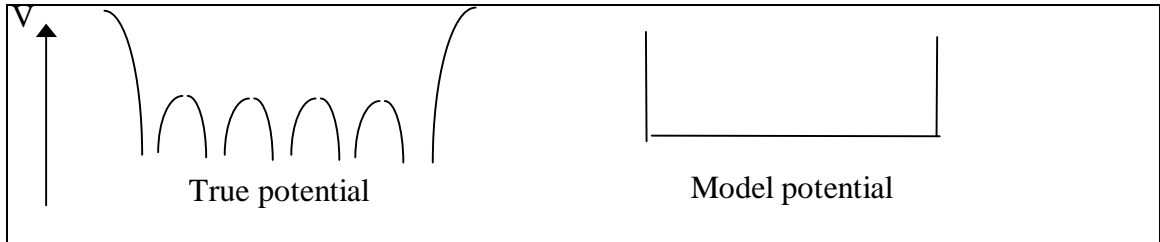


The free electron model

This is the simplest possible model for a metal. We shall make two fundamental (and very big) assumptions that are, in fact, much more reasonable than they look:

- the interactions between the electrons are irrelevant and can be ignored (the *independent electron approximation*)
- the electrons move in a constant potential $V(r)$ i.e. we can ignore everything about the structure of the material. In that case we might as well set $V(r)$ to zero.



These are heroic assumptions; but they do give a fair representation of a simple metal. If these assumptions are granted, the Schrodinger equation for a metal is simply that of a particle in a box

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E \psi \quad (1)$$

where ψ is the wavefunction of a single electron of mass m and E is the energy. This gives the wavefunctions as

$$\psi_{\mathbf{k}}(r) = \frac{1}{\sqrt{V}} \exp(i\mathbf{k} \cdot \mathbf{r}) \quad (2)$$

where V is the volume of the material and \mathbf{k} is the wavevector. The energy is given by $E = \hbar^2 \mathbf{k}^2 / 2m$ (remember that for this case the energy depends only on the magnitude of \mathbf{k}). This gives travelling (or stationary) waves as before and \mathbf{k} is, in effect, the wavenumber. If L is the periodic length-scale, we have the same restrictions on k_x, k_y, k_z as before: that they must equal $2\pi p / L$ where p is an integer. This gives a cubic lattice of points in k -space and for each state of the system described by (k_x, k_y, k_z) , the energy is

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2). \quad (3)$$

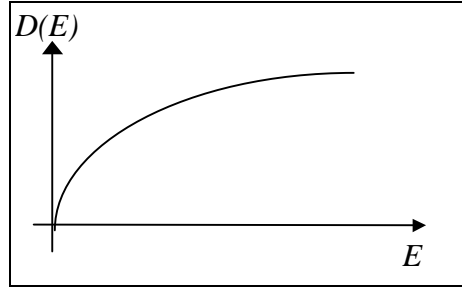
As before, we can use the idea of a density of states. Previously we showed that the density of states for lattice vibrations depended on the magnitude of the wavevector; $\rho(k) = V k^2 / 2\pi^2$. We can relate this density of states, $\rho(k)$, to the density of states expressed with respect to the energy E , $D(E)$. But now, for each value of k there are two electrons (one with spin up, once with spin down). We must therefore write $2\rho(k)dk = D(E)dE$ And, rearranging this in the usual way, we therefore have

$$D(E) = 2\rho(k) \frac{dk}{dE}. \quad (4)$$

For our particle in a box, we know that $E = \hbar^2 k^2 / 2m$ and so $dE / dk = \hbar^2 k / m$, and therefore, substituting for $\rho(k)$, we obtain

$$D(E) = \frac{Vkm}{\pi^2 \hbar^2} = \frac{Vm}{\pi^2 \hbar^3} \sqrt{2mE}. \quad (5)$$

