

Mathematical Aspects of Biomedical Electronic System Design
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Lecture No. 10
Percolation theory and its application in biological tissues

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**Mathematical Aspects of Biomedical Electronic
System Design**

**Percolation theory and its application in biological
tissues**

Hello, everyone, welcome to the course mathematical aspects of biomedical electronic systems design. This is a TA session and the topic that we are going to focus today is percolation theory and its application in biological tissues. Before we begin with this topic, this is in continuation with the application and how disorder exists in biological tissues, which we had covered in the previous TA session.

So, before we plunge into this particular aspect of charge transport in biological tissues, let us first have a quick recap of the disorder present in the biological tissues. And then we will move on to this new topic. For any kind of queries feel, please feel free to put your questions, or queries in the comment section.

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What is the meaning of **disorder?**

Answer: Anything not in **order**

Why study disorder in biological systems?

One of the most common reasons: **Cancer** is a cellular level disorder

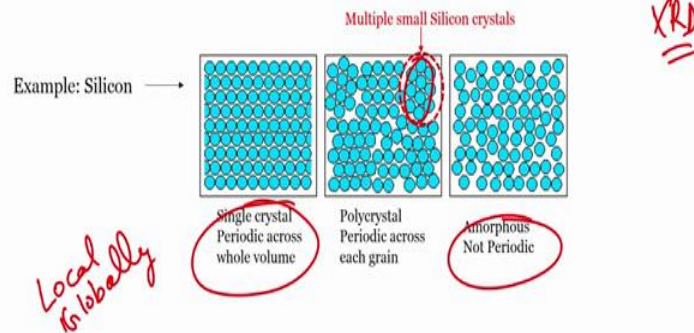
So, what is the meaning of disorder? We are talked about disordered systems, we first reasoned that what exactly means disorder, the most simple answer could be anything not in order. And then we try to motivate ourselves, that why study disorder in biological system, what is the reason, what is the importance of studying disorder in biological system? We study physics to understand our daily routine, that we do cycling, walking, everything is related to physics.

So in a similar way, why do we want to study so as biomedical engineers, or someone who is interested in the field of bioengineering, why disorder is important, why studying disorder is important? So, one of the most common reason, that we give is that cancer, a very widespread disease, and it is certainly a cause of large number of deaths in the world is a cellular level disorder. We will talk about it in some later a TA sessions. But, this itself is big motivation, to understand what exactly is disorder and why to study disorder.

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Example #1: Disordered semiconductors

Materials that do not have long range order of atoms and lack translational symmetry



Studying disorder in biology was, was a little big step. So, we went step by step by taking examples of existing systems, which have been completely established as far as their disorder is concerned. So, we began with first example, which was disordered semiconductors, disordered semiconductors have been used in applications such as flexible, flexible displays, which you may have seen in recent in the recent media.

And what is the difference and we talked about what is the difference between disordered semiconductors, we took example of amorphous silicon and we tried to reason, that how amorphous silicon, which is mentioned here is different than single crystal, or periodic silicon, the reason that, there are 3 different kinds of structurally different kinds of silicon available, first a single crystal which is locally as well as globally, a globally ordered. Whereas, in the case of polycrystalline, there are local patches, which are ordered.

But overall, if you see the crystal, if you take a wafer of poly silicon, then and if you do studies like X ray diffraction, we will find that the structure is not continuously ordered, but there are some patches, which presents ordered structure. And then there are some patches, which does not present ordered structure. Overall, it is not an ordered structure, but locally it is ordered. Whereas, in the case of amorphous, which is completely disordered system, even local ordering is absent.

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Disordered semiconductors

Types of **disordered** semiconductors

→ Inorganic (eg. Amorphous Silicon, Polysilicon)

→ Organic (Conducting polymers (eg. PEDOT:PSS))

flexible displays

Table 1. Structural characteristics of solids.

Comparison of characteristics of crystalline and non-crystalline solids

Structural subsystems	Solid states			
	ideal single crystal	real single crystal	polycrystal	non-crystalline solid
short-range order	+	+	+	+
defects' subsystem	-	+	+	+
morphology	-	-	+	+
medium-range order	-	-	-	+

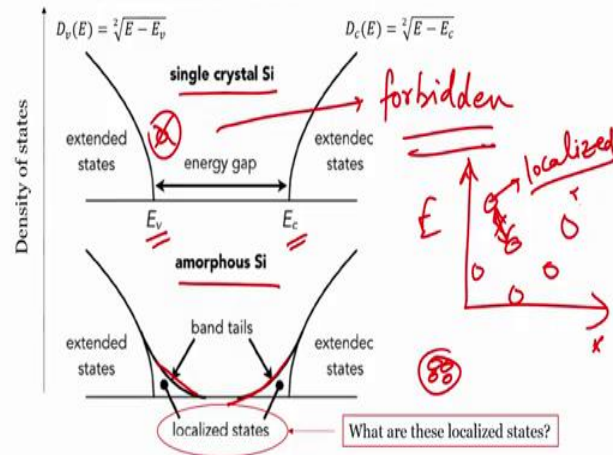
Then we try to understand that what kind of disordered semiconductors are, are available, inorganic like amorphous silicon, and poly silicon and then organic conducting polymers such as PEDOT:PSS. So, when I was referring to flexible ovulates flexible displays, or even flexible devices, if you happen to design some biomedical devices, it is good to have flexibility. Because our skin is not planar and whatever sensor we fabricate it has to be conformal.

So, another reason why we included disordered semiconductors in this particular session. And then we presented a comparative analysis of how these three different kinds of structurally different kinds of silicon fair in terms of their subsystems, which is short range order, which is present in all of them, defects of system, it is present it is present in again all of them, morphologically single crystal silicon stands out compared to poly crystalline and amorphous silicon. And then medium range order, medium range order as we discussed, which is, which is even not even locally disordered is a present only in amorphous silicon.

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Electronic structure of a disordered semiconductor

Comparison of band structure of crystalline and disordered semiconductor



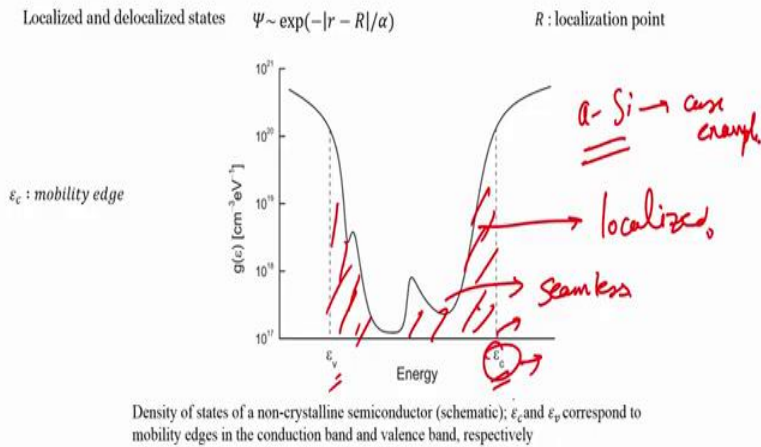
Now, these kinds of systems also translate into different kinds of band structure arrangement, this is what we studied last time, we study that how in case of single crystal silicon the band diagrams, which is valence band and conduction band are clearly separated and in between there is something called as forbidden gap, there are no energy levels which are allowed, there are no states which are available, for any charge carrier to, to occupy this particular location. Whereas, in the case of disordered semiconductor, we took an example of amorphous silicon.

