Class 21: Anisotropy and Periodic Potential in a Solid

In the progress made so far in trying to build a model for the properties displayed by materials, an underlying theme is that we wish to build the simplest model that we can get away with. This is the reason we examined the Drude model, which is very simple, but still makes good predictions. However, we have been able to identify its limitations as well. It is worth noting that in the approach we have taken so far, we typically start by assuming that the system follows specific rules and then build equations consistent with these rules. In this process, the equations are typically 'correct' within the context of the rules assumed, and hence when the predictions do not turn out to be accurate, it is not the equations, but the rules themselves, that need to be re-examined. In other words, the rules chosen for the system, are themselves not appropriate for the system, and hence need to be modified. It is in this vein that the Drude-Sommerfeld model, differs from the Classical Drude model. The Drude–Sommerfeld model relinquishes the assumption of classical behavior of the electrons and imposes the assumption of quantum mechanical behavior of electrons, thereby changing the rules for the system. The new rules result in improved predictions.

In the further refinements that we will make as we proceed, the overall approach will be the same. Limitations of models that we will try to overcome will come about due to changes or modifications in the rules we will expect the system to obey, and hence equations that will result, will differ.

We note that the Drude-Somerfeld model is still a 'free electron model'. There is no variation in the potential experienced by electrons in the solid as they traverse the extent of the solid. The justification for this assumption is that all of the negative charges in the solid, from the free electron cloud, will be neutralized by all of the positive charges in the solid, from the ionic cores, since the solid is charge neutral. Therefore the free electron model is not unreasonable at first glance. However, it is also true, that while the overall material is charge neutral, the positive and negative charges are not distributed uniformly across the extent of the solid, when examined at an atomic level. The ionic cores occupy specific locations within the solid, and their influence is more strongly prevalent in the vicinity of their locations. Therefore, when an electron moves through the solid, although the solid is charge neutral from an overall perspective, the potential the electron experiences is a very strong function of its position – i.e., a flat uniform potential is far from reality.

Having recognized that the flat potential model is too simplistic, it is also of interest to identify specific aspects of material properties that the Drude-Sommerfeld model may not be in a position to address. Perhaps the most prominent aspect of material properties that cannot be addressed by the Drude-Sommerfeld model in its present form is the anisotropy, or dependence on direction, in properties displayed by most materials. Let us briefly examine how anisotropy manifests itself in material properties, and why we may not always notice it, even though the material is inherently anisotropic.

Consider the samples shown in Figure 21.1 below:

