reversible electrochemical insertion of Li and K into single-walled nanotube bundles has been investigated by galvanostatic charge–discharge on half-cells consisting of purified single-walled nanotube buckypaper and Li or K metal, using LiPF\(_6\) or KCN salts in organic solvents. In situ acquisition of x-ray scattering data used a magnetically actuated piston to raise and lower the electrolyte (Claye et al 2000). Figure 13 plots the x-ray results across one lithium charge/discharge cycle. The reference spectrum shows a broad (1, 0) reflection at \( q = 0.43 \, \text{Å}^{-1} \) from the 2D triangular rope lattice and a sharp (002) peak at \( q = 1.87 \, \text{Å}^{-1} \) from residual graphite impurities. Doping reduces the intensities of these peaks, but does not change their positions. Near the maximum doping level (i.e. the lowest cell potential), the (002) peak develops a shoulder at lower \( q \); this signature of the \( \sim 10\% \) c-axis dilation of stage-1 LiC\(_6\) confirms the proper operation of the cell. Reversing the current recovers pristine graphite, but not ordered bundles: the (1, 0) peak does not recover. Bundle crystallinity was restored only by high-temperature annealing after disassembling the cell. Similar results for potassium, (whose higher scattering power would certainly reveal 2D lattice gas filling or lattice dilation), suggest that electrochemical doping simply frays the bundles somewhat by progressive solvent co-intercalation rather than irreversibly exfoliating them. In contrast, samples that are vapor-doped by alkali atoms retain crystalline bundles, but the relative x-ray peak intensities are inconsistent with appreciably filled channels in the doped state (Gao et al 1998, Fischer et al 2000).

A convincing fit of scattering data has not yet been achieved for any structural model for any dopant. Charge transfer in these electrochemically K-doped nanotube arrays has been studied by several in situ probes: four-probe conductivity, microwave conductivity, electron paramagnetic resonance spectroscopy and Raman spectroscopy (Claye et al 2000). Samples of a given concentration were anaerobically transferred to a cryostat for temperature-dependent measurements. An EPR signal is a definitive proof of a metallic state, since it measures the temperature-independent concentration of Pauli spins, which is proportional to the density of states at the Fermi energy. In addition, doping-induced redshifts of certain Raman-active modes reflect carbon–carbon bond softening due to n-doping, or conversely for p-doping (Rao et al 1997a). Figure 14 collects the room-temperature results. The top panel shows a smooth 15-fold increase in the conductivity (normalized to graphite) with increasing K concentration from zero to about KC\(_{27}\), a quarter of the saturation doping. For comparison,
conductivity enhancement saturates at by coinsertion of the THF solvent. Panel (a) shows that the controlled insertion and de-insertion. The maximum $K$ microwave and low audio frequencies. Panel (b) shows that the spin signature of charge transfer, also evolves continuously (and since THF (tetrahydrofuran) co-intercalates to form a partially solvated ternary compound at higher doping levels. The conductivity provides no evidence for phase transitions or staging under doping, consistent with the x-ray results showed during galvanostatically

de-doping. The conductivity is linear in cell potential but nonlinear in potassium concentration, since most of the K uptake occurs below 0.5 V. The smooth evolution of the conductivity provides no evidence for phase transitions or staging under doping, consistent with the x-ray results discussed previously.

Microwave ESR measurements required the weakly polar KCN electrolyte, for which the maximum $K/C$ ratio is 1/24, since THF (tetrahydrofuran) co-intercalates to form a partially solvated ternary compound at higher doping levels. The middle panel of figure 14 plots the Pauli spin susceptibility $\chi_p$, proportional to $\chi_p(E_F)$, as a function of doping. No conduction electron signal was detected in the undoped state due to dephasing of the induced spin alignment through interaction with approximately 1 at% of ferromagnetic Ni impurity from the catalyst. A well-defined resonance emerges upon doping, with a monotonically increasing intensity. Despite the large error bars, one is tempted to identify an induction period below K:C $\sim 0.007$ after which the susceptibility increases rapidly. However, the threshold at 0.007 most likely simply represents the potassium concentration at which all of the semiconducting tubes are doped into the metallic regime. The Raman shift shows a similar threshold, above which a continuous and reversible redshift reflects charge-transfer-induced softening of the carbon–carbon bonds, consistent with the behavior of the conductivity and Pauli susceptibility. Below this doping threshold the Raman shift is not monotonic; this is also the region where $\chi_p$ depends only weakly on K:C.