And what we found? We found that there are, there are localized states, which extend into the forbidden gap when compared to the single crystal silicon. And what are these localized states? These localized states are non-continuous patches with allowed levels of energy within the forbidden zone, you can imagine it in this way, then we saw that if it is E versus X , within that, you can have multiple energy levels within the forbidden zone and these are all allowed state and they are not connected. And that is why they are called localized states.

Again, we just we are just scraping through the surface, there is a lot more that goes into understanding these localized states, the foundations are the foundations lie in the in the field of quantum mechanics, but just to appreciate the structural difference between single crystal silicon and amorphous silicon and how it affects the band structure arrangement, which will eventually affect the transport properties, we are trying to understand at first order.

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Electronic structure of a disordered semiconductor

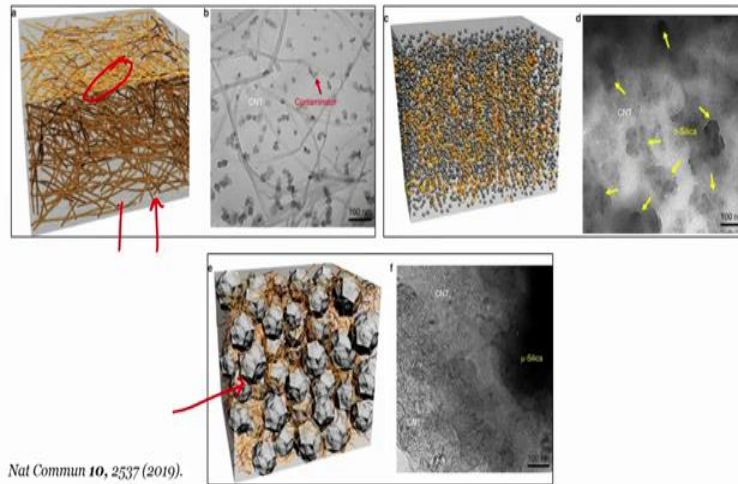


Then we try to understand, what are these localized states in terms of a clear band diagram, which we can, which we can assume for disordered semiconductor, which is amorphous silicon that is the case example here. So, what we found? We found that, like we have bands, valence bands and conduction band, in case of single crystal silicon, in case of amorphous silicon, we have something called as mobility edge.

The mobility edge is something, where after if the electron is transported here, then the conduction will be seamless. But somewhere here, where the states are localized, the conduction will be unlike the way when it is after the mobility edge, which means, here the conduction will be the way electrons transport will be different, the way they transport when they cross this mobility edge.

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Example #2: Polymer composites



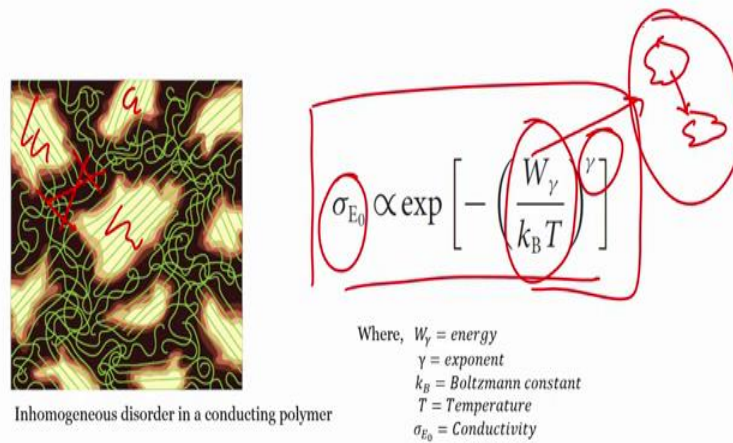
Nat Commun 10, 2537 (2019).

Then, we also looked at another example of polymer composite, we had discussed that polymer composite resemble to some extent the structure of tissues and can be modeled and therefore, are useful in understanding the structure of biological tissues, by the means that they capture the complexity and the associated randomness. We took three examples here. The first example was there is this polymer composite, which contains polymer and nano fibers as filler material.

So, these nano fibers as you see are filler materials, which are electrically conducting, which are carbon nano tubes here. And in the second structure, we introduced small silicon nano particles, which are insulating, and in the third figure, we found that, they have introduced larger silica particles.

And why did we discuss all these things? We were discussing, that how structure can affect the physical property, what is the structure property co relationship as far as polymer composite is concerned. Similar things, similar concepts can also be applied to biological tissues and how the structure property co relationship exists, there is something we are going to see today.

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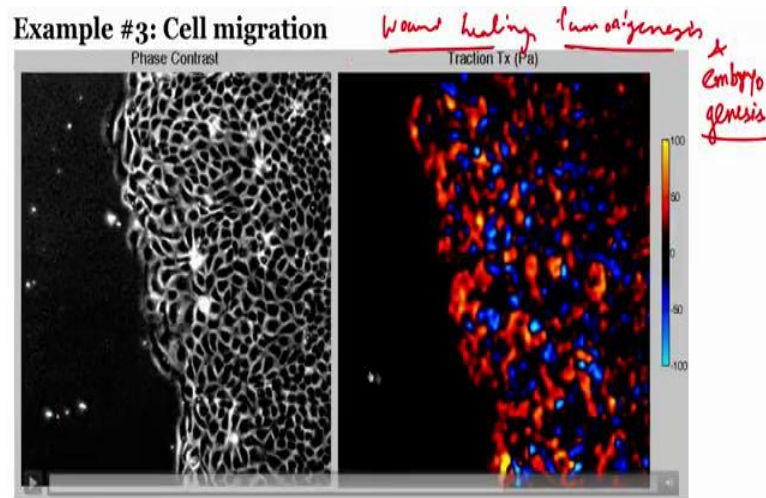
Nature Materials, 16, 252–257 (2017)

We then also try to understand, then if given a polymer composite, which has conducting islands in patches, which are connected, loosely connected, when I say loosely connected it means, there is no, there is no continuation continuous path between these two, this part does not exist. But there are some fine conducting islands, which are present in between these two conducting islands, through which the conduction happens. And how the conduction happens is something we are going to understand today.

Then, we try to then in the previous session, we try to understand that how the equations of conduction work as far as such a disordered conducting polymer system is concerned, we talked about an exponent, which is dependent on temperature and then we found how this particular conductivity, which is again temperature dependent can be expressed in terms of exponential of this particular function.

Whereas, this energy, which is required for the charge carriers to transport from one conducting island to another conducting Island is again dependent on temperature and is also a function of this exponent. Please keep this picture in mind, because in next few minutes, we are going to delve in more detail, keeping in mind this particular picture.

