

Lecture 17 – Introduction to Quantum Theory of Solids

3/13/09

Notes by MIT Student (and MZB)

*Note on last lecture: while we gave a simple model for phase-separating electrodes, the reality of how to handle this situation can be quite involved. This is because there is a boundary between the phase separated regions, and thus we no longer have a single reaction rate and we need to start thinking about the dynamics of the two-phase reaction. These aspects were neglected in the short discussion we had.

Last time, we finished our discussion of compositional variations on overpotential. The next topics we will tackle involve quantum effects on voltage and reaction rates. This lecture will cover some introductory material in quantum mechanics to set up some of the discussion later on electrochemistry topics. Specifically, we will be looking at energy levels for electrons in solids, and the statistics of electron filling in these energy levels.

1. Quantum Mechanics and the Fermi-Dirac distribution

The most fundamental postulate of quantum mechanics is that variables which were continuous in classical mechanics are actually discrete, or *quantized*. This includes several variables (e.g. momentum), though we will focus on the quantization of *energy*. In quantum mechanics, a system (such as a harmonic oscillator) is only allowed to exist within a discrete set of energy states, which can be determined by solving the *Schrödinger equation* with appropriate boundary conditions. One way of thinking about this is to envision energy as carried by discrete objects. Thus, a system will have $\{E_n\}$ discrete energy states at which particles are allowed to exist, where the subscript n describes the energy level.

Without going into the details yet of specific systems, or how to solve for such allowed energy levels, we will assume that we already have solved for the discrete set of energy levels in some system. We can then focus on how such energy levels will become filled by particles. It turns out that different types of particles will fill the energy levels in different ways. Namely:

- **bosons** (e.g. photons) can have more than one particle in one energy level. Thus, it is possible for all bosons in a system to occupy, for example, the lowest energy level of the system.
- **fermions** (e.g. electrons) can only have one particle per energy level. Fermions obey the *Pauli-exclusion principle*, which stipulates that no two particles can occupy the same quantum state. Because each quantum state will have a corresponding energy level, only one fermion can occupy each energy level. Note that it is in fact possible for two quantum states to be degenerate in energy, and thus two fermions may in fact have the same energy (but still belong to different quantum states). We'll briefly mention this situation in the context of *electron spin* a little later.

Though the Pauli-exclusion principle may appear to be a small distinction between fermions and bosons, it is in fact responsible for the structure of matter, the periodic table, and all chemical properties!

Given the properties of fermions, we now seek to derive the *Fermi-Dirac distribution*, which describes the temperature dependence of the probability of a fermion occupying an energy level at energy E . We will be using this distribution extensively in our later analysis of electrochemical systems. Note that classically the distribution of particles over energies is described by the Boltzmann probability distribution:

$$f(E) = Ae^{\frac{-E}{kT}}$$

where A is a normalization constant such that the integration over all energies yields a probability of 1. In a Boltzmann distribution, the probability of a particle having a certain energy follows an Arrhenius-type dependence. The Boltzmann distribution does not apply directly in quantum mechanics because it does not account for the fact that particles are inherently *indistinguishable*.

We'll start our derivation of the Fermi-Dirac distribution by picking an arbitrary distribution of energy levels that may or may not later be occupied fermions. However, each fermion can only occupy one of these energy levels via the Pauli exclusion principle. Because the energy levels have discrete spacings between them, it is useful to think in terms of the number of states having an energy between energy E and some small interval dE . Thus, we'll define the function $g(E)$ to be the number of states with energy between energy E and $E+dE$. Note that the spacing between energy states is generally quite small, so it is feasible that many of them may be present within a small energy interval dE . A parabolic $g(E)$, typical of free electrons, is shown in Figure 1.

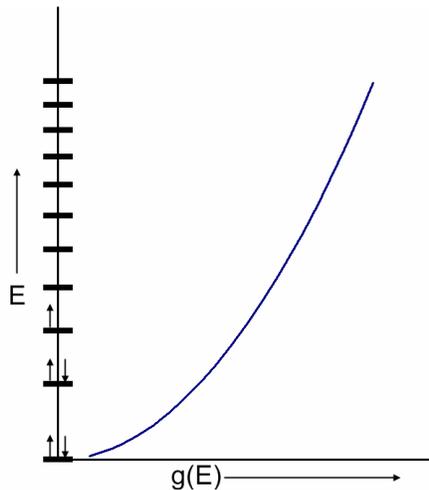


Figure 1: The function $g(E)$, chosen arbitrarily to be parabolic for this diagram, which describes the density of available energy levels in a chosen system. To the left of the graph, several discrete energy levels are shown as black horizontal bars. Note that our chosen $g(E)$ stipulates that the density of energy levels increases as a function of energy, and thus our energy levels grow more closely spaced at higher energies. We represent electrons occupying discrete energy levels as

small arrows, with the sign of the arrow representing either spin up or spin down electrons. Each spin represents a separate quantum state, and thus we do not violate the Pauli exclusion principle by putting two electrons with opposite spin at the same energy level.