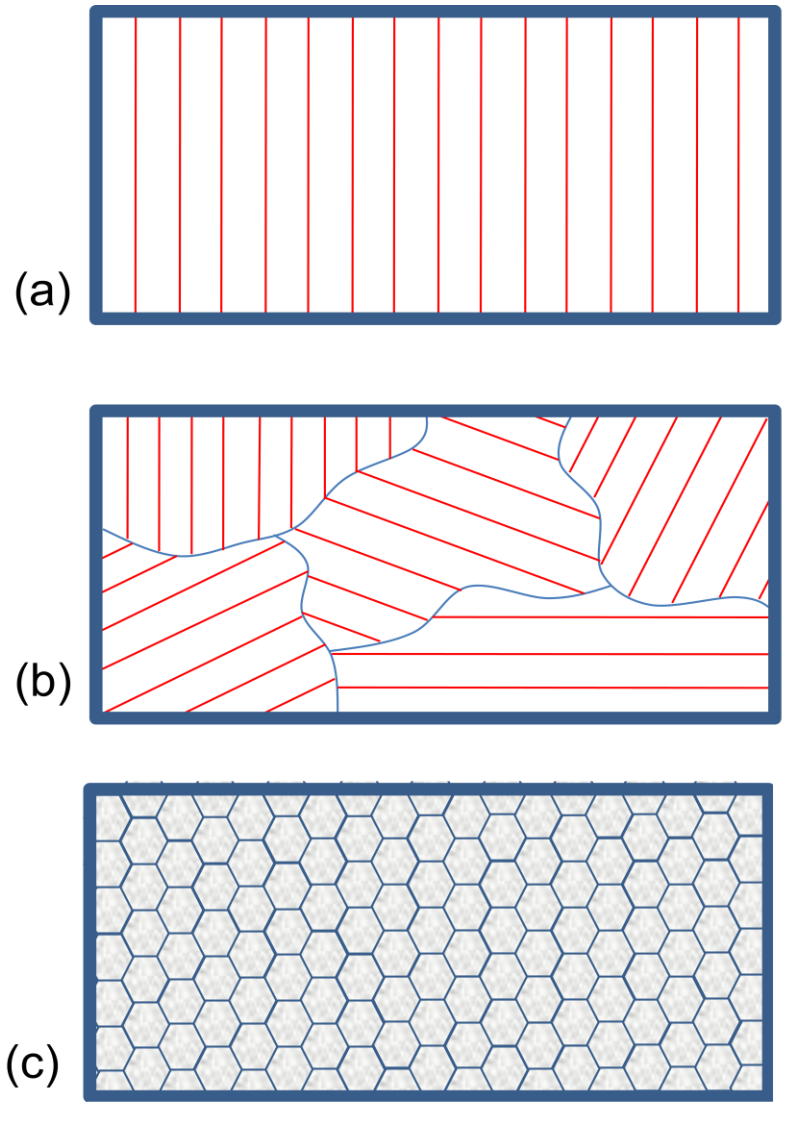


Figure21.1: a) A single crystal; b) A polycrystal with large crystal sizes; c) A polycrystal with very small crystal sizes. The lines and shading within the crystals are representative of crystal planes. The direction of the lines is representative of the orientation of the crystal planes.

In a single crystal, shown in Figure 21.1a, the atoms are in perfect crystallographic order from one end of the sample to the other. Therefore each direction in the sample that is a single crystal, represents a specific order of atoms and atomic planes. Therefore, a single crystal sample typically shows strong directionality, or anisotropy, in its properties. The sample properties represent inherent material properties.

In a polycrystal with large crystal sizes as shown in Figure 21.1b, assuming that the crystals are randomly oriented, there is an increased chance that the sample properties are averaged versions of the material properties across a few different directions. The same sample direction will likely be different crystallographic directions in each of the crystals. Therefore the overall property displayed in a given direction by the sample, will have contributions from different crystallographic directions from each of the crystals making up the sample.

In a polycrystal with very small crystal sizes as shown in Figure 21.1c, assuming that the crystals are randomly oriented, the sample properties will necessarily be averaged versions of the material properties across many different crystallographic directions. This averaging is a direct result of the fact that a given direction in the sample, will have contributions from a very large number of crystallographic directions corresponding to the many randomly oriented crystals making up the sample.

So while Figure 21.1a results in the display of ‘material properties’ during measurements, Figures 21.1b and 21.1c progressively result in the display of ‘sample properties’ rather than the inherent ‘material properties’ during measurements. While the sample properties do originate from the inherent material properties, averaging of the properties due to the polycrystalline nature of the samples, masks details of the directionality of the inherent material properties. The sample may be isotropic while the material itself is anisotropic.

A classic example of a material that shows significant anisotropy, is graphite. Figure 21.2 below shows the layered structure of graphite.