This is parabolic and does look roughly like the bottom of a band. Note that, since $D(E)$ is proportional to V , the more material we have, the more states there are. Suppose that we have a material with N electrons in it. Then we proceed as before, filling up the states. The



energy of the highest filled state at zero temperature is, by definition, the *Fermi energy* E_F . We can obtain this since we know

$$N = \int_{E=0}^{E_F} D(E)dE = \frac{V\sqrt{2m^3}}{\pi^2 \hbar^3} \int_{E=0}^{E_F} \sqrt{E}dE \quad (6)$$

and so, performing the integral and rearranging it,

$$E_F = \frac{\hbar^2}{2m} (3\pi^2 N / V)^{2/3} \quad (7)$$

where (N/V) is the density of electrons in the material. Two quantities are closely related to this. First, the *Fermi temperature*, T_F is defined by the relation $E_F = k_B T_F$ and the *Fermi wavevector*, k_F is defined as the magnitude of wavevector of the state with energy E_F . This can be calculated since we know that $E_F = \hbar^2 k_F^2 / 2m$ and,

combining this with the result for k_F we get $k_F = (3\pi^2 N / V)^{1/3}$. Since we have ignored

everything about the structure, the occupied states are described by \mathbf{k} values in a sphere of radius k_F - the *Fermi sphere*. For a typical metal, with electron density (N/V) about 10^{28}m^{-3} , E_F is about 2eV and k_F is about 6.7nm^{-1} ; roughly the reciprocal of a lattice spacing. We can easily obtain the velocity of the electrons at the Fermi surface, either by considering them as particles, in which case, the kinetic energy, $\frac{1}{2} m v_F^2 = E_F$

or as a wave, in which case the group velocity is given by

$$v_F = d\omega / dk = (1 / \hbar)(dE / dk)_{k=k_F} = \hbar k_F / m \quad (8)$$

either way. This is about 10^6m/sec which is well below relativistic velocities; but is above thermal velocities (i.e. velocities given by $3kT/2 = mv^2/2$; for 300K this is about 10^5m/sec . Another way of putting this is to say that the Fermi temperature is high; about 10^5K . This means that, under terrestrial conditions, the behaviour of the electrons is dominated by the Pauli principle. The electrons form a degenerate quantum gas. They generate a huge outward pressure and can be seen by the following argument. Ignoring the heat term, the first law of thermodynamics states that $dE = -$

PdV . The total energy of the electrons is given by $\int_0^{E_F} E D(E)dE = 3NE_F / 5$. Hence

the pressure is $(-3N/5)(dE_F/dV) = 2NE_F/5V$. Putting in the figures quoted above, this gives a pressure of about 10GPa. This is what keeps the ears of a white dwarf apart (remember your 1st year 1B23 course on the evolution of stars).

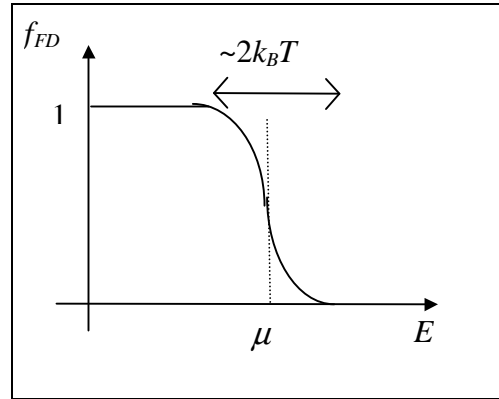
There remains the problem of what keeps a metal together. In a solid, there are two competing effects; as the electrons spread out in the material as a 'gas', the kinetic energy is lowered ($E \propto V^{-2/3}$). On the other hand, as they move away from the nuclei, the potential energy is raised. For the inner electrons, tightly bound to the nucleus, the potential energy is the stronger effect and the spreading out of the electrons is minimal. The nuclei plus inner electrons form a positively charged 'core'. For the outer

(valence) electrons, the kinetic energy effect is much stronger and the electrons spread throughout the metal like a gas. However, they cannot spread out infinitely far, they are still held within the material by the Coulombic attraction of the positively charged cores. The tendency of the kinetic term to spread the electrons out balances the Coulombic attraction of the cores at the experimental volume of the material.

Finite temperature.

