PHYS4450 Solid State Physics **Problem Set 1** **Due: 1 February 2013 (Friday)**

All problem sets should be handed in not later than 5pm on the due date. Drop your assignment in the Box labeled PHYS4450 in SC 213. Late submission within Due+2 days from the due date will receive a discounted score.

Important: You MUST attached a SIGNED declaration on academic honesty to every problem set. Homework without a signed declaration form will NOT be graded. A form is attached at the end of the Problem Set.

Please work out the steps of the calculations in detail.

1.0 *Reading Assignment: Don't need to hand in anything.* Read Chapter 1 of Kittel and/or Chapter 2 of Christman. Chapter 1 of the e-book of Quinn and Yi also covers the same materials (deeper in some topics). Read also Kittel's Chapter 3 (early sections) for a review on different types of bonding (see Problem 1.1). The part on bonding will not be discussed in class, yet it is part of our course. Read Kittel or Christman's discussion on bonding in solids. You are assumed to know the basics of bonding, e.g. ionic, covalent, metallic, and molecular (Van der Waals) bonding (see Quantum Physics II).

1.0' Read all the problems at the end of Kittel's Chapter 1. You should be able to do all that (don't need to hand them in), and the answers are scattered in our class notes.

1.0" *Action:* (a) Go to the library (reserved books section) and browse the standard textbooks reserved under PHYS4450. Get a feeling of the style of the books. There must be one that fits your taste. (b) Click on the link in course page to browse the e-book *Solid State Physics: Principles and Modern Applications* by JJ Quinn and KS Yi. The first 9 chapters are standard topics in a basic course like ours. It is a good book.

1.1 **Self-study on Cohesive Energy I.** This is related to the fundamental question of why atoms (or molecules) come together to form a regular array (i.e., solids). You have learnt this in Quantum Physics (on bonding). Let's review and learn something new. (Your Quantum Physics textbook and Kittel's Ch.3 may be useful.) In Nature, when you see some basic entities coming together to form a stable group, there must be a potential energy function $u_{pair}(r)$ (which indicates the interaction between two entities as a function of their separation r) of the form that the two entities experience an attractive force when they are close to each other and a repulsive force when they are TOO close to each other. The origin of these forces depends on the physical situation (e.g., the nucleons in a nucleus, atoms in a molecule, ions in a ionic crystal, molecules in a molecular crystal, etc.), but the shape of $u_{pair}(r)$ is general.

In this problem, we consider **molecular crystals** or crystals in which the atoms are only weakly interacting. In molecular crystals, i.e., a regular array of molecules, the bonding is typically weak and a popular form of the pairwise interaction is

$$u_{pair}(r) = -4\epsilon\{\left(\frac{\sigma}{r}\right)^6 - \left(\frac{\sigma}{r}\right)^{12}\}, \tag{1}$$

where ϵ has the units of energy and σ carries the units of a length. Equation (1) is called the **Lennard-Jones potential** or simply the "6-12 potential". This is the interaction between gas molecules in a jar of air. Usually, we simple IGNORE this interaction and treat a jar of air as an IDEAL GAS. This assumption works OK for the air in our classroom. However, as temperature is lowered, it is this interaction that leads to a phase transition, e.g., from gas to liquid and from liquid to solid, in systems where the basic entities are charge neutral. This is the $u(r_{ij})$ we had in mind when deriving the van-der-Waals gas law in statistical mechanics. And molecular solids do exist.

(a) Without knowing the values of ϵ and σ, sketch Eq.(1) and indicate ϵ and σ in your sketch.

(b) Consider a molecular solid. We need not specify the lattice structure at the moment. Argue that the energy (due to the pairwise interaction) in one mole is given by

$$U = -\frac{N_A}{2}\sum_{j\neq i} 4\epsilon\{\left(\frac{\sigma}{r_{ij}}\right)^6 - \left(\frac{\sigma}{r_{ij}}\right)^{12}\}, \tag{2}$$

where r_{ij} is the separation between molecules i and j in the solid and N_A is the Avogadro number. Why is there a factor of 1/2?