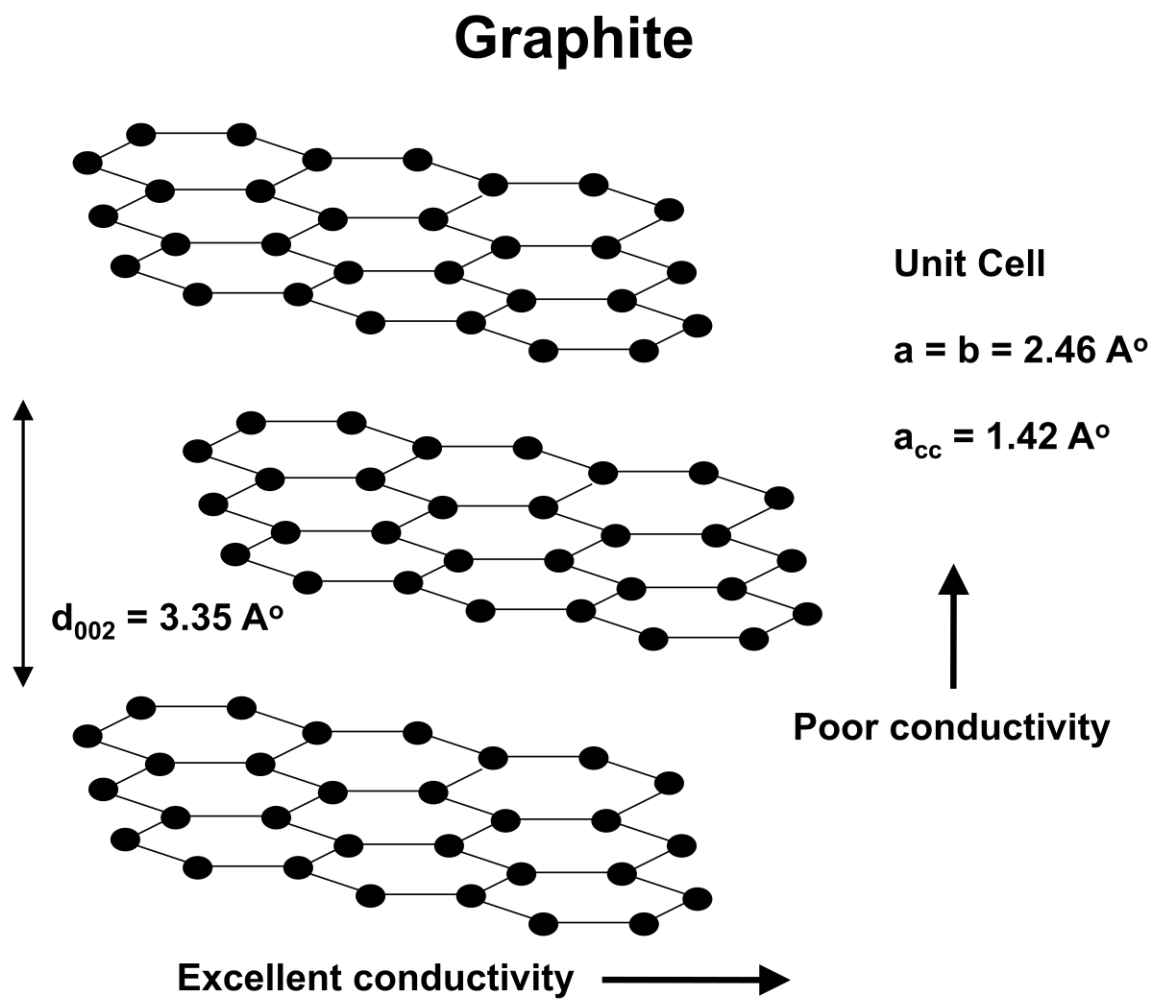


Figure 21.2: The layered structure of graphite. Graphite displays poor electronic conductivity perpendicular to the sheets of carbon atoms, and excellent electronic conductivity parallel to the sheets of carbon atoms.

Graphite has excellent electronic conductivity parallel to the sheets of graphite, and very poor conductivity perpendicular to the sheets.

There is nothing in the Drude-Sommerfeld model to suggest anisotropy. The model assumes a uniform field within the material and ignores the ionic arrangements. The model has therefore effectively enforced isotropy. The model assumes isotropy, therefore the results are isotropic.

Therefore there is a need to develop a better picture of the potential an electron experiences as it travels through the solid. In other words we need to incorporate into the model the dependence of potential on the position of the electron.

Let us first consider a single ionic core and examine the potential the electron experiences as it moves from infinity, towards the ionic core. The energy, or potential, due to the coulombic force

of attraction between the negatively charged electron and the positively charged ionic core is given by the expression:

$$E = -\frac{1}{4\pi\varepsilon_0}\frac{e^2}{r}$$

Where ε_0 is the permittivity of free space, e is the charge of the electron, and r is the distance between the electron and the ionic core. The electron will experience the above potential as a function of position, regardless of the direction from which it approaches the ionic core. For simplicities sake a one dimensional example is taken and the potential experienced by the electron as a function of position, as it approaches the ionic core from the positive x direction and the negative x direction, is shown in Figure 21.3 below.

