Doctoral Qualifying Examination, January 2015

Mechanical Engineering Department, Columbia University

CARBON NANOTUBES AND GRAPHENE

Question 1: Electronic Structure of Diatomic Molecule

Consider a simple 'tight binding' model of a diatomic molecule, with a state that is a superposition of identical states on atoms 1 and 2, with complex coefficients u_1 and u_2.

$$\Psi(r) = u_1\varphi_1 + u_2\varphi_2$$

a) Provide an expression for the expectation value of energy $\langle E \rangle$ in terms of the overlap integrals $H_{ij} = \langle \varphi_i | H | \varphi_j \rangle$.
b) For identical atoms, set the zero of energy such that $H_{11} = H_{22} = 0$. Find the extrema of $\langle E \rangle$ -- i.e. the bonding and antibonding energies. Show all major steps in the derivation.
c) Derive the bonding and antibonding wavefunctions (i.e. u_1 and u_2).

Question 2: Crystal Structure and Electronic Structure of Graphene

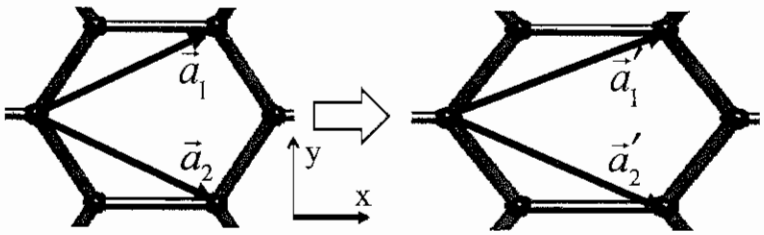
a) Sketch the crystal lattice of graphene, and the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of the graphene unit cell. Choose one atom as the origin and provide the coordinates $\mathbf{R}_i$ of its three nearest neighbors (in terms of a)
b) Sketch the reciprocal lattice of graphene and give the values of the reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$. Sketch the first Brillouin zone, and determine the coordinates of the K points at the corners of the BZ.
c) In the tight binding model, the electronic states of graphene are given by:
$$\varepsilon(\boldsymbol{k}) = \pm t\sqrt{f(\boldsymbol{k})} \text{ where } f(\boldsymbol{k}) = \sum e^{i\boldsymbol{k}\cdot\boldsymbol{R}_i}$$
Show that $\varepsilon(\boldsymbol{k}) = 0$ at the K points, and expand around one of these points to give an expression of the linear bandstructure (Dirac cone).

Question 3: Electronic Density of States

a) Consider a 1-D lattice with periodic boundary conditions and length L. Give the number of states N(k) with $|\boldsymbol{k}| < k$. Repeat for a 2-D lattice with area L^2.
b) For a system with a linear bandstructure $\varepsilon = v|\boldsymbol{k}|$, calculate and sketch the electronic density of states in 1D and 2D.
c) Now consider a gapped system with $\varepsilon = \sqrt{\Delta^2 + v^2k^2}$. Expand around k=0 to show that the bandstructure is parabolic. Give an expression for the effective mass.
d) For the gapped system, calculate and sketch the electronic density of states in 1D and 2D.

2012 ME PhD Qualifying Exam: Carbon Nanotubes questions

Question 1:



A graphene sheet with unit vector length a=2.46 Å is subjected to 20% uniaxial strain in the armchair (x) direction, as shown. Assume that there is no strain in the y direction, and that all of the carbon-carbon bond distances remain equal (which would not actually be the case).

a) Find the length a' of the strained unit vectors, and the new carbon-carbon bond length.
b) Sketch the reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$, and give their Cartesian components. Sketch the 1st Brillouin zone.
c) For a nanotube constructed from the strained lattice with circumferential vector $C_h = n\mathbf{a}_1' + m\mathbf{a}_2'$ derive expressions (in terms of n and m) for:

1. The circumference C_h
2. The components t_1 and t_2 of the translation vector $\mathbf{T}=t_1\mathbf{a}'_1 + t_2\mathbf{a}'_2$

Question 2:

A one-dimensional semiconductor has a unit vector length a, and a total length L = Na. Its conduction and valence bands have electronic dispersion relations given by:

$$E_c = \frac{1}{2}E_g + \frac{\hbar^2 k^2}{2m_e^*} \qquad E_v = -\frac{1}{2}E_g - \frac{\hbar^2 k^2}{2m_h^*}, \text{ with } m_h^* = 2m_e^*$$

a) Sketch the electronic dispersion in the first Brillouin zone. Identify the edge of the B.Z., and give the width (in k) of one electronic state.
b) Calculate the electronic density of states in the conduction and valence bands, and sketch.
c) Repeat the same calculation and sketch for an equivalent 2D material with a square lattice and size LXL.

Question 3:

a) For a nanotube of radius R, what is the spacing between 1D bands (in k-space)?
b) For a semiconducting nanotube, sketch the first few bands near the K point, and state their perpendicular spacing from the K point.
c) Calculate the energies of the band minima / maxima for these bands. Ignore trigonal warping, and leave your answer in terms of constants such as h-bar and v_F.
d) Describe the series of optical transitions expected between these states, and why some are generally allowed vs. not allowed.
e) Explain how the real optical transitions observed in nanotubes are different from these single-particle transitions. What is the physical explanation for this difference?