So far, we have completely ignored the effect of temperature. We have assumed that the occupation of the density of states falls instantly to zero at E_F and there is no thermal distribution of states at this point. This is untrue, of course. The necessary correction is given by the *Fermi-Dirac function* f_{FD} given by

$$f_{FD}(E) = \frac{1}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1} \quad (9)$$



where μ is the chemical potential of an electron (in effect the Gibbs free energy of the electron gas per electron; strictly speaking the Gibbs free energy change when one more electron is added to an N electron system under stated conditions of temperature and pressure). If $E \ll \mu$, $f_{FD}(E)$ goes to unity. Even if E is only slightly below μ , $f_{FD}(E)$ is still approximately unity at low enough temperature. In the other limit, when $E \gg \mu$ or the temperature is high, $f_{FD}(E)$ goes to zero. If the energy is equal to the chemical potential, $f_{FD}(E) = 1/2$. The shape of the function is shown in the diagram above. As can be seen, for many purposes, the step function is not a bad approximation. However, the true spectrum of electron energies should be written as $D(E, T) = D(E)f_{FD}(E)$. We can now calculate the electronic specific heat directly, since

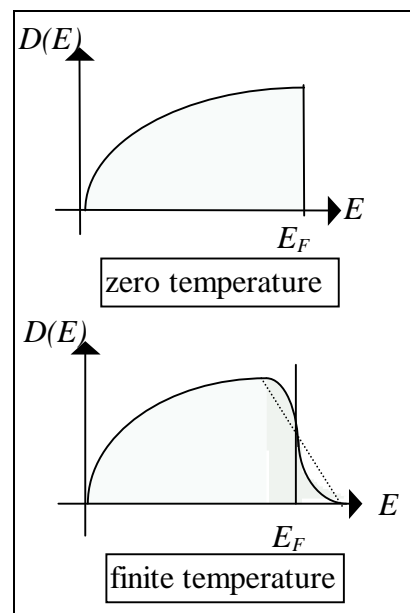
$$C_V = dE/dT \text{ and } E(T) = \int_0^{E_F} E D(E, T) dE .$$

This is doable, but the integral is a mess. A reasonable approximation can be obtained by assuming that $f_{FD}(E)$ can be replaced by a straight line passing through the point when $f_{FD}(E) = 1/2$ and cutting the lines $f_{FD}(E) = 1$ for $E = E_F - k_B T$ and the line $f_{FD}(E) = 0$ at

$E = E_F + k_B T$ (dashed line on the diagram). In this case, the thermal excitation involves altering the vertical cutoff by removing a triangle at the top and putting it at the bottom. The number of electrons promoted is the area of a triangle of height $D(E_F)/2$ and width $k_B T$ i.e. $D(E_F)k_B T/4$ and they each gain about $k_B T$. Thus $E(T) = E(0) + D(E_F)k_B^2 T^2/4$. The specific heat is therefore

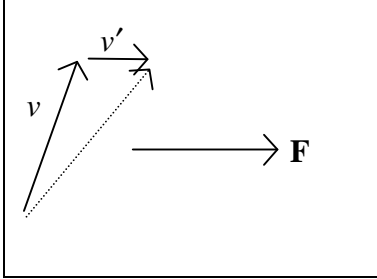
$$C_V = dE/dT \sim D(E_F)k_B^2 T/2 = 3Nk_B^2 T/4E_F. \quad (10)$$

Doing the job properly gives an extra factor of $2\pi^2/3$. The important point is that the specific heat is *linear in temperature*. If we recall that, at low temperatures, the phonons give a term proportional to T^3 , we can write the specific heat of a metal at



low temperatures as $C_V = AT + BT^3$. Experimentally, the functional form is obeyed very well, but our calculated value of A is out by about 25%. This was one of the first triumphs of quantum theory, since a classical theory would give $3Nk_B T/2$ from classical equipartition.

Transport



We showed above that the electrons could be considered as a gas of particles. However, they have a non-Maxwellian velocity distribution since the particle velocities are given by $v = \hbar k / m$ with a maximum when $k = k_F$. We will continue this analogy by assuming that we can use the classical equations of motion for a charged particle, $\mathbf{F} = m(dv'/dt)$ where v' is the *extra velocity due to the force* \mathbf{F} . This is NOT the

same as v used above. Thus $v'(t) = \int (\mathbf{F} dt) / m$. The question is what to use for the limits. The electrons collide with each other and with the lattice. The important interaction is between the electrons and the lattice vibrations. If we assume, continuing the classical analogy, that each interaction randomises the velocities (i.e. that the electron loses all the velocity v' due to the force \mathbf{F}), then the integral should be over the time between interactions. The mean of these velocities, called the *drift velocity*, is approximately

$$\mathbf{v}_D = \mathbf{F} \tau / m \quad (11)$$

where τ is the mean time between collisions, called the *relaxation time*. If the force varies, so must the drift velocity. This can be described by a *transport equation* of the form

$$m((d\mathbf{v}_D / dt) + \mathbf{v}_D / \tau) = \mathbf{F} \quad (12)$$

In the steady state, we get $\mathbf{v}_D = \mathbf{F} \tau / m$, and if $\mathbf{F} = 0$, then

$$\mathbf{v}_D = \mathbf{v}_D(t=0) \exp(-t / \tau), \quad (13)$$

illustrating the relaxation of drift to zero upon the removal of the driving force.