The function $g(E)$ describes the energy levels in the system, but says nothing about which energy levels the particles in the system (e.g. electrons) will actually occupy. Therefore, we define another function, $n(E)$, which describes the *number* of particles actually occupying energy levels with energy between E and $E+dE$. From these two quantities, we can define the function $f(E)$, which describes the *probability* of a particle occupying an energy level at energy E :

$$f(E) = \frac{n(E)}{g(E)}$$

Next, we will find an expression for $f(E)$ by considering an ideal solution of particles in a “lattice gas” of energy levels. Note that such a treatment is applicable to fermions, where the Pauli-Exclusion principle acts as sort of an ‘excluded volume effect’ for energy levels. In such a scheme, the chemical potential of a particle is:

$$\mu_{fermion} = kT \ln\left(\frac{n(E)}{g(E) - n(E)}\right) + E$$

The second term in the equation, E , is simply the enthalpic effect of adding a new particle. The first term in this expression is an entropic effect, where $g(E)$ is the maximum number of filled states and $n(E)$ is the actual number of filled states. Thus the term inside the log is analogous to an $[x/(1-x)]$ term. This is perhaps clearer after dividing the numerator and denominator in the log term by $g(E)$:

$$\mu_{fermion} = kT \ln\left(\frac{f(E)}{1 - f(E)}\right) + E$$

Rearranging the above expression:

$$f(E) = [1 - f(E)]e^{\frac{\mu - E}{kT}}$$

and solving for $f(E)$, we get:

$$f(E) = \frac{1}{1 + e^{\frac{E - \mu}{kT}}}$$

which is the Fermi-Dirac distribution! This distribution describes the probability of a single fermion occupying an energy level at energy E at a certain temperature T . To better understand this distribution, we plot it at various temperatures in Figure 2.

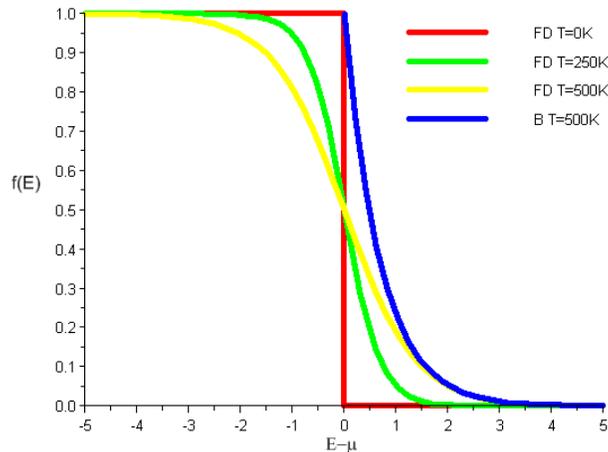


Figure 2: The Fermi-Dirac distribution for $T=0\text{K}$, 250K , and 500K . The Boltzmann distribution, which applies classically, is shown in blue for 500K . The width of the transition region from high to low probabilities is approximately kT . Note that at high energies (or $E-\mu \gg kT$), the Boltzmann distribution is an excellent approximation to the Fermi function. Thus we retain classical limits.

The preceding analysis was crucial in solving the mystery of predicting the heat capacities of solids. Classically, it was believed that every electron would contribute to $3k_B$ to the heat capacity, but this led to large overestimations. However, the Fermi-Dirac distribution shows that the vast majority of electrons will be ‘frozen’ at low energies even at moderate temperatures. Only the electrons near the Fermi energy transition to higher energy levels; thus only a portion of electrons (those near the Fermi energy) will contribute to the heat capacity at lower temperatures. By taking this into account, we can often obtain very good estimates of the temperature dependence of heat capacity.