Alternatively, the induction period might suggest behavior reminiscent of the soliton doping regime in polyacetylene, i.e. a large conductivity enhancement with no spins. Charge transfer in doped conjugated polymers, in particular polyacetylene, is more subtle than in graphite due to the existence of solitons: one-dimensional objects, spread over about ten carbon sites on the (CH)$_1$ chain, which carry charge but no spin (Chi et al 1977, Heeger et al 1988). Solitons can originate at defects or can be induced by doping up to some maximum concentration above which the conductivity increases dramatically, with the onset of Pauli spins signaling the transition from a soliton-doped semiconductor to a normal metal. Nanotubes do exhibit a low energy elastic excitation, the twiston, which might provide the necessary quenched distortion to stabilize a localized lattice distortion on individual tubes (Kane and Mele 1997).

With the advent of graphene as the latest nanocarbon possessing readily tunable properties, we have come full circle. Wallace’s landmark band structure published 63 years ago contained the seeds of graphene physics, in particular band degeneracy and linear dispersion at the Fermi energy (Wallace 1947). It significantly influenced Peter’s early work on intercalation compounds. We now describe graphene as unrolled nanotubes; less than 20 years ago nanotube concepts were introduced by starting from the fiction of rolled-up single-layer graphite. For now graphene doping is generally limited to modulation by a capacitively coupled gate, as in field effect transistors. One suspects that it would not be long before someone rediscovers the surface science literature devoted to alkali metal adlayers (see, for example, Ancilotto and Toigo 1993) and develops a chemical procedure to induce permanent property changes in graphene.

Effects more dramatic even than intercalant doping are possible through chemisorption to graphene sheets (Boukhvalov and Katsnelson 2009). Chemisorption is more complex than physisorption, since one must explicitly account for the pronounced electronic and ionic response of the carbon atoms. One striking prediction of chemisorption models is graphene, in which hydrogen reacts with graphene to form an infinite, buckled sequence of C–H bonds, a giant planar molecule (Soto et al 2007, Flores et al 2009). Tentative experimental evidence for this novel two-dimensional crystal exists (Elias et al 2009), in that graphene reacts reversibly with atomic hydrogen. Exposure to cold-hydrogen plasma increases the electrical resistivity of graphene by two orders of magnitude. The resulting insulator remains a

Figure 14. In situ measurements of the electrical conductivity (a), spin susceptibility (b) and shift of the Raman-active G-band (c) as functions of $K/C$ ratio during galvanostatically controlled insertion and de-insertion. The maximum $K/C$ is limited by coinsertion of the THF solvent. Panel (a) shows that the conductivity enhancement saturates at $K/C \sim 0.04$, is completely reversible (solid and open circles), and is the same when measured at microwave and low audio frequencies. Panel (b) shows that the spin susceptibility also evolves reversibly with K concentration, more rapidly above $K/C = 0.007$. Panel (c) shows that the Raman shift, a signature of charge transfer, also evolves continuously (and reversibly, not shown) and exhibits non-monotonic behavior below $K/C = 0.007$. Adapted from Claye et al (2000).
hexagonal crystal, and the Raman spectrum shows vibrational characteristics of fully hydrogenated graphene. This material returns to its pristine graphene form after thermal annealing (Elias et al. 2009), without substantial damage to the graphene lattice. However, the lattice constant of the hydrogenated material currently presents an interesting puzzle. Transmission electron microscopy indicates that the insulating material produced by graphene hydrogenation has a lattice constant almost 5% smaller than graphene, but theory predicts that the lattice constant should be 3% larger than graphene (Sofo et al. 2007). Also unknown is the maximum degree of hydrogenation that can be obtained by this method.