Electrical conductivity ($\mathbf{F} = -e\mathbf{E}$).

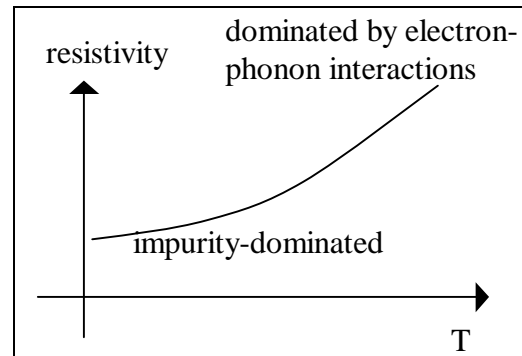
Substituting into the above, this gives the steady-state solution of

$$\mathbf{v}_D = -e \tau \mathbf{E} / m \quad (14)$$

(Note that e is the magnitude of the fundamental electronic charge and is therefore positive). If we define the *mobility* $\mu_e = |\mathbf{v}_D|/|\mathbf{E}|$, then, comparing with the previous equation, we have the mobility of an electron in an electron gas as $\mu_e = e \tau / m$. The electric current, the rate of flow of charge, $\mathbf{j} = -ne\mathbf{v}_D$ where $n=N/V$, the density of electrons. Putting in the expression for \mathbf{v}_D , we get $\mathbf{j} = \frac{ne^2 \tau}{m} \mathbf{E} = \sigma \mathbf{E}$ which is Ohm's

Law where σ is the conductivity. We can use this to get an idea of the relaxation time. For a typical metal, $\sigma \approx 10^7 \Omega^{-1} \text{m}^{-1}$ and taking our previous estimate for the density of electrons of 10^{28}m^{-3} , this gives $\tau \approx 10^{-14}$ seconds. The mean free path λ is clearly $\mathbf{v}_F \tau$, about 10nm. This is tens to hundreds of lattice spacings. This is obviously consistent with the idea that we can to a great extent ignore the lattice, but does not explain why.

There are two main effects dominating the value of τ ; one is scattering off impurities, the other is scattering off phonons. The first effect is temperature-independent; the second depends on temperature because the number of phonons depends on temperature. This explains the qualitative shape of the conductivity curve.



Thermal conductivity. We have already discussed thermal conductivity when we considered phonons. This effect dominates the thermal conductivity of insulators. When considering metals, we must consider the thermal conductivity of the electrons. We can still use the expression for the coefficient of thermal conductivity obtained from the kinetic theory of gases; $\kappa_T = \lambda \bar{v} C / 3$. Here we identify the mean velocity with the Fermi velocity since only electrons near the Fermi level can change their electronic state at thermal energies. The specific heat per unit volume of the electrons is nC_V where C_V is the heat capacity of one electron and n is the density of electrons (N/V). We have derived expressions for C_V and λ above, so we can obtain an expression for the thermal conductivity due to the electrons as

$$\kappa_T = (\mathbf{v}_F \tau) (\pi^2 k_B^2 T / 2E_F) (v_F n / 3) \quad (15)$$

which reduces to $\kappa_T = n \pi^2 k_B^2 T \tau / 3m$ when we take into account the fact that the Fermi energy is the kinetic energy of the electrons and so; $E_F = mv_F^2/2$. In metals, this tends to dominate the phonon contribution. Taking our usual values; we get $100 \text{ Wm}^{-1}\text{K}^{-1}$. To get this, we have assumed that one relaxation time is valid for both thermal and electrical conductivity. Then we examine the following combination;