2. Free electron gas (model for a metal)

So far, we have assumed that the function $g(E)$ describing density of the energy levels in a system was somehow given to us, and solved for the probability of filling these energy levels. Next, we will look at how to derive $g(E)$ in a particular system – the free electron gas. In this model system, the particles we are modeling are electrons, and they do not interact with each other outside of the Pauli exclusion principle. Thus, the electrons do not feel Coulombic repulsions from one another, and effects of *correlation* between electrons is neglected. Note that if we modeled electron-electron interactions in a uniform (positive) background charge, we would arrive at the *jellium* model, which is more involved and will not be discussed further here. The free electron gas we will discuss is still a good approximation to the conduction electrons in a metal.

In order to get the allowed energy levels of the free electron gas, we must solve the *Schrödinger equation* for this system. The Schrödinger equation is a partial differential equation in space and time, and the fundamental equation of quantum mechanics. Without getting into details, it can often be solved via separation of variables, in which the time-dependent portion is always the same and is easily solved. Then, the only task necessary is to solve the *time-independent* form of the Schrödinger equation:

$$H_{op}\psi = E\psi$$

This equation requires a little explanation. First, ψ is the (space-dependent) quantity we are solving for. If we solve for this quantity, the solution to the full Schrödinger equation is then given by:

$$\Psi = \psi e^{-i\omega t}$$

where Ψ is the solution to the full (time-dependent) Schrödinger equation. Thus, the full solution can be viewed as a wave oscillating in time and space, with the wave amplitude given by ψ . We note that ψ is actually a complex quantity which can lead to some interesting behavior. Also, the quantity $|\Psi|^2$, when evaluated at a particular region in space, gives the probability density of the electron existing at that region of space. Thus, the solution to the Schrödinger equation has some physical meaning relating to the position of the electron.

Next, we describe H_{op} . This quantity is dubbed the *Hamiltonian operator*. It can be found by writing an expression for the classical energy of the electron in our system, and then performing appropriate transformations to that energy to arrive at the correct quantum Hamiltonian operator. The only transformation we'll discuss is that of the momentum of the electron, p :

$$p_{op} = -i\hbar\nabla$$

In our free electron gas, the only energy is the kinetic energy of the electron. Thus, the energy of the electron can be written as:

$$H = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

giving us the Hamiltonian operator:

$$H_{op} = \frac{p_{op}^2}{2m} = \frac{-\hbar^2}{2m}\nabla^2$$

Finally, we discuss the energy E in the time-independent Schrödinger equation. The time-independent Schrödinger equation is an eigenvalue equation, and *when coupled with appropriate boundary conditions*, has solutions for discrete eigenvalues E . These discrete eigenvalues E describe the possible energies of our system, and are the energy levels that we are looking for.

Thus, from our discussion, we are looking for solutions ψ to the equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi = E\psi$$

in order to arrive at the energy levels E of our system.

There are a few ways to solve this differential equation; we'll take the *Fourier transform approach*, as it will naturally lead us to a concept called *k-space*. In the Fourier transform approach, the functions $\psi(\mathbf{x})$ and $\psi(\mathbf{k})$ are related by:

$$\hat{\psi}(\vec{k}) = \int_{-\infty}^{\infty} e^{-i\vec{k}\cdot\vec{x}} \psi(\vec{x}) d\vec{x}$$

$$\psi(\vec{x}) = \int_{-\infty}^{\infty} e^{i\vec{k}\cdot\vec{x}} \hat{\psi}(\vec{k}) \frac{d\vec{x}}{(2\pi)^d}$$

where d is the dimensionality of the problem. Recall that when taking the Fourier transform approach, each spatial derivative becomes a multiplication by $-ik$:

$$\frac{-\hbar^2}{2m} \nabla^2 \psi(\vec{x}) = E \psi(\vec{x})$$

$$\frac{\hbar^2 \|\vec{k}\|^2}{2m} \hat{\psi}(\vec{k}) = E \hat{\psi}(\vec{k})$$

The latter equation can then be solved algebraically for E , rather than as a differential equation:

$$\frac{\hbar^2 \|\vec{k}\|^2}{2m} = E(\vec{k})$$

giving us the following (graphic) relationship between E and $\|\mathbf{k}\|$ in Figure 3:

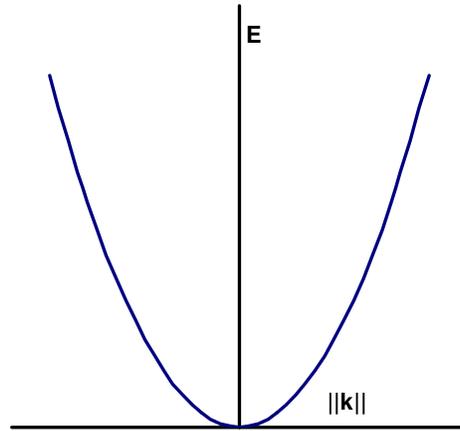


Figure 3: E vs $\|\mathbf{k}\|$ diagram for free electron gas.