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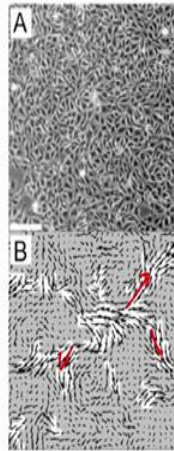
Nature Phys **5**, 426–430 (2009)

Then, we moved on to an example of explaining disorder in biological system, we will took example of cell migration, why cell migration, we tried to reason that cell migration is a very common phenomenon, which is observed in processes like wound healing, tumorigenesis, tumorigenesis and embryogenesis.

So, these are the three main processes, where cell migration is commonly observed. And then we saw this clip, wherein we could see that there is structural variation, that is happening across the cells and we found that there is no specific order, or there is no specific direction in which these cells are moving, or these cells are changing the shape in order to migrate from point A to point B.

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Example #3: Cell migration



The way cells migrate in scenarios such as tumorigenesis, wound healing and embryonic development resemble formation of "glassy systems"

As the particle (cells here) density reaches a particular density ϕ_c there occurs a transition from fluid-like state to solid-like state

$$\frac{S(q, \omega)}{S(q)} = \underbrace{f_0(q) \frac{\frac{1}{2}\Gamma_0(q)}{\omega^2 + (\frac{1}{2}\Gamma_0(q))^2}}_{\text{Rayleigh scattering term (Random and uncorrelated scattering)}} + \underbrace{f(q) \frac{\Omega(q)\Gamma^2(q)}{[\omega^2 - \Omega^2(q)]^2 + \omega^2\Gamma^2(q)}}_{\text{Brillouin scattering term (Periodic and correlated scattering)}}$$

X-Ray Neutron Scattering
Spatial Temporal
Fourier Transform

Proceedings of the National Academy of Sciences, 2011, 108 (12) 4714-4719

Then, in the next part, we try to understand that what really governs this particular cell migration, and how can we characterize the structure of cells and associated disorder. For that, we also looked into a vector plot, which gave us further detail about the extent of disorder in the cell migration, where we could see that the vector fields associated with the migration, or the movement of cells in different direction gave us a very clear idea, that there is no specific direction in which the cells are migrating rather, it is very disoriented.

And how we can understand the structural property? We can understand the structural property, by using this equation structure factor. Structure factor is generally used for understanding crystal structure by the means of techniques like X-ray diffraction and neutron scattering. Though in this particular study, it was done by image analysis, it can also be done by image analysis. And what we try to reason is how these cells when they migrate, have both spatial as well as temporal variation.

Now, what is something that can correlate both spatial and temporal variation, this is Fourier transform. So, we did a Fourier analysis, we tried to understand that, how it can be explained by combining these two aspects. And that is why this particular structure factor contains both spatial and temporal terms. And these two parts of this equation, the first part contains Rayleigh scattering term, which is associated with random and uncorrelated scattering.

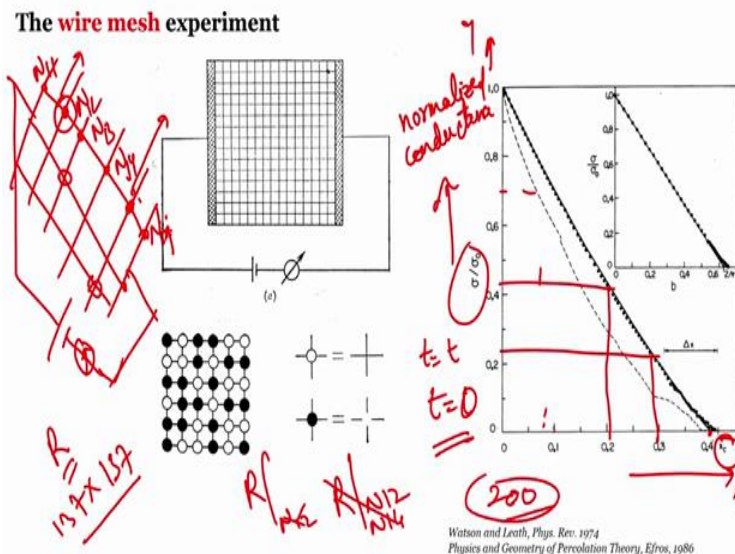
And then the second part is associated with Brillouin scattering term, which is periodic uncorrelated scattering. We do not have to go into the details, this is just to give you a glimpse, that how one can understand, or appreciate the extent of disorder in different kinds of system and this is where we ended.

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Percolation Theory

So, let us now understand what exactly percolation means, what is percolation theory and finally, we will try to look for some examples in both existing and established system as well as biological systems. So, let us begin with understanding percolation theory.

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So, one very interesting way of understanding percolation theory is to do a wire mesh experiment. So, what you do, you take different strains of wires, and then you solder them, or you connect them by some other means, and then you have a common end at each side and then you apply potential.

Now, what you do? You measure, what is the voltage drop and hence, eventually the resistance. So, you can measure the resistance of this wire mesh. So, let us call these junctions as nodes. So, I will name them as node 1, node 2, node 3, node 4. And let us say there are n junctions. So, this will be node n . And it is a matrix. So, there will be a component ij . So, it can be termed as node 1, 1, node 1, 2, node 1, 3, node 1, 4 and node N_{ij} , where i corresponds to the row and j corresponds to the column.

Now, you will measure that resistor, resistance for this entire mesh circuit. Now, what you do, you remove selectively any node that you feel like it is a random phenomenon. Because if you let us say have 137 by 137 matrix, which was the case in this particular example, when the authors did the experiment, it is difficult to select that why particular node will be removed.

So, you associate some randomness to it, which we will discuss now, and then we remove a particular node. So, let us say I remove node, node 1, 2, then I removed node 1, 4, after removing node 1, 2, I will measure the resistance. So, there will be a resistance after node 1, 2, is removed and then there will be a resistance after node 1, 2, and 1, 4 is removed. And then you plot resistance versus such node removal instances and what you will get is a graph looking something like this.

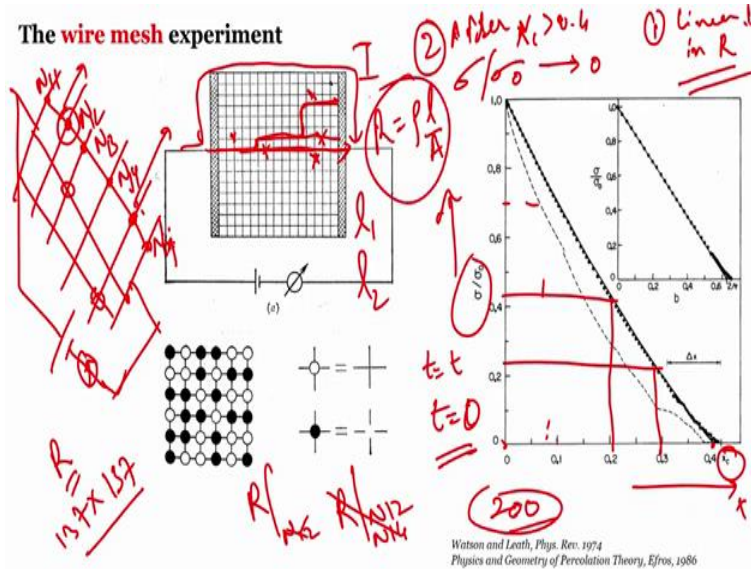
So, this is normalized conductance. So, when I say normalized conductance, it is the conductance at that instance of time divided by the conductance at $t = 0$, $t = 0$ means, the instance where this experiment was started. And $t = t$, is the time when we are, when we are looking at the conductance such, at each instance of the X axis, this is X, this is Y.