(c) For any lattice, there is a nearest neighbor distance (from any point, one can find the nearest neighbor(s) and then find the distance). Let r_0 be the nearest neighboring distance, which as yet is an UNKNOWN. In terms of r_0, each r_{ij} can be written as $r_{ij} = \alpha_{ij} r_0$, where α_{ij} is a NUMBER. (That is to say, we can measure r_{ij} using r_0.) Show that U in Eq.(2) can be rewritten as

$$U = -2\epsilon N_A \left(\frac{\sigma}{r_0}\right)^6 A_6 + 2\epsilon N_A \left(\frac{\sigma}{r_0}\right)^{12} A_{12}, \tag{3}$$

where A_6 and A_{12} are two numbers given by

$$A_6 = \sum_{j\neq i} \left(\frac{1}{\alpha_{ij}}\right)^6 \tag{4}$$

$$A_{12} = \sum_{j\neq i} \left(\frac{1}{\alpha_{ij}}\right)^{12}. \tag{5}$$

Note that up to now, we need NOT specify the lattice.

(d) For a given lattice, A_6 and A_{12} can be evaluated (at least numerically). So let's assume that they are known. U becomes a function of σ/r_0. We look for the value of r_0 such that U is a minimum, i.e., what is the nearest neighboring separation r_0 in a molecular solid taking on the assumed lattice? By minimizing U with respect to σ/r_0, show that the equilibrium nearest neighboring separation is given by

$$r_0 = \sigma \left(\frac{2A_{12}}{A_6}\right)^{1/6}. \tag{6}$$

Hence, show that the **cohesive energy per mole** is given by

$$U = -N_A \epsilon \left(\frac{A_6^2}{2A_{12}}\right), \tag{7}$$

and the **cohesive energy per molecule** in the solid is given by

$$u = -\epsilon \left(\frac{A_6^2}{2A_{12}}\right). \tag{8}$$

The **cohesive energy** is a measure of how stable the solid is, as compared to the molecules being far apart (where the interaction is negligible). A more negative cohesive energy implies a more stable solid. Therefore, a solid that results from a stronger bonding mechanism will have a more negative cohesive energy. Note that up to now, we need NOT specify the lattice.

(e) To proceed, we specify the lattice. Let's consider the case where the molecules sit on the points forming a **face-centered cubic** lattice. Write down mathematical expressions for A_6 and A_{12} (recall that they are numbers) by including the first FIVE TERMS (meaning: five "shells" of neighbors of increasing distance) in the sums in Eqs.(4) and (5). Sum the terms up and get the numerical values for A_6 and A_{12}. By comparing the results for retaining FEWER TERMS, are the sums converging rapidly? The calculations here are referred to as "doing lattice sums". [**OPTIONAL - no bonus**: Write a small computer program to obtain A_6 and A_{12} to high accuracy and also work out A_6 and A_{12} for the body-centered cubic lattice.]

(f) What you obtained for A_6 and A_{12} is good for ALL face-centered cubic lattices (regardless of the actual value of the lattice constant). Now, let's apply the results to real solids with very weak interaction. Xenon forms a face-centered cubic solid. Xenon atom has a closed shell structure.

Thus, the interaction between xenon atoms is very weak and the Lennard-Jones interaction is applicable. (Note we are applying the results to a solid form by atoms.) If we know the values of the parameters ϵ and σ from experiments, then we can obtain an estimate for the nearest neighboring separation r_0 from Eq.(6) and for the cohesive energy U or u from Eq.(7) or (8). From experimental studies on Xenon **gas** (not from solids), it was found that $\sigma = 3.98 \times 10^{-10}$ m and $\epsilon = 0.02\ eV$. ESTIMATE r_0 and u (cohesive energy per atom) for xenon. [For your information, using X-ray diffraction, $r_0(expt)$ was found to be $4.33 \times 10^{-10}\ m$, and by measuring the latent heat of vaporization, $u(expt)$ was found to be $-0.17\ eV$.]

(g) Don't need to do anything. Read parts (a) to (f) again and understand the steps in the calculation of cohesive energy of a solid, given a form of pairwise interaction. The steps are general and applicable to other solids. Chapter 3 of Kittel discusses cohesive energy. In the next Problem Set, you will play around with ionic crystals in a similar fashion.