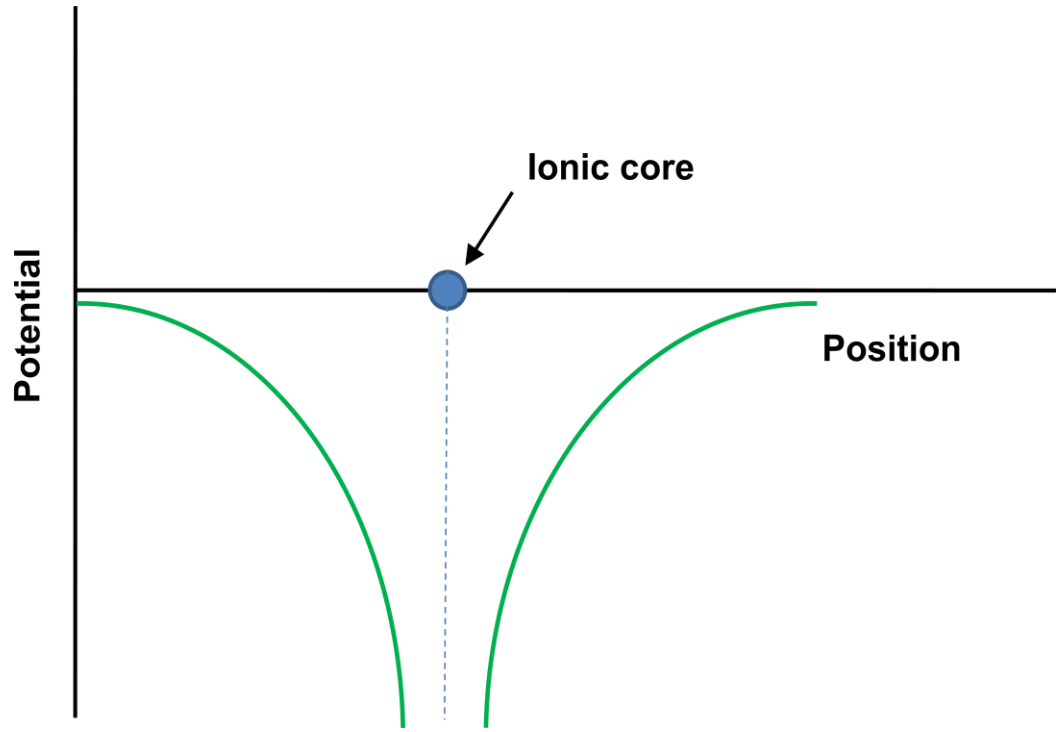


Figure 21.3: A one dimensional example of potential experienced by an electron, as a function of position with respect to an ionic core.

In reality, if the electron gets extremely close to the ionic core, it will start interacting with the electron cloud around the ionic core and a repulsive force will result. For the purposes of the present discussion, this repulsive interaction is being ignored based on the idea that only 'free' electrons are being examined and hence they can be expected to not get very close to any particular ionic core.

If we extend the above analysis to a one dimensional lattice, with regularly spaced ionic cores, we can expect the interaction of the electron with each of the ionic cores to be identical to that

described above for the single ionic core. Figure 21.4a shows the interaction of the electron with each individual ionic core, neglecting the influence of the remaining ionic cores on the electron.