So, what do we see here, we see that as we remove the number of nodes, so this resembles how many such fractions of nodes of the total nodes? So, let us say if there are 200 nodes. So, point one would mean 10 percent of these many nodes, 10 percent of 200 nodes are removed at this particular point and then they are measuring the resistance.

So, something here at 10 percent, then if I look out for 20 percent, it will be somewhere here and then 30 percent, it will be somewhere here, 20 percent is here, 30 percent is there. And finally,

when I go to around 40 percent, this is the most interesting aspect. Finally, when I go to almost 50 percent, reduction in the overall number of nodes, the normalized conductivity almost drops to 0.

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So, there are two observations here one, there is a linear decrease in resistance. And second, more important observation is after let us say X_C , or the fraction of nodes, which are removed greater than 0.4, my σ by σ_0 is tending to 0. Let us discuss this observation in sequence. So, if it is linear reduction, how is it possible?

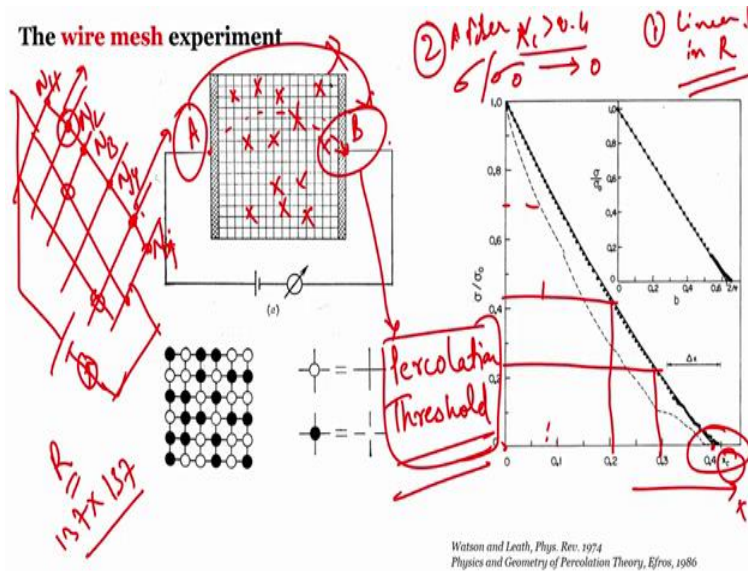
So, let us look at this particular diagram, what are we doing, we are breaking some electrical junctions, which are contributing flow of current from this point to this point. And this is just to show the flow of current, it does not necessarily go like this, it will definitely go through this and the shortest, shortest resistance path, which all of you would know, but just to illustrate the point.

So, as, as soon as I start removing each node from here, the number of junctions, which are contributing to the conduction are reducing, which means they are increasing the overall resistance of the circuit. Why, because the overall path length, which now the current has to take is increasing.

For example, if the current was flowing like this and if I broke this node in between, it is possible, as I discussed, it is a random experiment. I am removing any node at random, if I have removed this, then the current has to go from here to here. And then if I have removed this junction here, then it will have to find another route, which is from here to here.

So, what is the overall length, if you check here and the overall length if you compare. Let us say the length at this particular point was l_1 , and at this particular point is l_2 , considering the, considering the radius does not change, then by $R = \rho \frac{l}{A}$, if length is increasing the overall resistance will also increase. So, now we have understood the linear increase in the resistance as a function of removal of nodes or conducting nodes in this particular section.

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Watson and Leath, Phys. Rev. 1974
Physics and Geometry of Percolation Theory, Efros, 1986

Now, what happens when a particular fraction percentage is reached, I am referring to the point number two, wherein after X_C crosses 0.4, there is there the resistance sorry the normalize conductivity comes back to 0, or approaches 0, they have not zoomed in this particular graph otherwise, you would see that how it is approaching 0 very small values of conductance conductivity.

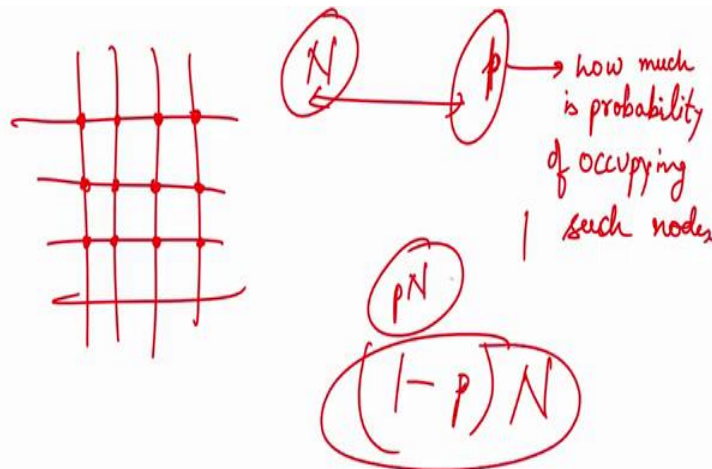
Now, why is that happening? So, let us understand this fact and this is these forms the basis of percolation theory. So, I am removing node after node from here, from here, from here, from here, from here, from here.

Now, if I keep doing and repeating this process, I will be left at a particular point, where there is no single line, which can continuously connect, if I call this point A and this point B, there would not be any single line, which can continuously form a network of such nodes from point A to point B. And at this point, and remember at this particular point, the conductivity drops to 0. And this particular point where conductivity drops to 0 is something called as percolation threshold.

So, what we are trying to say that, if there are nodes in the network and the conduction is happening through the connected nodes and if we keep tripping the nodes one after the other, we will reach a point, we will reach a point and that point which is termed as percolation threshold after which there would not be any path, there would not be any continuous path, which can provide conduction from point A to point B for the current to pass through.

So, let us understand this briefly, I am not going into the detail in terms of probability, why probability, because it is more of a random experiment, you cannot, you cannot say that in a structure in a real, in a real world in a practical world, you cannot really say that, when you are making such, when you are making such structure, which has, which has nodes, interconnected nodes which contribute to the conduction will snap off, or will not be connected at this particular point. And that is why you need to associate that probability to each of such nodes.

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So, how we can do that, so let us assume that probably, that there are N number of nodes. So, we will see that there are N number of nodes, the same diagram I am drawing just for the sake of repetition and familiarity. And let us say that there is a probability p , probability p , which is associated with, how much is the probability, this is the probability of occupying each of occupying one node occupying such nodes.

So, if there are N such nodes and in the probability for one was this for, one such node is this, then the overall probability for N such nodes, which are occupied would be pN , on the other side, there

will be nodes which are not, which are not connected, which are not occupied. So, what will be the probability for that? It will be $(1-p)N$. So, now we have with two probabilities $(1-p)N$, and pN to N .

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What does it mean by the term “percolation”?