1.2 (See Sample Question SQ1) Someone tells you tell he found a crystal with the following primitive lattice vectors:

$$\mathbf{a}_1 = (a/2)\hat{\mathbf{x}} + (a/2)\hat{\mathbf{y}},$$
$$\mathbf{a}_2 = a\hat{\mathbf{y}},$$
$$\mathbf{a}_3 = (a/\sqrt{2})\hat{\mathbf{z}}.$$

where $\hat{\mathbf{x}}$, $\hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$ are unit vectors in the x, y, and z directions of a Cartesian coordinate system.

(a) Identify the Bravais lattice. [Drawing a picture may help.]

(b) Evaluate the volume of the primitive cell.

(c) Decide whether there is a conventional unit cell for this lattice. If yes, find the volume of the conventional unit cell.

(d) The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ define a plane (two non-colinear vectors define a plane) and it also defines a set (infinitely many of them) of crystal planes that are parallel. Find the separation between adjacent planes. [Using the picture in (a) may help.]

(e) We discussed that the choice of primitive vectors for a lattice is NOT unique. Write down another possible choice of the primitive lattice vectors and evaluate the volume of the primitive cell again using your set of primitive vectors.

1.3 The face-centered cubic lattice is important for the reason that many semiconductors take on the fcc lattice. Take the primitive lattice vectors for a fcc lattice to be $\mathbf{a}_1 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{y}})$, $\mathbf{a}_2 = \frac{1}{2}a(\hat{\mathbf{y}} + \hat{\mathbf{z}})$ and $\mathbf{a}_3 = \frac{1}{2}a(\hat{\mathbf{x}} + \hat{\mathbf{z}})$. Express the following vectors as linear combinations of the primitive vectors: [it is useful to make a sketch of the lattice and the vectors] (a) the position vectors for the eight cube corners (thinking about the conventional cubic unit cell); (b) the position vectors for the six cube face centers; (c) the positive vector of the point that is 3/4 on the line that goes from a lattice point (the origin) diagonally across the cube to the opposite corner (we are not saying that there is a lattice point at this location, we simply want to describe this location using primitive lattice vectors).

Finally, look up a picture for diamond (carbon crystal) and silicon. Describe the crystal structure by (i) specifying the Bravais lattice and (ii) specifying the basis set of atoms decorating each lattice point and where they sit relative to a lattice point.

1.4 (See Sample Question SQ2)

(a) Consider a two-dimensional (2D) square lattice as shown in the attached page. Five sets of crystal planes (lines) are shown. Taking the separation between neighboring lattice points as a (called the lattice constant). find the distance between adjacent planes for cases (b)-(e), using **elementary mathematics (e.g., trigonometry)**. [Remark: You can also regard the system as three-dimensional by stacking up layers. See (b).]

(b) Consider a three-dimensional cubic lattice. The attached page (again) shows the lattice points on the x-y plane and the three-dimensional system is formed by stacking up layers one on top of another. The z-direction is pointing out of the page. The natural choice of primitive vectors is $\mathbf{a}_1 = a\hat{x}$, $\mathbf{a}_2 = a\hat{y}$, and $\mathbf{a}_3 = a\hat{z}$.

(i) Find the Miller indices for the planes in cases (b)-(e) on the attached page. [Remark: Important to convince yourself that the Miller indices actually define an infinite set of parallel planes AND that the planes contain all the lattice points (no points are left out).]

(ii) Starting with the formula for the separation between adjacent planes (see class notes) which is valid for any lattice type, find the separation for the sets of crystal planes in cases (b)-(e) shown on the attached page.

1.5 (See Sample Question SQ3)

Find the Miller indices for the following lattice planes: The plane containing the points $3\mathbf{a}_1$, $2\mathbf{a}_2$, and $\frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$, in ANY lattice.

1.6 (Structure of Graphene) The attached page shows where the carbon atoms in graphene (which is a single sheet of graphite) sit. The atoms labelled A and B are both carbon atoms. The labels emphasize that the local environment of A and B atoms are different. Therefore, we need to (i) identify the underlying 2D lattice; and (ii) decorating each lattice point with a basis of two carbon atoms and specifying their positions relative to a lattice point. The carbon-carbon separation is 1.42Å. **Describe** the crystal structure of graphene completely.