Thus, we now have solved our differential equation problem. Our $\psi(\mathbf{x})$ is just a superposition of plane waves of the form $e^{i\mathbf{k}\cdot\mathbf{x}-\omega t}$ (where the ωt term comes from the time-dependent part of our Schrodinger equation). Note that we can use any $\psi(\mathbf{k})$, so long as we have the correct energy given by our algebraic equation.

Now that we have solved our differential equation, we need to apply boundary conditions to our problem. So far, any \mathbf{k} value, and thus any energy level, is allowed. It will turn out the boundary conditions will in fact be what leads to quantization of the energy levels, and this will in turn allow us to find $g(E)$.

As our boundary condition, we consider the free electrons existing within a box with dimensions L . If the dimension L is much much greater than the wavelength of our wavefunction (equal to $2\pi/\|\mathbf{k}\|$), which is generally the case, then the exact form of our

boundary condition won't matter. We will in fact be using periodic boundary conditions at the edges of the box; that is, the wave function at the right-face of the box will in fact "wrap around" to the left-face of the box. This may not seem to make much intuitive sense; it may seem a more reasonable choice to set $\psi=0$ outside the box (corresponding, for example, to electrons that cannot escape a big hunk of metal). However, the periodic boundary conditions will give the same essential results while being easier to treat.

Our periodic boundary conditions then stipulate that going from one face of the box to the other will not change the wavefunction, or that:

$$\psi(x) = \psi(x + L)$$

thus

$$\cos(kx) = 0$$

or

$$\cos(kx) = \cos(k[x + L])$$

where the cosine terms come in because the wavefunction $\psi(x)$ was a superposition of waves of the form e^{ikx} . Note in particular what our last equation implies. In order for this equation to hold true:

$$kL = 2\pi n$$

$$k = \frac{2\pi n}{L}$$

where n must be an integer. What this condition therefore tells us that k is no longer allowed to be continuous, but must be integer multiples of $(2\pi/L)$! This in turn restricts the allowed energy levels, as the allowed energies E are a function of the allowed k . Note also that as we increase the size of the box L , the distance between energy levels grows smaller.

In three dimensions, our expression for the quantization of k generalizes to:

$$\vec{k} = \left\{ \frac{2\pi}{L} n_x, \frac{2\pi}{L} n_y, \frac{2\pi}{L} n_z \right\}$$

where n_x, n_y, n_z are (independently varied) integers.

Note that although we have only considered the case of a cubic box, it is possible to extend this analysis to many different crystal symmetries, leading to the concept of *Brillouin zones* in solid state physics. We will not pursue this avenue in this class.

Given our derivation, we can now solve for the density of states $g(E)$ in an arbitrary number of dimensions. To aid us in our derivation, we plot in two dimensions the allowed k values in k -space in Figure 4:

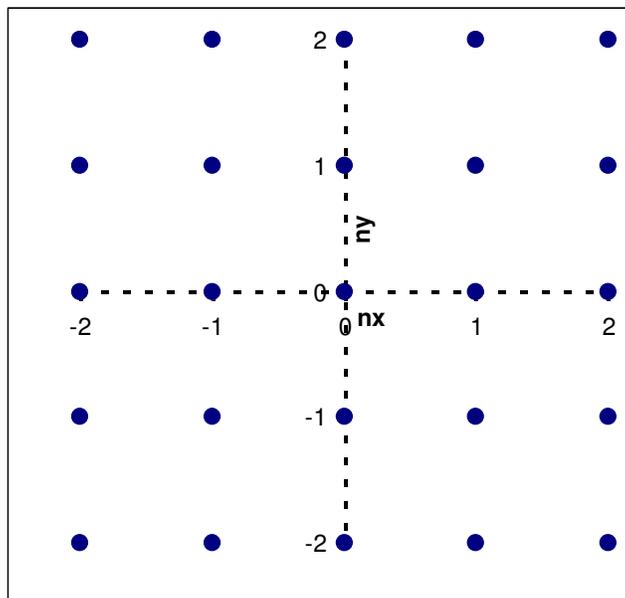


Figure 4: A visual representation of allowed states in two-dimensional k -space. Each circle represents one allowed value of n_x and n_y , corresponding to one allowable \mathbf{k} vector or state. The spacing between the states is $2\pi/L$. In three dimensions, another axis for n_z would be needed, and the allowed states would form a simple cubic lattice.