Let each site be associated with a probability p of being occupied with charge

Let be N such sites in a square lattice

Then pN sites are occupied and $(1 - p)N$ are empty

(a) $p < p_c$

(b) $p > p_c$

$\sigma \propto (p - p_c)^t$

For: $p > p_c$ and $(p - p_c)$ is very small

Each site of a very large lattice is occupied randomly with probability p , independent of its neighbours. Percolation theory deals with the clusters thus formed, in other words with the groups of neighbouring occupied sites.

Journal of Applied Physics, 92, 7, 2002

Reviews of Modern Physics, 72, 3, 2000

Introduction to percolation theory, Dietrich Stauffer and Amnon Abraham

And let us understand this particular in terms of the percolation threshold. Now, when this N , reaches the value of percolation threshold denoted by P_c here, the conduction from point A to point B happens. So, this is an example of a maze, which is generally used in different papers, or research articles to emphasize the percolator aspect of any kind of system.

Similar is the case used here, that when the percolation, the, the fraction, or the number of nodes, if we continue with the same terminology, the number of nodes, if they are less than the percolation threshold number, then there would not be a completely connected path. Whereas, if the number of nodes interconnected nodes are larger than the percolation threshold, then the percolation, or transport would happen from point A to point B.

So, this is what we were discussing, that each side is associated with the probability p let N sites such in a square lattice. So, one more point that I want to emphasize here is, we are all discussing the first order problem, that is why we are taking the simplest case, which is square lattice. In real life, there may be honeycomb lattice, which will look something like this and these lattices will be interconnected.

So, these hexagons when interconnected will form honeycomb lattice and then there will be triangular lattice is also, where will form structures, where the unit, where the unit cell of that particular sector will be a triangle for that, these values would definitely change and have to be calculated.

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What does it mean by the term "percolation"?

Let each site be associated with a probability p of being occupied with charge

Let be N such sites in a **square lattice**

Then pN sites are occupied and $(1-p)N$ are empty

$\sigma \propto (p - p_c)^t$

For: $p > p_c$ and $(p - p_c)$ is very small

Each site of a very large lattice is occupied randomly with probability p , independent of its neighbours. Percolation theory deals with the clusters thus formed, in other words with the groups of neighbouring occupied sites.

Journal of Applied Physics, 92, 7, 2002
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Introduction to percolation theory, Dietrich Stauffer and Amnon Abraham

Handwritten notes: $p > p_c$, $p < p_c$, $0.04g$ (CN?) $\rightarrow < p_c$, $1g$, $\rightarrow < p_c$, \rightarrow Condens, \rightarrow Carbon Nanotubes, S_1, S_2, S_3, S_4 , $S_1 \rightarrow S_2 \rightarrow NN$, $S_1 \rightarrow S_3 \rightarrow NN$.

But just to begin with, we are going for square lattice. For more references into triangular and hexagonal lattice, you can please refer to this book it is quite rigor, rigorously explained all these processes and how you can associate probabilities for each such type of lattice, whether it is square, honeycomb, or triangular.

Now, when we talk in terms of biological tissues, or before that let us talk about the polymer composites that we had discussed, we talked about conductive, we talked about a cuboid, which was the polymer and then there were carbon nano tubes filled in this, in this particular case, this was the filler material, the carbon nano tube, the conducting filler material, this was the conducting part.

Now, why I am discussing this, I am trying to draw parallel between the percolation that we just studied and this polymer composites. How we can draw parallels? We can consider that in a matrix, in a polymer matrix which is insulating we have induced some carbonaceous elements, in this case, carbon nano tubes, which are electrically conducting, and till a particular fraction is reached, which is P_C .

So, let us say I am taking 1 gram of polymer, and I am putting 0.01 gram of CNT. And if this particular volume fraction corresponds to less something which is less than P_C , then in this particular polymer composite, if I apply, if I apply current, there would not be a continuous path, I would not be reading any potential at a voltmeter, if I put here.

So, just to make it more clear, if this is a polymer composite, and I am applying a potential here, and I am reading, what is the current here, if I go for this particular part, where $P < P_C$, which means the number of carbon nano tubes, which are mixed in this particular composite are less than P_C , then I would not be able to form any single conductive path, which can complete the circuit.

Whereas, if I increase, let us say, this is just an example, these are not some real values, let us say increase to 0.04, for example, so I increase it by four times, and for four times let us say, let us suppose, we know that for four times this particular value will cross P_C . So, we have a condition of P greater than P_C , in this particular case, what we will find, there is a continuous path and the charge particles are able to cross from point A here to point B, why, because now there is a continuous percolative path between point A to point B.

So, this is a kind of formal definition, which has been described in this particular book, each side of a very large lattice in terms of lattice, it means it is a kind of solid, even this can be considered as a description of lattice, or occupied randomly with probability p , independent of its neighbors. Percolation theory deals with us the clusters, thus formed in other words with the group of neighboring occupied sites.

So, here, if you would have paid attention to the previous, previous slide, you would have appreciated that how adjacent nodes, how adjacent nodes are very important, because if I have short this particular adjacent node, then there would not be any continuity between this node and this node.

So, this adjacent, which is also called as nearest, nearest neighbor node. So, this node which is also called as nearest neighbor node is very important in, in percolative transport. So, this particular node means, you share an edge, if you are sharing a node with this particular cell, it does not mean that it is nearest neighbor. I will draw that again here.

So, these two can be considered as adjacent nodes, whereas the adjacent, or nearest neighboring nodes, whereas these two are not sharing an edge, they are sharing a node and that is why these two, if I were to name it, one S_1, S_2 and $S, S_1,$ and S_2 are nearest neighbors, whereas S_1 and S_3 are not nearest neighbors. So, this is what was about particulative transport.

Now, we will try to understand, we have seen how percolation happens, but at the level of conducting islands, which in this particular case was carbon nano tube to carbon nano tube, how transport happens, that we will now try to understand.

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Hopping

Diagram 1: Shows two sites A and B with an energy barrier. A red arrow indicates the hopping distance x_{AB} . A handwritten note says "① Hopping length x ".

Diagram 2: Shows energy levels with two peaks representing sites. A red arrow indicates the energy barrier E between them. A handwritten note says "② E".