The graphene structure results from covalent bonding between carbon atoms. In chemistry language, each atom undergoes sp^2 hybridization. With what you know about carbon atoms (6 electrons per atom) and sp^2 hybridization, **describe** clearly why there is such a crystal structure and where the electrons are. In particular, discuss what happens to the electron in a carbon atom that is not involved in forming the honeycomb structure of graphene.

SAMPLE QUESTIONS FOR DISCUSSION IN WEEK 2 (23 Jan 2013) EXERCISE CLASS

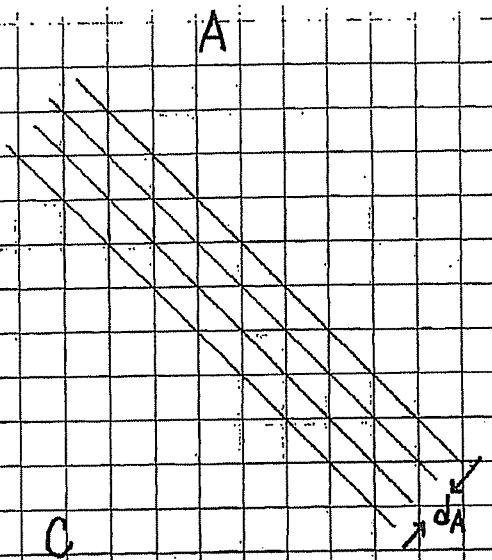
You may want to think about them before attending exercise class and discuss them with the TA.

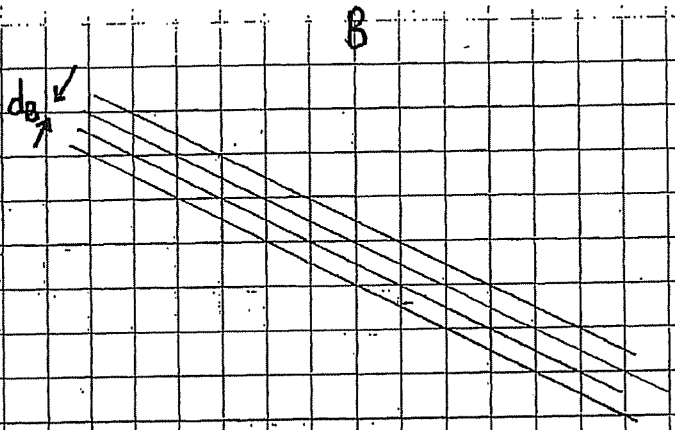
SQ1 (Related to Question 1.2.) Identify the following Bravais lattice in 3D given the following primitive lattice vectors. Evaluate the volume of the primitive cell and find the volume of the conventional unit cell (if there exists one).

$$\begin{aligned} \mathbf{a}_1 &= a(-\hat{\mathbf{x}} + \hat{\mathbf{z}}), \\ \mathbf{a}_2 &= a(-\hat{\mathbf{x}} + \hat{\mathbf{y}}), \\ \mathbf{a}_3 &= \tfrac{a}{2}(-\hat{\mathbf{x}} + \hat{\mathbf{y}} + \hat{\mathbf{z}}), \end{aligned}$$

SQ2 (Related to Question 1.4.) TA will illustrate how to do Problem 1.4 part (a) and part (b) for the planes in case (a) in the figure. [You are asked to do cases (b)-(e).]

SQ3 (Related to Question 1.5.) Find the Miller indices for the following lattice planes: The plane that is parallel to both $\mathbf{a}_1$ and $\mathbf{a}_3$, in ANY lattice.