4. Electron energy-loss spectroscopy at the nanoscale

As an excellent experimentalist, Peter was always aware that a complete picture of nature required one to correlate a nanostructure’s physical behavior with its structural, morphological and chemical characteristics. Although he appreciated the power of spectroscopic techniques such as Raman spectroscopy, Fourier transform infrared spectroscopy, photoluminescence and visible–UV absorption, these probes present intrinsic limitations in spatial resolution. Hence he also dedicated great attention to complementary techniques such as atomic force and electron microscopy that offer much higher spatial resolution, whether studying ensembles (Adu et al. 2008, W u et al. 2009) or individual (Chen et al. 2008, Wu et al. 2009) nanostructures.

In the later years of his career, Peter expanded his research interests to encompass many new kinds of nanostructures. He studied plasmons in nanoparticles, magnetic doping of semiconductor nanowires (Wu et al. 2009), the local properties of graphene (Gupta et al. 2009) and boron doping in carbon nanotubes (Liu et al. 2008). In many cases he successfully correlated, one-to-one, the physical behavior of individual nanostructures with their structure, chemistry and morphology, combining optical techniques with electron microscopy. We now review how recent technological advances in electron microscopy will advance Peter’s vision of the scientific method for research in nanoscience.

Spectroscopic techniques of absorption exploit the inelastic scattering suffered by the probe (photons or electrons) while traveling across a material, through interactions with vibrational modes (i.e. phonons), electronic transitions (excitons), and collective oscillations of free charge carriers (plasmons). Here we survey recent advances in using electron probes to study the physical and chemical properties of individual nano-objects, focusing on electron energy-loss spectroscopy (EELS) as performed in a transmission electron microscope.

The synthesis and fabrication of novel nanostructures imposes a growing need for analytical techniques with very high spatial resolution. Recently, electron energy-loss spectroscopy performed in a spherical aberration (Cs) corrected scanning transmission electron microscope (STEM) has reached record sub-nanometer, even atomic resolutions (Haider et al. 1998, Krivanek et al. 1999, 2003, Muller et al. 2006, Muller 2009, Maigne and Twesten 2009, Pennycook et al. 2009). An electron beam with an energy of a few hundred keV can be focused to a scanned probe ∼0.1 nm in diameter, making possible a transmitted image of a sample with atomic spatial resolution.

Figure 15 shows the main components of an STEM-EELS system. The high energy electron beam is focused to a sub-nanometer spot and can be passed through a thin crystalline sample along a single atom column. An annular dark field detector collects electrons elastically scattered at high angles by Rutherford scattering, forming an image as the probe scans the sample. Simultaneously, inelastically scattered electrons are collected in the forward direction; an electron spectrometer disperses these to resolve the energy-loss spectrum, correlated directly to the position of the beam on the sample.

Elastic scattering mainly arises from interactions with atomic nuclei. Since a nucleus has a much higher rest mass than an electron, the energy exchanged between them is too small to resolve in a TEM-EELS system. Elastic scattering produces the so-called zero-loss peak; in a very thin sample, this peak essentially reproduces the energy distribution of the electron source. Inelastic scattering arises from the interactions with conduction, valence and inner-shell electrons. The EELS spectrum presents two important regimes of inelastic scattering: the low-loss and high-loss regions. The low-loss region up to ∼50 eV involves interactions with the least-bound atomic orbitals, transferring energy into plasmons, inter-band transitions, and intra-band excitations. The high-loss region above 50 eV is associated with inner-shell electrons and hence it reveals the elemental composition of the sample.

The electrons in the outer shells (i.e. conduction electrons in a metal or valence electrons in a semiconductor) are weakly bound to the atoms, with significant delocalization into energy bands. Since they couple to each other by Coulomb forces, an electromagnetic perturbation (via photons or electrons) can induce collective oscillations with a characteristic energy...
signature. Fast electrons from the probe can displace outer-shell electrons in the specimen through Coulomb interaction, leaving behind a positively charged correlation hole. This perturbation can initiate a longitudinal charge oscillation along the probe trajectory (Egerton 2009): a plasmon wake oscillating at a frequency ωp.