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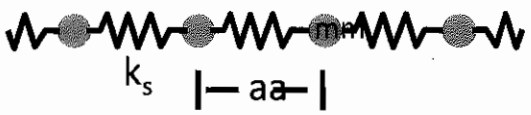
2013 ME PhD Qualifying Exam: Carbon Nanotubes / Graphene questions

Question 1:

Consider a 1D chain of identical atoms with bond length a, mass m, and spring constant k_s between the atoms, with a total length L, as shown:



a) Give the length of the reciprocal lattice vector.

b) Assuming periodic boundary conditions, give the spacing between allowed values of the wavevector **k**. (not the same as spring constant)

c) The phonon dispersion in a solid is given by setting det (D) = 0, where the dynamical matrix D is given by:

$$D^{(ij)}(\mathbf{k}) = \left(\sum_{j''} K^{(ij'')} - M_i \omega^2(\mathbf{k}) I \right) \delta_{ij} - \sum_{j'} K^{(ij')} e^{i\mathbf{k}\cdot\Delta\mathbf{R}_{ij'}}$$

where K is the force constant tensor between atoms i and j. Solve for the dispersion relation ω(k), for the 1D chain above, in the case in which the atoms are constrained to move only in the direction of the lattice. Sketch ω(k) in the first Brillouin zone.

d) For the solution to c) above, calculate the phonon density of states D(ω).

e) The energy of the phonon system is given by $U(T) = \int n(E) D(E) dE$, where the phonon occupation is given by the Bose-Einstein distribution $n(E) = \frac{1}{e^{E/k_B T} - 1}$. Derive an expression for the phonon specific heat C=dU/dT. Show that C(T) is linear in T at low temperature (i.e. well below the energy of the zone-edge phonon).

Question 2:

Near the Dirac (K) point, graphene has a conical bandstructure $\varepsilon(\mathbf{k}) = \pm \hbar v_F |\delta\mathbf{k}|$, where δ**k** is the wave-vector relative to the K point, and the Fermi velocity v_F is ~10^6 m/s (which can also be expressed as $\hbar v_F = 0.65$ eV-nm).

a) For a 2D graphene sheet of area A, calculate position of the Fermi level ε(n), as a function of 2D charge density in electrons / cm^{-2}.

b) Calculate the 2D electronic density of states D(ε) near the Dirac point.

c) For a sheet of graphene placed on a conducting Si substrate with 285 nm of SiO_2, calculate the position of the Fermi level as a function of back-gate voltage ε(V_g). The dielectric constant of oxide is ~ 35 X 10^{-12} F/m, and the charge on the electron is e = 1.6 X 10^{-19} C.

Question 3: (note, see question 2 for bandstructure of graphene)

a) Describe (i.e. in words and sketch) how rolling graphene into a nanotube causes the 2D Dirac cone to split into 1D bands.

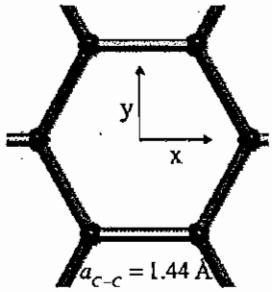
b) Find the electronic bandgap of semiconducting nanotubes, as a function of nanotube diameter.

c) Describe how the symmetry of the electronic states near the Dirac point leads to suppressed scattering in graphene and nanotubes. What types of disorder can either weakly or strongly scatter electrons?

d) Consider a strip of graphene with a width of 1 μm to be quantized in the same way as a rolled nanotube (i.e. periodic boundary conditions). Find the number of conducting channels in the strip as a function of Fermi energy. Assuming the graphene is ballistic, calculate the 2-terminal conductance as a function of Fermi energy.

2012 ME PhD Qualifying Exam: Carbon Nanotubes questions

Question 1:
For a graphene lattice with carbon-carbon bond length a_{cc}, as shown:



a) Sketch the lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$, and give their Cartesian components.
b) Calculate the sheet density (in kg/m^2) of graphene
c) Sketch the reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$, and give their Cartesian components. Sketch the 1st Brillouin zone.
d) For a nanotube with indices (n,m), derive expressions (in terms of n and m) for:

1. The circumference C_h
2. The components t_1 and t_2 of the translation vector $T=t_1\mathbf{a}_1 + t_2\mathbf{a}_2$
3. The number of atoms in the unit cell
4. The reciprocal lattice vectors $\mathbf{K}_1$ and $\mathbf{K}_2$.

Question 2:
In the nearest-neighbor tight-binding model, the conduction and valence band energies of graphene are given by $\varepsilon(\mathbf{k}) = \pm t\left|f(\mathbf{k})\right|$, where $t \approx 3$eV and $f(\mathbf{k}) = \sum e^{i\mathbf{k}\cdot\Delta\mathbf{R}}$, with the sum taken over all three nearest-neighbor atoms.

a) Show that, near the K point, this expression produces a conical bandstructure $\varepsilon(\mathbf{k}) = \pm v_F\left|\delta\mathbf{k}\right|$, and provide an expression for the Fermi velocity v_F.

b) Calculate the electronic density of states D(E) near the Dirac point. Compare this to a 'normal' 2D system with $E = \frac{\hbar^2 k^2}{2m^*}$.

c) Use the results of b) to calculate the electronic heat capacity of graphene in the low-temperature limit. The occupation of electronic states (and therefore the electronic energy) is governed by the Fermi-Dirac distribution $f(\varepsilon) = \frac{1}{e^x + 1}$, where $x = \frac{(\varepsilon - \varepsilon_F)}{k_B T}$. You can leave as a

Question 3:

a) Show that nanotubes with (n-m) = 3 X integer are metallic.
b) Derive an expression for the bandgap in semiconducting nanotubes as a function of nanotube radius.
c) Describe the series of allowed optical transitions in a semiconducting nanotube. How do their energies scale with the index of the transition and with nanotube radius?
d) Explain why these optical transitions show a small dependence on chiral angle, that is different for nanotubes with $p = \pm 1$, where p=(n-m) mod 3. Describe how these 'family relations' are used to identify the chiral indices in one type of optical spectroscopy (e.g. fluorescence, Rayleigh scattering, or Raman scattering).