Note that in two dimensions, the area occupied by one state in k -space is simply the spacing between states squared, or $(2\pi/L)^2$. In three dimensions, each state occupies a volume in k -space of $(2\pi/L)^3$.

Next, we can look at, for a given vector magnitude k_E , the *number of states* having a magnitude in \mathbf{k} less than k_E . Because of the relationship between \mathbf{k} and E , this will later correspond very simply to the number of states with energy less than a given E , which (after taking a derivative) can be used to derive the density of states $g(E)$.

To find the number of states having magnitude in \mathbf{k} less than k_E , we can draw a sphere from the origin in k -space with a radius equal to k_E and count the number of states inside this sphere. In two dimensions, this would be akin to drawing a circle with radius k_E centered at the origin in Figure 4, and counting the number of points inside. Note that in three dimensions the volume of such a sphere in k -space will be $(4/3)\pi k_E^3$, and the number of states per unit volume is $1/[(2\pi/L)^3]$, or $(L/2\pi)^3$. Thus, the number of states inside such a sphere is just the product of the volume and density of states:

$$N_{states}(k_E) = \frac{4\pi}{3} k_E^3 \left(\frac{L}{2\pi}\right)^3 \text{ in 3-dimensions}$$

$$N_{states}(k_E) = \pi k_E^2 \left(\frac{L}{2\pi}\right)^2 \text{ in 2-dimensions}$$

Next, rather than express the number of states with a \mathbf{k} magnitude less than k_E , we desire the number of states with energy is less than E . This is straightforward using the relation between E and \mathbf{k} in a free electron gas we derived earlier:

$$\frac{\hbar^2 k_E^2}{2m} = E$$

$$k_E = \sqrt{\frac{2mE}{\hbar^2}}$$

Substituting back into our expression for N_{states} :

$$N_{\text{states}}(E) = \frac{4\pi}{3} \left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}} \left(\frac{L}{2\pi}\right)^3 \text{ in 3-dimensions}$$

$$N_{\text{states}}(E) = \pi \left(\frac{2mE}{\hbar^2}\right) \left(\frac{L}{2\pi}\right)^2 \text{ in 2-dimensions}$$

Note that the actual density of states N_{states} will be *twice* this value when we account for electron spin, as both a spin-up and a spin-down electron can occupy each of these states. Adding this factor of two, and cleaning up our expression:

$$N_{\text{states}}(E) = \frac{L^3}{3\pi^2} \left(\frac{2mE}{\hbar^2}\right)^{\frac{3}{2}} \text{ in 3-dimensions}$$

$$N_{\text{states}}(E) = \frac{L^2 m E}{\pi \hbar^2} \text{ in 2-dimensions}$$

This completes our analysis for the number of states enclosed within a certain energy cutoff. Finally, we derive $g(E)$. Recall that $g(E)$ is the number of states between energy E and $E+dE$. This is actually just the derivative of $N_{\text{states}}(E)$. One way to see this is to visualize extending the radius of the sphere we used to derive $N_{\text{states}}(E)$ by a small amount dE . The number of additional states picked up by that small extension of the radius is both mathematically the definition of the derivative of $N_{\text{states}}(E)$, and conceptually the number of states between E and $E+dE$, or $g(E)$.

Thus, after taking a derivative of $N_{\text{states}}(E)$, we have derived $g(E)$ in the free electron gas:

$$g(E) = \frac{L^3}{2\pi^2} \left(\frac{2mE}{\hbar^2}\right)^{\frac{1}{2}} \text{ in 3-dimensions}$$

$$g(E) = \frac{L^2 m}{\pi \hbar^2} \text{ in 2-dimensions}$$

The different behaviors of g versus E (square root dependence in 3-dimensions versus constant value in 2-dimensions) can give rise to interesting behaviors which are applicable to many fields including electrochemistry. Next time, we'll talk more about this topic.

MIT OpenCourseWare
<http://ocw.mit.edu>

10.626 Electrochemical Energy Systems
Spring 2014

For information about citing these materials or our Terms of Use, visit: <http://ocw.mit.edu/terms>.