The energy loss is proportional to \( \text{Im}[−1/\varepsilon(E)] = \varepsilon_2/(\varepsilon_1^2 + \varepsilon_2^2) \), where \( \varepsilon(E) = \varepsilon_1 + i\varepsilon_2 \) is the energy-dependent complex dielectric function of the medium. This quantity is routinely measured by optical techniques. Recently, techniques which exploit enhanced electromagnetic fields, such as resonant Rayleigh dark field optical microscopy, have measured the spatially averaged optical response from individual nano-objects (Sherry et al. 2006). However, even the most sophisticated optical methods, such as tip-enhanced optical spectroscopy (Cançado et al. 2009), cannot provide spatial resolution better than a few tens of nanometers. The sub-nanometer electron probe of an STEM-EELS system can also activate these optical excitations; this suggests the possibility of imaging localized excitations in a single nano-object through the near infrared, visible, and ultraviolet regions by STEM-EELS spectroscopy. Depending on the electron source, the lowest energy (i.e. near infrared) region of the EELS spectrum can be masked by the tail of the zero-loss peak. However, high-brightness, small-energy-dispersion electron sources, such as cold field-emission electron guns and e-beam monochromators (especially within C4-corrected STEMs), now provide the right tools to make these spatially resolved measurements. Note, however, that optical techniques like those that Peter pioneered still provide a finer energy resolution for measuring vibrational mode shifts.

For example, Nelayah et al (2007) mapped three distinct surface plasmon modes at 1.7, 2.7 and 3.2 eV within a single triangular Ag nanoparticle ~50 nm across, as depicted in figure 16. The lowest energy mode is confined to the corners of the triangle. The energy of this corner-localized mode strongly depends on the particle size and shape. Mapping plasmons in nanostructures facilitates plasmon engineering by tuning the nanoparticle geometry.

Recently, N’gom et al (2009) investigated the electromagnetic coupling of surface plasmon modes on two interacting Au nanorods. The isolated nanorods each show two plasmons, a longitudinal mode at ~1.9 eV that is confined to the rod ends and a transverse mode at ~2.4 eV that is homogeneously distributed along the nanorod. When two such rods are close to each other, the EELS spectrum measured in the gap between them shifts to lower energies. The experimental plasmon intensity distributions correlates well with the theoretical distribution of the electromagnetic field calculated by the discrete dipolar approximation method. The results also agree with previous optical measurements of interacting nanoparticles, wherein the spatially averaged plasmon intensity shows similar energy shifts (Rechberger et al. 2003,A tay et al. 2004).

The high-loss region of the EELS spectrum provides elemental analysis. The binding energies of inner-shell electrons (labeled K, L, M, N and O) range from hundreds to thousands of electron volts. When electrons from the beam ionize inner-shell electrons, the resulting features in the EELS spectrum, called ionization edges, characterize each
The material (and the basis of much of Peter’s research program). Anisotropic, with graphene being the ultimate two-dimensional sheets, such as graphite, nanotubes or nanohorns, are extremely orientation relative to the electron beam for isotropic materials annular dark field image. Individual Ti, O and Ca maps correlate with the high-resolution a misfit dislocation core at a SrTiO3/CaTiO3 interface. The STEM to obtain EELS spectrum images that clearly show a correction STEM. Figure 17 gives a beautiful example, where Pennycook et al corrected STEM. Atomic-resolution spectroscopic mapping of near-edge structures is now feasible with the new generation of Cs corrected STEM. Figure 17 gives a beautiful example, where Pennycook et al (2009) use a fifth-order aberration corrected STEM to obtain EELS spectrum images that clearly show a misfit dislocation core at a SrTiO3/CaTiO3 interface. The individual Ti, O and Ca maps correlate with the high-resolution annular dark field image.