A
d_A


B
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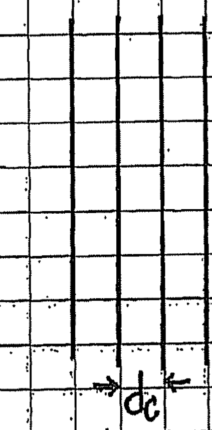
C
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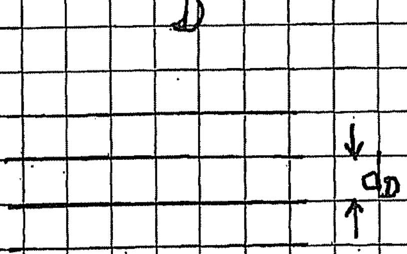
D
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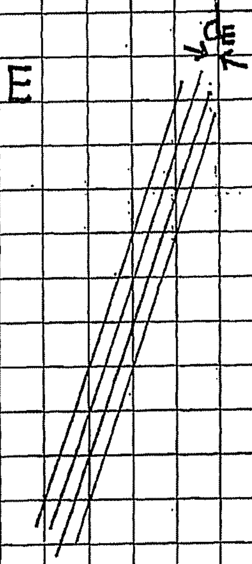
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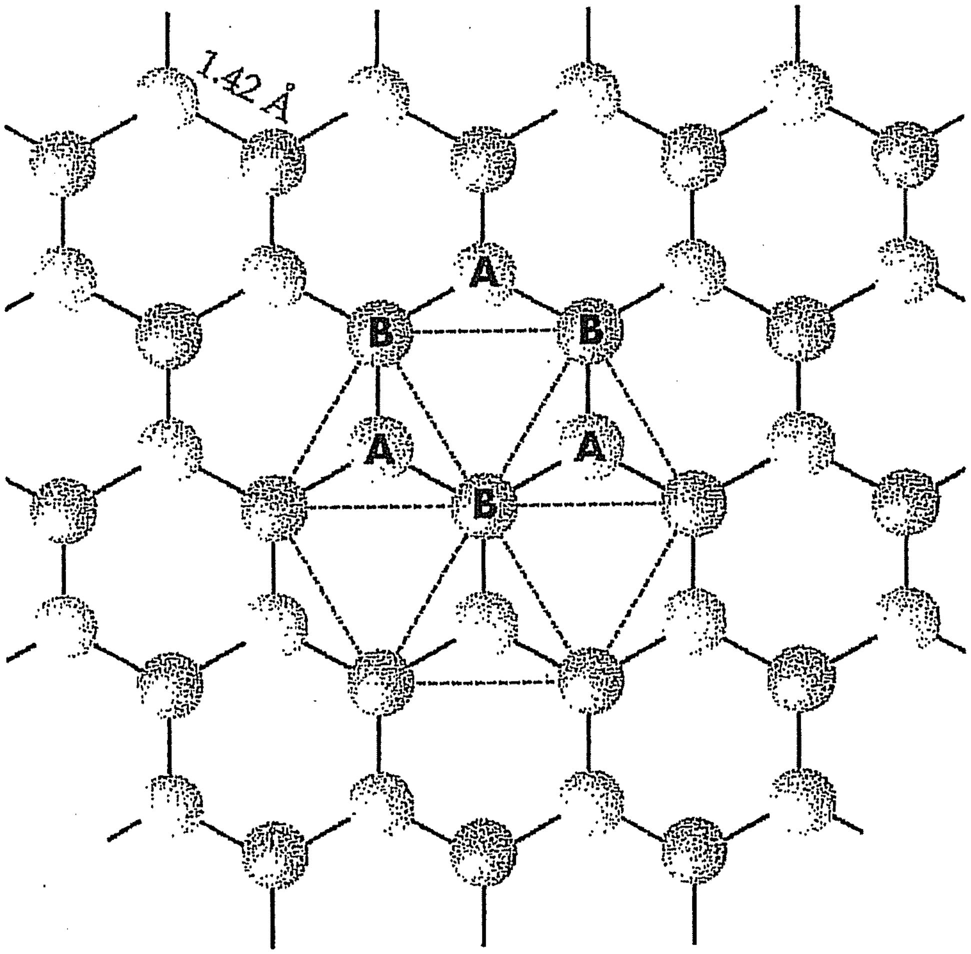

Figure showing carbon atoms in graphene

Further Reading on graphene:

A. K. Geim and A. H. MacDonald, "Graphene: Exploring carbon Flatland", Physics Today (August 2007), p. 35-41.

[Remark: A. K. Geim shared the 2010 Nobel Physics Prize.]

Important: You must attach a signed copy of the following declaration to your homework. You may also download the form in the website listed below.

I declare that the assignment here submitted is original except for source material explicitly acknowledged, and that the same or related material has not been previously submitted for another course. I also acknowledge that I am aware of University policy and regulations on honesty in academic work, and of the disciplinary guidelines and procedures applicable to breaches of such policy and regulations, as contained in the website http//www.cuhk.edu.hk/policy/academichonesty.

Signature

Name

PHYS4450 Solid State Physics

Date

Student ID

Problem Set Number