Utrecht University
Exam Solids & Solid Surfaces
Tuesday, January 27, 2015
Time: 13:30 - 16:30

Read the questions carefully. Answer the questions in the spaces provided on the question sheets. If you run out of room for an answer, continue on the back of the page.

Name and student number: _____

Good luck!

Question 1: **Wulff construction** ..... *12 points*

Consider the graphene lattice shown in Figure 1 below.

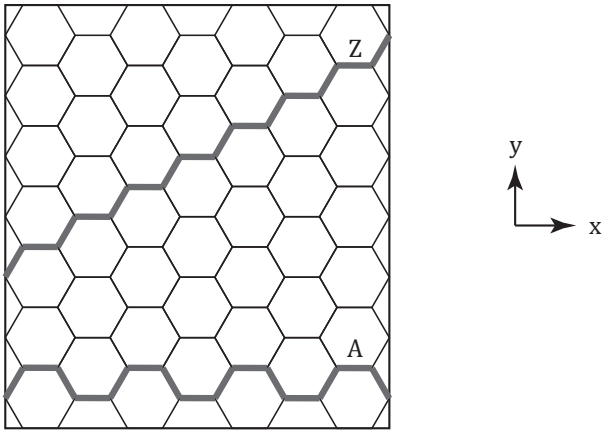

Figure 1: Geometry of a graphene sheet. Zigzag (Z) and armchair (A) directions indicated by a thick gray line. Orientation of x and y axes as indicated.

(a) (2 points) How many equivalent armchair directions are there in graphene? How many equivalent zigzag directions?

Answer: *There are 6 equivalent armchair directions (1 point) and 6 equivalent zigzag directions (1 point).*

(b) (10 points) Assume that the energies of the zigzag and armchair edges are $\gamma_Z = 1.2$ eV and $\gamma_A = 1.0$ eV, respectively. All other edge terminations have a much larger energy. Use the Wulff construction to predict the equilibrium structure of a graphene flake.

Answer: *The angle between the armchair and zig-zag direction is* $30°$ *(2 points).* $\Gamma_Z \cos 30 > \Gamma_A$ *(2 points). The hexagonal symmetry (2 points) implies that a graphene flakes should be terminated by 6 armchair edges (2 points), i.e. the flake is hexagonal. 2 points for the sketch.*

Question 2: **Miller indices** ..... *8 points*

Consider the crystals shown in Figure 2 below.

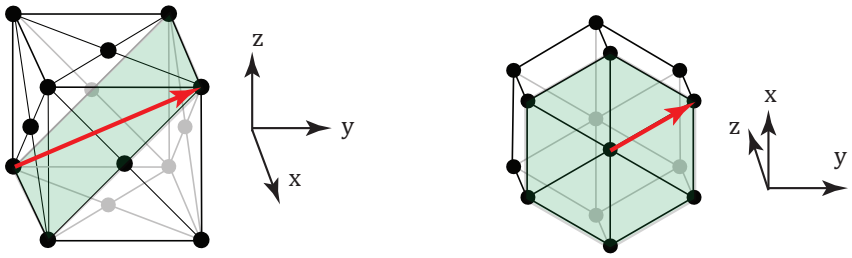

Figure 2: Crystals belonging to the face-centered cubic (left) and hexagonal class (right), respectively.

(a) (8 points) Give the Miller indices of the planes indicated in green and of the arrows indicated in red in Figure 2. Use the axes as indicated in the figure.

Answer: *Left plane: (*$0\bar{1}1$*), left direction: [111]. Right plane: (0001), right direction: [0100]. 2 points for each correct answer.*

Question 3: **Angle Resolved Photo Electron Spectroscopy** ..... *21 points*

(a) (8 points) Give two strong and two weak points of STM and ARPES.