Atomic-resolution spectroscopic mapping of near-edge structures does not depend on the crystal orientation relative to the electron beam for isotropic materials such as cubic crystals. However, structures based on graphene sheets, such as graphite, nanotubes or nanohorns, are extremely anisotropic, with graphene being the ultimate two-dimensional material (and the basis of much of Peter’s research program). The σ electrons of these sp2 hybridized carbon atoms provide strong inter-atomic bonding in the basal plane, while the π orbitals are oriented perpendicular to the plane. The K-edge of graphene-like materials is associated with transitions from the 1s state to empty π∗ and σ∗ anti-bonding orbitals. The π∗ component produces a sharp loss peak at 285.4 eV, while the broader σ∗ contribution centers around 292.5 eV. Scanning TEM-EELS of individual multi-walled carbon nanotubes reveals a strong orientation dependence to the K-edge (Stephan et al 2001, Maigne and Twosten 2009). Maigne and Twosten (2009) mapped the π∗/σ∗ K-edge intensities in an individual multi-walled carbon nanotube, showing maximum intensity when the beam is parallel to the graphene planes. A similar approach can in principle measure the sp2/sp3 ratio in hybrid nanostructures, but this experiment is more challenging (Berger et al 1988). The mapping of ionization edges has also revealed the chemical distribution and structure of multi-shell hybrid B–C–N nanotubes (Stephan et al 2001).

TEM instrumental development now enables scanned atomic-resolution EELS to reveal detailed field distributions in nanostructures, while simultaneously providing valuable information on their chemistry, structure and bonding at the atomic scale.

5. Defects in carbon nanostructures

A Stones–Wales defect can split into a dislocation dipole, the two dislocations gliding apart through a series of successive 90° bond rotations that shift bonds from the current seven-fold to the current five-fold ring.

Snapshots of atom emission from a bent double-walled nanotube in tight binding molecular dynamics in a microcanonical ensemble (Wako et al 2007). Dark gray, light gray, and black atoms denote the inner wall, outer wall, and emitted atoms, respectively. The arrow indicates a hole which relieves compressive stress.

Multi-vacancies produced by removing two, four, six or eight carbon atoms from a tube wall and subsequently relaxing the structure, all within an (8, 8) nanotube. Open circles on left denote removed atoms. The 5-8-5 defect of the di-vacancy evolves through dislocation climb as successive dimers marked in black are removed. Reproduced with permission from Wako et al (2008).


Figure 18 shows examples of point defects in a (6, 6) nanotube. The single-atom vacancy reconstructs to a more stable structure with a single dangling bond and a five-membered ring. A di-vacancy similarly reconstructs to form a 5-8-5 defect (which can be transformed into a 555-777 configuration by rotating a bond out of the eight-fold ring). A Stone–Wales defect comprises a 90° rotation of a C–C bond to create two oppositely-oriented 5–7 pair dislocations: a dislocation dipole. Finally, the last panel depicts an adatom–vacancy pair. Table 1 provides experimental and theoretical formation and migration energies for many of these defects. (Note that the reference state for the carbon chemical potential is not always explicitly described in the literature on defects with variable atom number, but one consistent definition could be the energy of an isolated carbon atom.) The vacancy and di-vacancy energies decrease with decreasing tube diameter due to the greater defect-induced release of curvature strain energy in narrower tubes; the di-vacancy energy is lower, since the dangling bonds can be satisfied under reconstruction. The Stone–Wales defect typically has the lowest formation energy, and hence is favored for formation under e.g. electron or ion irradiation. Helicity dependence arises from variations in the alignment of C–C bond relative to the tube axis and also electronic effects, visible most clearly in the period-three variation in figure 19 for zig-zag tubes.

Direct observations of point defects by scanning tunneling microscopy (Ouyang et al 2001, Ishigami et al 2004) and transmission electron microscopy (TEM) (Hashimoto et al 2004, Huang et al 2006) can image 5–7 pair defects and monitor the accumulation of topological defects near kinks in deformed nanotubes. Activation energies for vacancy–interstitial recombination (0.4 eV) and vacancy migration (0.7 eV) are also accessible to time-resolved, temperature-dependent Raman spectroscopy (Uchida et al 2007), as shown in table 1.