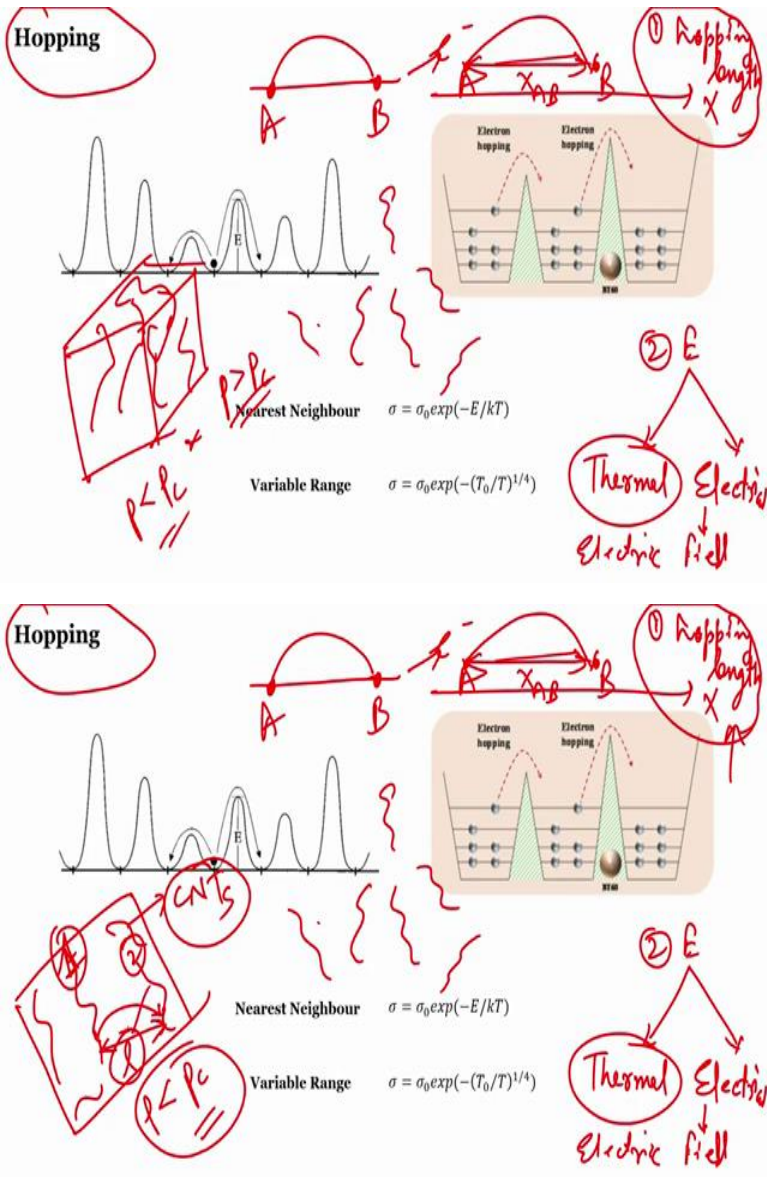
Diagram 3: Shows a series of energy levels with a red arrow indicating the hopping process. A handwritten note says "Electron hopping".

Equations:

- Nearest Neighbour: $\sigma = \sigma_0 \exp(-E/kT)$
- Variable Range: $\sigma = \sigma_0 \exp(-(T_0/T)^{1/4})$

Handwritten notes in red ink:

- $\sigma \propto \exp\left(\frac{W_p^2}{kT}\right)$
- Temperature Transport disordered system
- Thermal Electric
- Electric field



So, the process by which such kind of particulate of transport occurs is called hopping. Hopping by literally since it means jumping from one point to another point. So, let us say there is a point A and there is a point B, you hop means you jump from point A to point B. In the literal sense, it means that and even if we consider in terms of charged particles, let us say we consider electron, the same can be associated with holes. The hole jumps from one point A in space, in space.

So, this is space X, so electrons will jump from one point A to point B. So, what are the things which are and this is how the percolative transport is found. So, what are the things required, for the electron to achieve these jumps successfully, one as we would be able to appreciate is the

distance. So, let us say this distance is X_{AB} , which is called the hopping length. And second, how much energy has been given to this electron to jump from point A to point B.

So, this energy is mostly either thermal, or it is electrical, by electrical I mean it is electric field. And now if you are, if you are able to recall the equation, wherein there was a temperature component for the polymer composite, we had written that it is exponentially dependent on

$$\left(\frac{W^{\gamma}}{k_b T}\right)^{\gamma}$$

and there was a temperature dependence.

And this temperature dependence stems from the fact that, for an electron to hop from point A to point B, one of the factors which is required is energy and that one of the energy forms, which can do, or which can help electron achieve that hop is thermal energy and that is why there is a temperature dependence.

So, what do we conclude from this particular point, we conclude that temperature dependent, temperature dependent transport, when I say transport I am talking about electrical transport unless specified. Temperature dependent transport is a signature, is a signature of disordered system, as a disordered system, why, because if you are supplying some extra thermal energy to the system, you will find that the conductivity will increase.

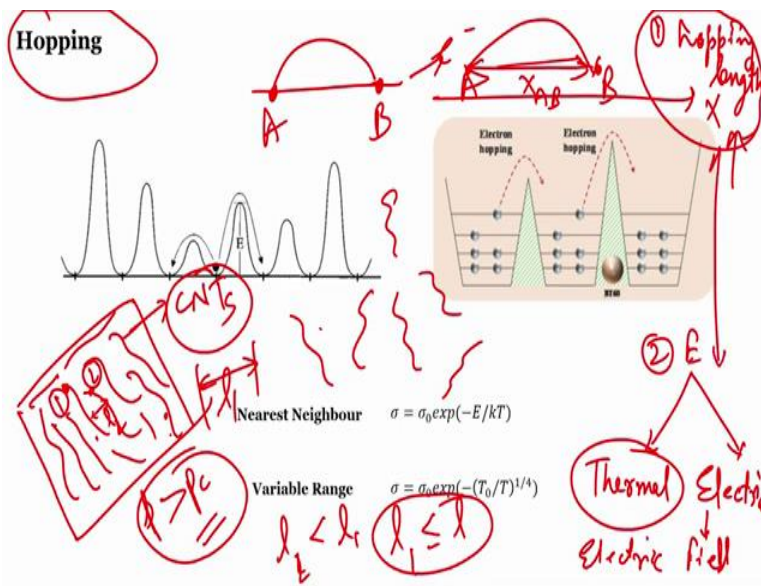
Now, what so this is one way, this is the second way. Now, let us go to first way, what does it mean by hopping length? Now, going back to the previous slide, where we had brought in that picture of polymer composite, where there was a polymer matrix and then there were carbon nano tubes filled and there were two cases that we discussed one was $P < P_C$ and second was $P > P_C$.

Now, let us try to understand these two cases in terms of hopping length. Let us say in case of $P < P_C$, I will just try to draw how it will look from a top view. So, I am trying top view here. So, this is the case for $P < P_C$. So, I put it inside a square box so that it does not confuse. So, these are all carbon nano tubes and this is the case for $P < P_C$, which means the conduction is not happening, one of the reasons why conduction would not happen and the fact that we said that it is less than volume fraction, what does it mean; the length.

So, this is a carbon nano tube, this is electrically conducting, this is another carbon nano tube, which is electrically conducting, to make a jump from one conducting island to another conducting island, electron not only needs energy, which we discuss, it also needs a particular length, which can make that jump feasible at this, this, this length, or the hopping length that we discussed cannot just be any value and that is dependent on different factors such as, what is the temperature, how is the fraction of carbon nano tubes arranged in a particular system.

And within the carbon nano tubes, how fast is the conduction possible, considering all these facts, there is a limitation to which electrons can make a jump from conducting island 1 to conducting island 2, and this limitation can directly be correlated with the volume fraction concept that we studied in previous slide, which says that if a particular volume fraction is not reached, if the number of conducting islands are not at a particular rate percentage in a matrix, then this conduction will not happen.