Answer:

STM strong	Very high spatial resolution (often atomic) Measure local density of states Visualize molecular orbitals in real space
STM weak	Sample needs to be conductive convolution of electronic structure and topography
ARPES strong	Band structure determination Momentum space microscopy Easy comparsion with theory
ARPES weak	surface sensitive single crystals only UHV required Occupied states only

1 point for each correct answer. Other answers are possible.

(b) (13 points) In ARPES experiments, the kinetic energy of the photo emitted electrons is given by:

$$E_{kin} = \frac{\hbar^2 \mathbf{k}_\parallel^2}{2m} \cdot \frac{1}{\sin^2 \theta} \tag{1}$$

Here, $\hbar$ and m are the reduced Planck constant and electron mass, respectively (with values 1.05×10^{-34} m^2 kg s^{-1} and 9.11×10^{-31} kg). Below is a projection of the graphene band structure onto the high symmetry directions of the 2D Brillouin zone. The work function of graphene is 5.11 eV. The coordinates of the K and M points are: $\left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right)$, and $\left(\frac{2\pi}{3a}, 0\right)$, respectively. a is the C-C bond length (1.42 Å). When performing an ARPES experiment on graphene with a Helium discharge lamp ($h\nu = 21.2$ eV), under what angles do you expect to detect electrons coming from the K, M and Γ points?

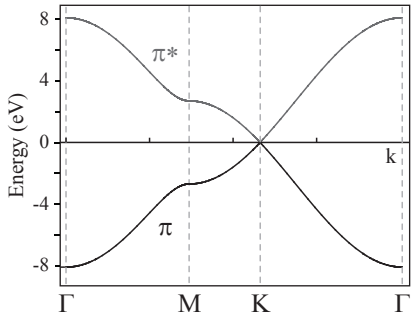

Figure 3: Band structure of graphene along high symmetry directions of the Brillouin zone.

Answer: *Rewrite the given expression:*

$$\theta = \arcsin \frac{\hbar \mathbf{k}_\parallel}{\sqrt{2mE_{kin}}} \tag{2}$$

(1 points). We need to determine the values of the kinetic energy and $\boldsymbol{k}_\parallel$ *for each point. The kinetic energy is given by:*

$$E_{kin} = E_{photon} - E_{binding} - \Phi \tag{3}$$

(3 points). The values of $E_{binding}$ *can be extracted from the band structure diagram. The values of* $\boldsymbol{k}_\parallel$ *can be calculated from the coordinates of the high symmetry points. We can now fill in the following table:*

Point	$\mathbf{E}_{Kin}$ (eV)	$\mathbf{k}_\parallel$(Å^{-1})	**Angle** (in °)
Γ	≈ 8.09	0	0
M	≈ 13.59	1.47	51.08
K	≈ 16.09	1.70	55.66

1 point for each correct value of the kinetic energy, parallel momentum, and angle (9 points in total).

Question 4: **Graphene rolled up to carbon nanotubes** ..... *18 points*

Carbon nanotubes (CNTs) can be considered as sheets of graphene rolled into a cylinder. There are various ways in which a sheet can be rolled into a tube, which can be defined using the lattice vector $\mathbf{c}_h = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$, see Figure 2 below. Here, n_1, n_2 are integers and $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit vectors of graphene. The CNT is formed by connecting the atoms indicated by the red dots, i.e. the cylinder joint is made along the dotted lines perpendicular to $\mathbf{c}_h$. The two limiting cases in which the graphene can be rolled are $\theta = 0$ (zigzag direction) and $\theta = \pm 30$ (armchair direction). The resulting tubes are called zigzag and armchair tubes, respectively. All other CNTs are called chiral. You will show that depending on how the sheet is folded, CNTs are either metallic or semiconducting.