A dislocation within the wall of a nanotube changes wrapping indices and hence is not point-like. (Dislocations also form perpendicular to the basal plane in multi-walled nanotubes, as seen by TEM (Huang et al 2006).) The lowest-energy edge dislocation core contains a 5–7 pair defect; two
such defects can originate from the splitting of a Stone–Wales defect, as shown in figure 20 (Yakobson 1998). Plastic tensile deformation is associated with the glide of these 5–7 pair dislocations—through successive bond rotations—to lengthen the tube (Dumitrica and Yakobson 2004, Dumitrica et al 2006, Jiang et al 2004, Nardelli et al 1998, 2000), particularly at elevated temperature; this process has also been seen in TEM (Huang et al 2008, 2006). If bond rotation cannot occur, a stretched nanotube may fracture (Tserpes and Papanikos 2007). While the 5–7 defect glides by the bond rotation, it climbs through emission or adsorption of atoms (Ding et al 2007).

Dislocation dipoles also form under bending (Mori et al 2006, 2007), either as the split Stone–Wales defect described above or as a reconstruction of a multi-vacancy (Wako et al 2007). While the 5–7 defect glides by the bond rotation, it climbs through emission or adsorption of atoms (Ding et al 2007).

Table 1. Formation energies for a range of defects in carbon nanotubes.

<table>
<thead>
<tr>
<th>Defect type:</th>
<th>Wrapping indices</th>
<th>Diameter (Å)</th>
<th>Formation energy (eV)</th>
<th>Migration energy (eV)</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacancy</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Berber and Oshiyama (2006)</td>
<td>(3, 3)–(6, 6) (6, 0)–(12, 0)</td>
<td>4–8</td>
<td>4.5–5.5</td>
<td>DFT</td>
<td></td>
</tr>
<tr>
<td>Carlsson (2006)</td>
<td>(n, n)</td>
<td>5.5–11</td>
<td>5.2–6.4</td>
<td>DFT</td>
<td></td>
</tr>
<tr>
<td>Krasheninnikov et al (2006)</td>
<td>(n, n)</td>
<td>6–17</td>
<td>5.4–6.7</td>
<td>0.5–2.1</td>
<td>Tight binding (TB), DFT</td>
</tr>
<tr>
<td>Kotakoski et al (2006)</td>
<td>(5, 5) and (10, 10)</td>
<td>4–16</td>
<td>5–6.8</td>
<td>0.3–1.0</td>
<td>TB, DFT</td>
</tr>
</tbody>
</table>

| Di-vacancy   |                  |              |                       |                      |        |
|--------------|------------------|--------------|-----------------------|                      |        |
| Carlsson (2006) | (n, n) | 5.5–11 | 3.6–4.4 | DFT |
| (and certain chiral tubes) | (n, 0) | 5.5–11 | 3.4–4.0 | DFT |
| (n, 0) | 4–16 | 2.7–4.7 |        |        |
| Kotakoski et al (2006) | (5, 5) and (10, 10) | 7 and 14 | 4.0 and 5.2 | DFT |
| Amorim et al (2007) | (5, 5)–(10, 10) | 7–14 | 4.1–4.9 | DFT |
| (8, 0)–(18, 0) | 6–14 | 3.6–4.4 |        |        |
| Berber and Oshiyama (2008) | (n, n) | 4–8 | 3.9–4.3 | DFT |
| (n, 0) | 5–9 | 3.5–3.8 |        |        |

| Stone–Wales  |                  |              |                       |                      |        |
|--------------|------------------|--------------|-----------------------|                      |        |
| Zhou and Shi (2003) | (12, 0)–(60, 42) | 9–70 | 4.5–7.5 | Extended Hückel |
| (curved clusters, not tubes) |              |              |                       |                      |        |
| Carlsson (2006) | (n, n) | 5.5–11 | 2.6–3.4 | DFT |
| (n, 0) | 5.5–11 | 2.2–3.4 |        |        |
| Dinadayalan and Leszczynski (2007) | (5, 5) | 7 | 1.4–2.3 | DFT, MP2 |
| Ertkin et al (2009) | (6, 6)–(10, 10) | 8–14 | 2.8–4.1 | Continuum mechanics |
| (8, 0)–(20, 0) | 6–16 | 3.0–4.5 |        |        |

| Adatom-vacancy |                  |              |                       |                      |        |
|----------------|------------------|--------------|-----------------------|                      |        |
| Okada (2007) | (9, 0)–(11, 0) | 7–9 | 8.1–10.0 | DFT |