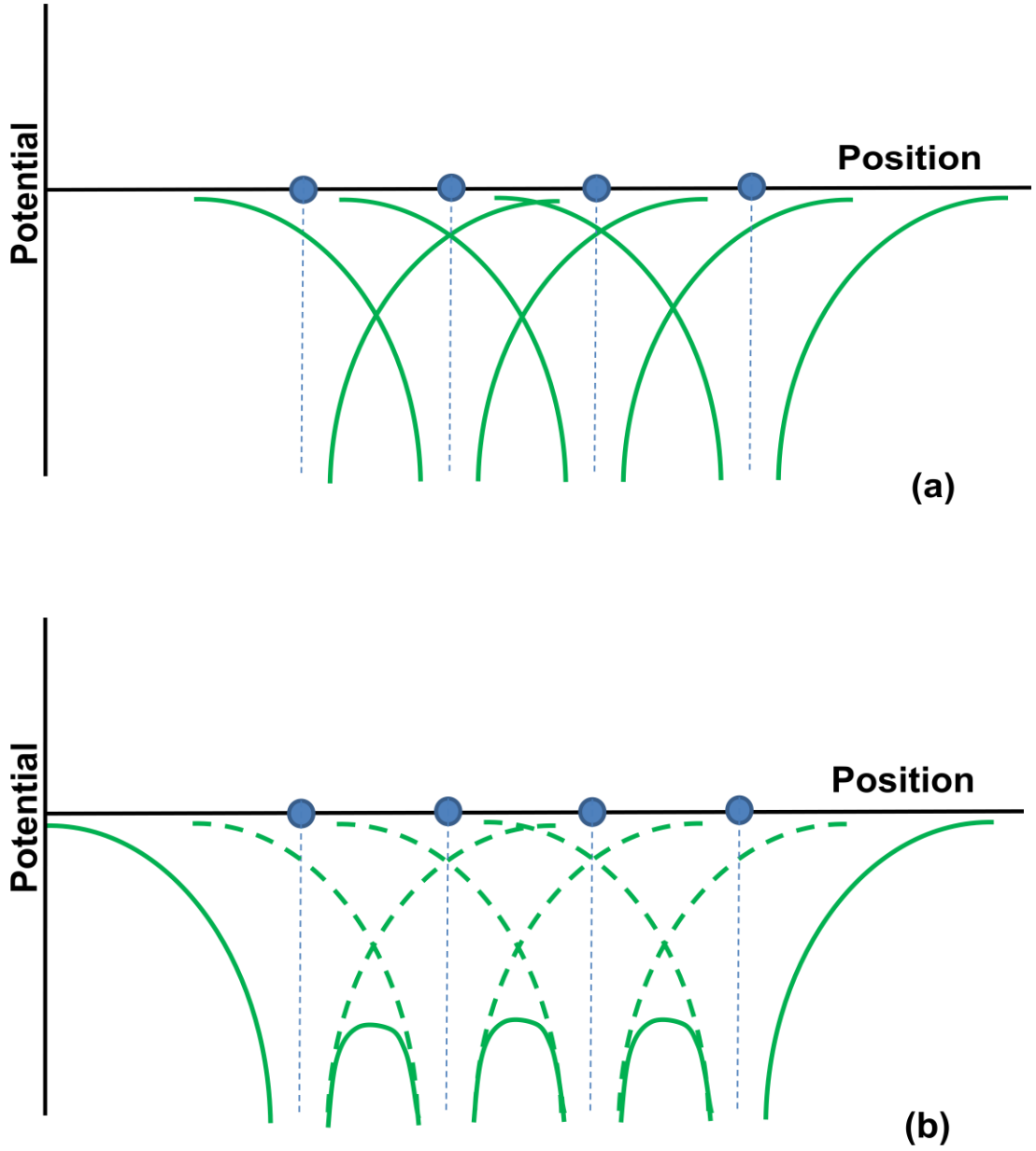


Figure 21.4: The potential experienced by an electron, as a function of position with respect to a one dimensional lattice of uniformly spaced ionic cores; a) interaction with each ionic core, ignoring the impact of the other ionic cores; b) interaction with the lattice as a whole

In reality, since the ionic cores are relatively close to each other, as the electron moves from left to right in the figure above, it will begin to experience the presence of each succeeding ionic core, before it has fully escaped from the influence of the preceding ionic core. The interaction of the electron with the one dimensional lattice as a whole is shown in Figure 21.4b above.

The steep fall in potential close to each ionic core, is called a ‘potential well’. As seen from Figure 21.4 above, the potential inside a solid is not constant or ‘flat’. It is therefore necessary to build enough detail into the model to incorporate the potential experienced by an electron as a function of position in the one dimensional lattice.

However, it turns out that while it is important to capture the reality of potential wells in the model, it is not necessary to immediately focus on the exact shape of the curve associated with the formation of the potential well. It will be adequate if we can make a reasonable approximation of the potential landscape experienced by an electron in the solid. The approximation we make should capture enough detail of the reality of the situation while minimizing the associated complexity.

Figure 21.5 below represents an approximation of the potential landscape experienced by an electron in a one dimensional solid.