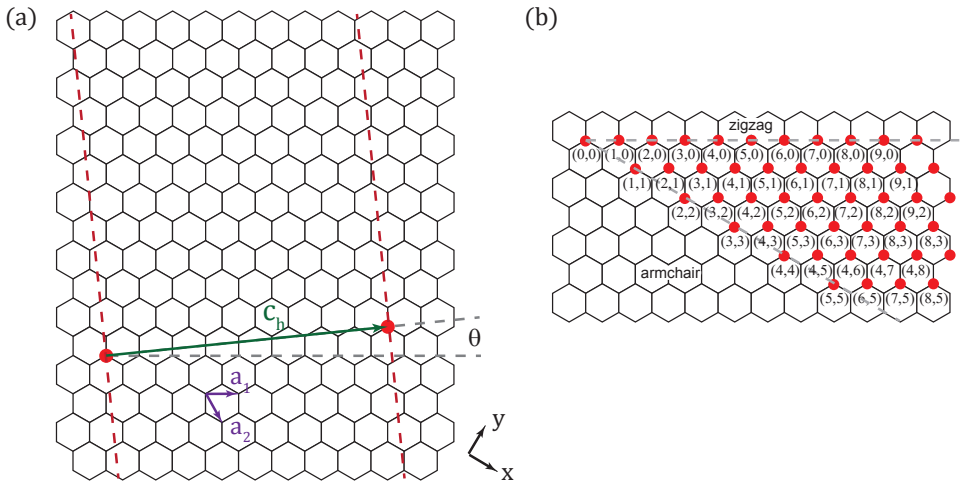

Figure 4: **(a)** Carbon nanotubes are made by rolling a graphene sheet into a cylinder. CNTs are uniquely defined by the lattice vector $\mathbf{c}_h$. The chiral angle is denoted by θ, while $\mathbf{a}_1$ and $\mathbf{a}_2$ indicate unit vectors of graphene. The x- and y-directions are indicated (same as in exercise 1). **(b)**Possible vectors for chiral fibers. Armchair and zigzag directions are indicated by dotted lines.

(a) (6 points) Use Blochs' theorem (a wave function in a crystal can change under translation only by a phase factor), together with periodic boundary conditions to show that the following equation holds for carbon nanotubes:

$$\mathbf{c}_h \cdot \mathbf{k} = 2\pi m \tag{4}$$

***answer**: The Bloch theorem states that:*

$$\psi(\mathbf{r} + \mathbf{c}_h) = \psi(\mathbf{r}) e^{i\mathbf{k}\mathbf{c}_h} \tag{5}$$

(2 points) From the periodic boundary condition:

$$\psi(\mathbf{r} + \mathbf{c}_h) = \psi(\mathbf{r}) \tag{6}$$

(2 points) These two requirements can only be satisfied if the following condition is satisfied:

$$\mathbf{c}_h \cdot \mathbf{k} = 2\pi m \tag{7}$$

(2 points) with m an integer.

(b) (2 points) What is needed for a material to be metallic? Which points in the Brillouin zone of graphene fullfill this requirement?

***answer**: A metal has unoccupied states at the Fermi level (1 points). For graphene, this only occurs at the K- and K'-points (1 point).*

(c) (6 points) The Dirac cones are located at $\left(\frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a}\right)$. Show that the condition for a fiber to be metallic is:

$$2n_1 + n_2 = 3q \tag{8}$$

where q is an integer.

***answer**: The lattice vectors are: $\boldsymbol{a}_1 = \left(\frac{3a}{2}, \frac{\sqrt{3}a}{2}\right)$ (1 point) and $\boldsymbol{a}_2 = \left(\frac{3a}{2}, \frac{-\sqrt{3}a}{2}\right)$ (1 point). Inserting these expressions, together with K-point (2 points), into the equation found under 4(a), directly gives the condition (2 points).*

(d) (4 points) Show that this implies that all armchair-CNTs are metallic, while every other third zigzag tube is metallic.

***answer**: For armchair ribbons $n_1 = n_2$ (1 point), so armchair CNTs are always metallic (0.5 point). For zigzag CNTs $n_2 = 0$ (1 point). For these tubes to be metallic the condition transforms to: $2n_1 = 3m$ (1 point). This holds for every third zigzag CNT (0.5 point).*