Vacancy recombination and migration

| Uchida et al (2007) | Mixed | 0.4 and 0.7 | Raman pulsed laser, T-dependent |

Figure 22 depicts the formation and migration of this dislocation dipole due to successive atom emission. The left-hand panels show initial states for successively larger multi-vacancies in a (8, 8) nanotube, with their relaxed structures—minimizing dangling bond energy—shown on the right. The di-vacancy reconstructs as a 5-8-5 defect. Tetra-, hexa- and octa-vacancies all reconstruct as 5–7 defect dipoles. Treating the 5-8-5 defect as a special case of coincident 5–7 defects, the distance between the constituent 5–7 pairs in the dislocation dipole increases with increasing number of removed atoms. These separated 5–7 defect dipoles—formed from linear multi-vacancies—are more stable than comparable structures formed by relaxing more compact multi-vacancy clusters (Sammalkorpi et al 2004, Kotakoski et al 2006, Lee et al 2009). The dislocation dipoles stabilize the bent tube, with larger separations generating larger bend angles, as shown in figure 23 for a (5, 5) tube (Wako et al 2008). Hence the
Figure 23. The bending angle and binding energy of a (5, 5) nanotube with a 5–7 dislocation dipole as functions of the number of atoms removed from one side. The nanotube shown has the maximum bending angle, 24.2°, caused by the removal of 8 atoms. The original unit cell contains 400 atoms. Reproduced with permission from Wako et al (2008).

Figure 24. Snapshots of the annihilation of a 5-8-5 defect through collision with a carbon dimer (in black), in tight binding molecular dynamics. The dimer has an incident kinetic energy of 18 eV.

As we look back on Eklund’s scientific career, his contributions had a large impact on carbon nanostructures, from his earliest attempts to probe single-layer and few-layer graphene in graphite intercalation compounds; to his studies on fullerenes in their pristine, doped and polymerized forms; to carbon nanotubes as they appear in their single-walled, double-walled and multi-wall pristine and doped forms; and finally to graphene which again appears in the corresponding layered forms. Although his own research work largely focused on optical and spectroscopic studies, where he did pioneering work, he followed the entire field of nanocarbons broadly and related his own scientific advances to this broader context. This approach was also apparent in his pioneering work on nanowires, to which he brought to bear his extensive knowledge about carbon nanostructures to search for quantum confinement phenomena in other nanowire systems. He applied his deep appreciation for the design of clever experiments and new experimental approaches to advancing research and in discovering new physics in quantum wires during the last decade of his career.

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5–7 defect dipole facilitates plastic bending, in addition to axial extension.

Being formed by atom emission, these same defects can be annihilated through atom addition. To simulate this process, carbon dimers were impacted onto a 5-8-5 defect in tight-binding molecular dynamics (Xu et al 1992) (the following describes new work by KW, MT and KK, not previously published). A relaxed 5-8-5 defect within a (5, 5) nanotube is impacted at the site of the eight-fold ring by C$_2$ dimers with kinetic energies from 8 to 30 eV. Figure 24 depicts the resulting defect annihilation: for initial kinetic energies above 18 eV, the dimer successfully inserts into the 5-membered rings.

Electron and ion beams can cut and weld carbon-based nano- and micro-devices (Jang et al 2004, Krasheninnikov and Banhart 2007, Kosynkin et al 2009, Elias et al 2010), perforce introducing defects during these operations; these must be understood and controlled to produce reliable devices. Computational studies currently dominate research on such defects in carbon nanotubes, revealing strong effects of tube diameter and helicity, and underpinning emerging experimental efforts in resolving and characterizing these defects.

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