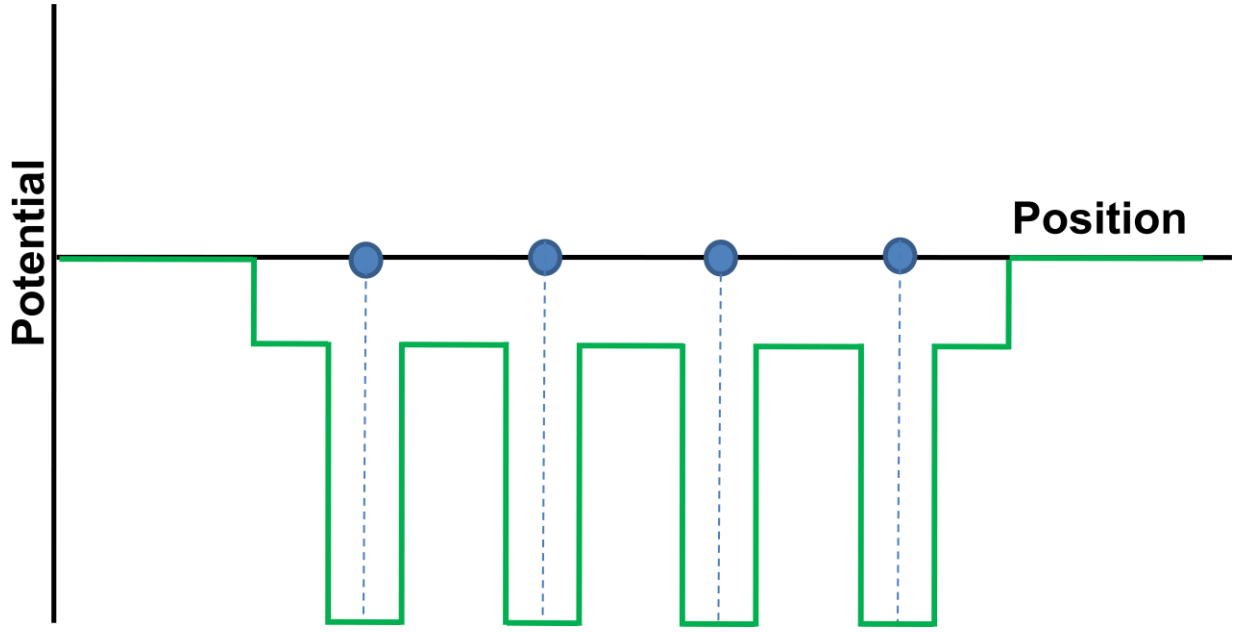


Figure 21.5: An approximation of the potential landscape experienced by an electron, moving along the x-direction, due to the presence of a one dimensional solid which is also aligned along the x-direction.

The primary features of the above approximation are as follows:

> When the electron is very far from the one dimensional solid, it experiences zero potential due to lack of interaction with the solid. This is true on either side of this hypothetical one dimensional solid.

This situation represents the electron having completely escaped from the solid, such as in the case of a photo electron. Such an electron is a truly free electron.

As the electron gets closer to the solid, it experiences a slight drop in potential due to its interaction with the overall solid.

This situation represents the electron being confined to the solid, but not attached to any specific ionic core. Such electrons are ‘nearly free’ electrons, and are the electrons that participate in the electronic conductivity process since they are free to roam through the solid. The ‘free electron gas’ of the Drude model also referred to these nearly free electrons only.

When the electron gets very close to an ionic core, it experiences a very sharp drop in potential.

The electrons trapped in this deep potential well represent ‘bound electrons’. These are electrons which are confined to each individual ionic core. In a typical metallic solid, these represent the majority of the electrons, but they do not contribute to the electronic conductivity of the solid since they are unable to move through the solid.

In the approximation above, the curves corresponding to the actual potential experienced by the electron, have been approximated to straight lines. This approximation results in the potential wells becoming ‘square potential wells’ (in view of their rectangular shape), and makes subsequent calculations simpler. It will be necessary to judge at a later stage if this approximation is reasonable.

In the next class we will examine more features of the above picture and see how it relates to parameters we have discussed so far such as the Fermi energy and the work function of the solid.