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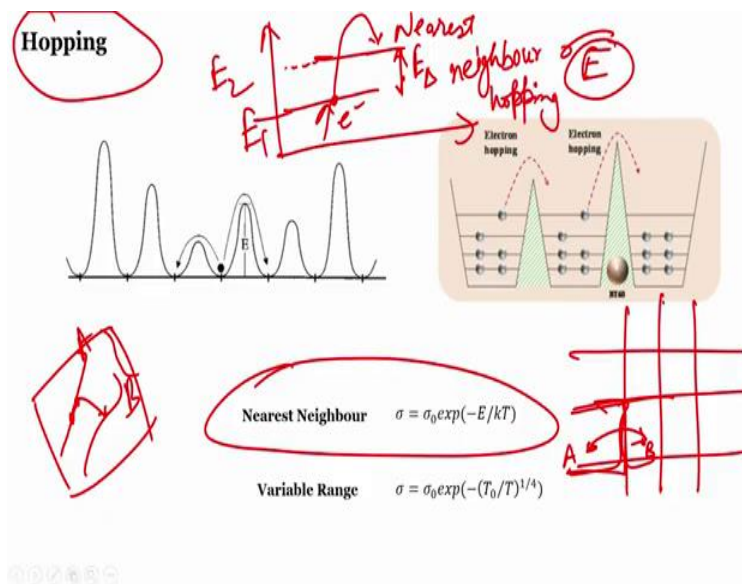


Now, similarly, let us try to take the case, where this volume fraction is enough to form a percolative path. So, I am just drawing a denser carbon nano tube system in the same polymer composite. And what here happens is? If previously, the, the mean length for the electron to hope was l_1 , and here the mean length is l_2 here $l_2 < l_1$ and l_2 should be less than or equal to the hopping length, which is the length required for the electron to make that hop to make that jump from point 1 to point 2.

So, we saw how these concepts of polymer composites their structure, their electrical transport, and how the transport happens, how percolation theory comes into the play, and how that percolation theory is connected to the fundamentals of charge transport in such systems, which is percolative, all this overall picture is now clear to you, this is what we do.

Now, just to give you a little more glimpse, we would not go into the detail, we will talk about two different types of hoppings, which can happen in a system. This will again make use of the previous slides discussion that we had, where I asked you to pay some more attention on the concept of nearest neighbor.

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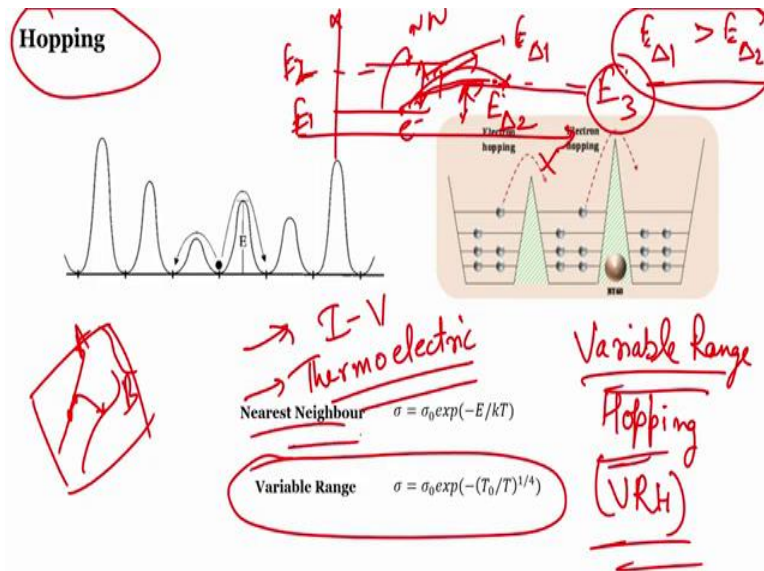


So, the first hopping itself, first type of hopping is called nearest neighbor hopping. So, the name itself suggests again we go back to that picture our same old picture, this is a conducting part, this is another conducting part, and this is a nearest neighbor. So, this is the point where electron is located, the electron will make a jump from point A to point B, this is a, this is, an idea system does not exist.

So, if we look in terms of polymer system, this is a carbon nano tube an electron is making a jump from point A to point B. This is the nearest neighbor, this is A, this is B, the highlight of nearest neighbor, if I were to draw it in terms of energy. So, let us say this is E_1 and this is E_2 , this is E_1 and E_2 , the electron let us say is here and this separation, let us say is E_Δ .

So, when you increase the temperature sufficiently, if you remember that σE equation, that we had discussed for disordered composite, this E corresponds to the energy, which is required for that electron to make this jump. So, if you supply enough temperature here, which is thermal energy, it can make this jump from here to here, such a jump would be called nearest neighbor hopping.

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Now, let us look at the second type of hopping. In this type of hopping, this type of hopping generally observed when the temperatures are not elevated, you do not have that high amount of thermal energy to provide enough, enough input to the electron to make that jump. So, if I draw the same diagram, if this was, if this was the energy E_2 and this was energy E_1 , then the jump made from here to here is nearest neighbor.

And let us say there is an intermediate energy level. Let us say this is E_3 , which is available because it is a disordered systems, in a single space energy domains can lie E_1 within the forbidden zone. So, let us say I have energy level E_3 , and my electron is cell here, this jumper is not possible because I do not have this temperature with me. In that case what would happen is? This is a probabilistic event, which means there is a probability associated with this particular electron making a jump from here to here.

Now, why this jump looks more feasible, there is one important reason here which can easily be seen, just by the look of it, that the overall energy required for the electron to make this jump. Let

us say this is $E_{\Delta 2}$ and this energy is $E_{\Delta 1}$. So, $E_{\Delta 1} > E_{\Delta 2}$. So, even if though, even if they, they are spatially, that they are spatially located at different instances electron.

Because of its low energy state for this particular level, it can jump, I am saying it can jump, because again there is a probability associated with that, it can jump from this state to this state, such a jump when made is called variable range hopping, or VRH. And these two hoping type are the hallmark of any kind of disordered semiconductor, or disk, or polymer composite, or any kind of disordered system when you consider its transport behavior.

So, whenever one has to study a disordered system and one has to characterize the physical properties, such as I-V, or thermoelectric behavior. Because as we discussed such disordered system were very temperature sensitive, for these two and many other types of studies, variable range hopping and nearest neighbor hopping is something that one should look for.

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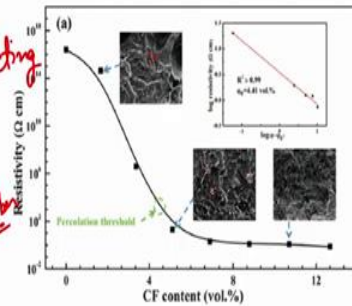
Examples from the literature

Polymer-Carbon Nanofiber composite

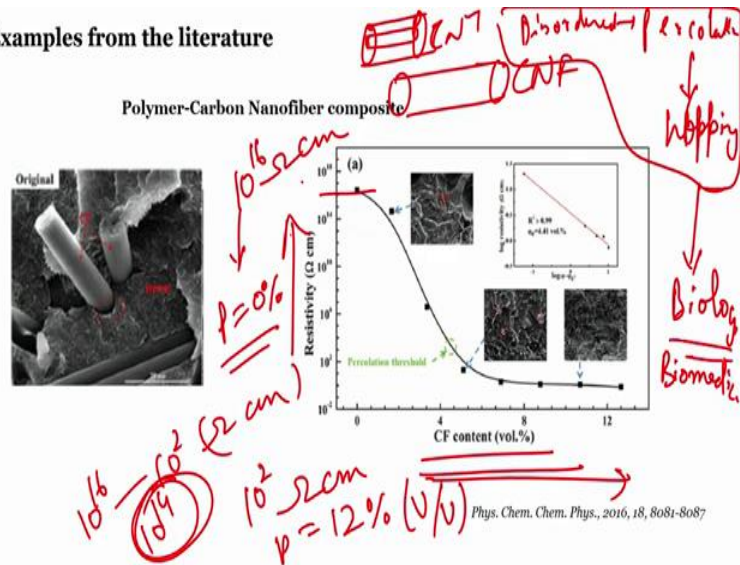


conducting
Carbon Nanofiber

Polymer Composites



Examples from the literature



So, having understood and study some aspects of percolation theory and how the charge transfers from point A to point B, what are the different hopping mechanisms that using which the charge can hop from point A to point B. Let us now look at some examples, which have been cited in the literature.

So, this is one example and I chose this example, because it resonates with the previous discussion on polymer composites, why I keep choosing polymer composites will be clear very soon to you in the next slide. So, in this polymer composite, this is a conducting part, it is a carbon nanofiber, I am not going to the detail of carbon nanofiber, the difference between carbon nano tubes and carbon nanofiber is that carbon nano tubes are hollow carbon nanofiber is a proper fiber, which is solid all throughout.

So, this is a carbon nano tube and this is a carbon nanofiber. So, what they did? They, they took a polymer and then they kept filling this carbon nanofiber and then they measured the resistivity of the composite at different filling fractions. This filling fraction is the same volume fraction, or packing fraction there are different names to it. So, please do not get confused. So, they kept filling at different concentrations.

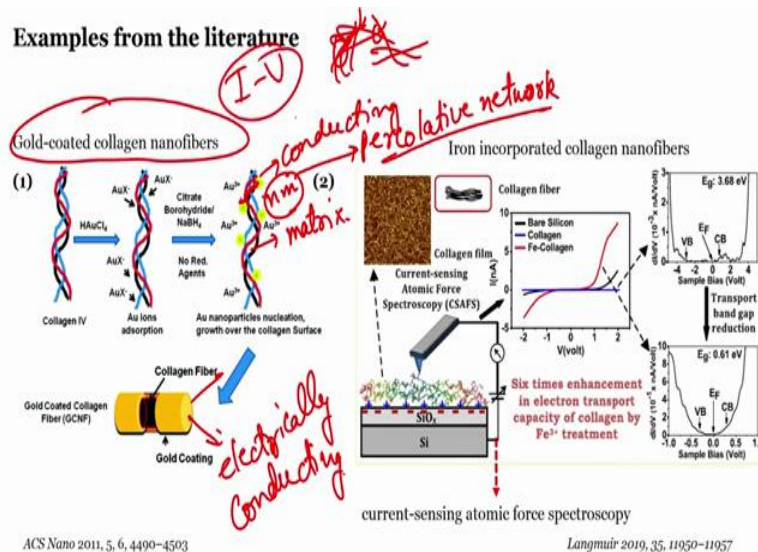
So, this is plotted for at X axis and the resistivity is plotted on Y, on Y axis. So, when they kept filling and increasing the concentration of this carbon nanofiber in this polymer composite, what they found was, the resistivity which was around 10^{16} ohms centimeter at $P = 0\%$, there was no carbon fiber, it reached to 10^2 ohms per centimeter, when P was increased to 12 %, which is volume

by volume. If you see this value 10^{16} to 10^2 ohms centimeter, there is a staggering change of 10^{14} times between the conductivity values.

So, just by increase of conductive fraction in the polymer composites, you can achieve very high resistivity, very from we can convert a material with very high resistivity to a material with very high conductivity. Now, such systems, because they are primarily composed of polymer can be used for many applications, such as flexible devices, stretchable devices, and as we have discussed such flexible and stretchable devices are very useful in designing biomedical sensors.

So, now all these things, if you see in a single picture, percolation begin with disordered, then percolation, then we are talking about hopping, if you see this in a single picture, we find that it is very much related to biology and biomedical systems alike. The relevance in biologic will be appreciating more when you go to the next example.

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So, next example is chosen again from the literature. And here we have taken the example, where collagen, which is the most abundant type of protein found in animals has been modified by introducing metal elements by decorating it or encapsulating it with metal elements and then they have studied its electrical properties.

First, we will try to see what exactly has been reported and then we will try to understand and appreciate this work, how is this important. This slide will also found the culmination of our

In a similar work, in a similar work, they introduced iron into collagen fiber network. And then they compared the I-V characteristic of collagen decorated of collagen decorated with iron and collagen by itself without any kind of metal nano particles. When they compared and they used a kind of current sensing atomic force spectroscopy, which means there is a very small tip by very small means, this tip diameter would be around hundreds of nanometers, or maybe less than that, with this they apply.

So, this they bring to the surface very close, this separation would be around 10 nanometers, or 20 nanometers. And then they apply field, since the separation is very less they could even since the current, which is generated after completing the circuit. And when they did this experiment, what they found was? There was a 6 times enhancement after iron nano particles were introduced in the collagen nanofibers.

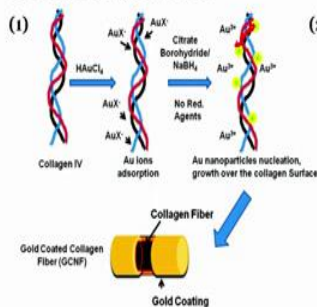
This is similar to the result that we saw for polymer nano composite in the previous slide, where there was around 14 times change 10^{14} times change in the resistivity values, when the packing fraction of conductive filler elements were increased. So, this is a similar situation just that here collagen, which is a kind of animal protein is used.

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Examples from the literature

14 years

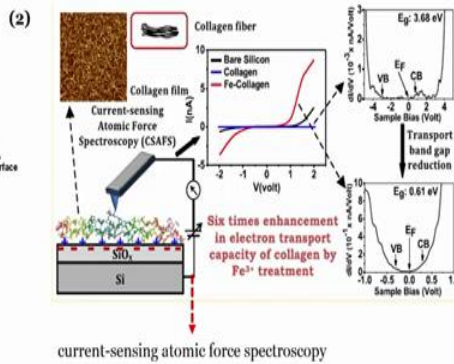
Gold-coated collagen nanofibers



ACS Nano 2011, 5, 6, 4490-4503



Iron incorporated collagen nanofibers



current-sensing atomic force spectroscopy

Langmuir 2019, 35, 11950-11957

for any biomedical engineer to design such biocompatible systems with using biomaterials, or biocompatible polymer composites.

And once we understand the electronic transport properties, we can engineer the structure by modifying. Let us say the percentage composition of filler elements that we just saw, it can affect the conductivity, we can also change its structure all these, all these modifications can be performed and different novel kind of devices can be developed. So, I hope you enjoyed this lecture. If you have any kind of doubt, please feel free to put your questions in the forum. Thank you so much.