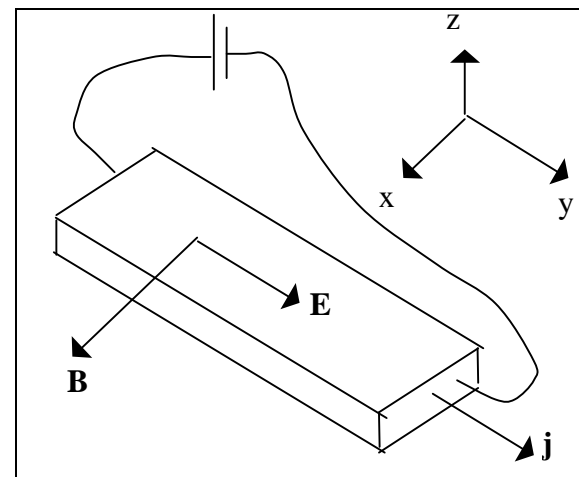
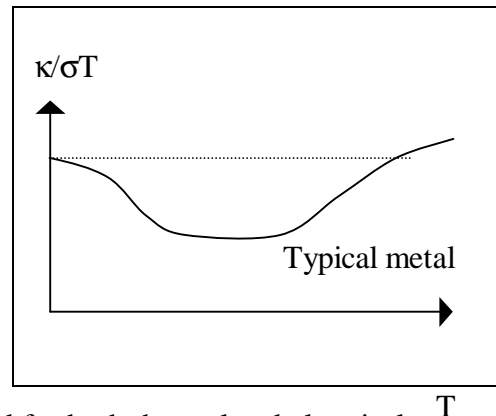
$$\frac{\kappa_T}{\sigma T} = \left(\frac{\pi^2 n k_B^2 T \tau}{3m} \right) \left(\frac{m}{ne^2 \tau} \right) \left(\frac{1}{T} \right) = \frac{\pi^2 k_B^2}{3e^2} = 2.45 \times 10^{-8} \text{ W}\Omega\text{K}^{-1} \quad (16)$$

- the Lorenz constant. This experimental correlation is at least approximately obeyed for a variety of metals and is called the *Wiedemann-Franz Law*.

The Hall effect. We consider the transport of electrons in a slab of when a magnetic field is applied at right-angles to the direction of motion. In this case, we must put the Lorentz expression for the force in the transport equation we derived above i.e.

$$m \left(\frac{d\mathbf{v}_D}{dt} \right) + \mathbf{v}_D / \tau = -e(\mathbf{E} + \mathbf{v}_D \times \mathbf{B})$$

If we write this out in components we have



$$m \frac{dv_{Dx}}{dt} + \frac{mv_{Dx}}{\tau} = -e(E_x + v_{Dy}B_z - v_{Dz}B_y)$$

$$m \frac{dv_{Dy}}{dt} + \frac{mv_{Dy}}{\tau} = -e(E_y + v_{Dz}B_x - v_{Dx}B_z)$$

$$m \frac{dv_{Dz}}{dt} + \frac{mv_{Dz}}{\tau} = -e(E_z + v_{Dx}B_y - v_{Dy}B_x)$$

If the current goes down the wire, then $v_{Dx} = v_{Dz} = 0$. From the diagram, $B_y = B_z = 0$

In the steady state, the acceleration in the x and z directions of the electrons must be zero. Thus equation (17) reduces to

$$0 = -eE_x \quad ; \quad \frac{mv_{Dy}}{\tau} = -eE_y \quad ; \quad 0 = -e(E_z - v_{Dy}B_x)$$

The first equation states that there is no current in the x direction; the second equation is simply that of the current down the wire. The third states that there must be a field perpendicular to the current $E_z = v_{Dy}B_x$ or, substituting for the velocity,

$E_z = (-1/ne)\mathbf{j}_y \cdot \mathbf{B}_z = R_H \mathbf{j}_y \cdot \mathbf{B}_x$ where R_H is the Hall coefficient and is obviously given by $R_H = -1/ne$ in the free electron model. The tendency of the magnetic force to bend the direction of the current must be balanced by an induced electric field if the current is to go down the wire. This is the *Hall effect*. In general, the Hall field is written as $\mathbf{E}_H = R_H \mathbf{B} \times \mathbf{j}$. This can be obtained from the transverse potential across the slab of conductor and can be used to deduce n , the electron density. However, the electron density comes from the valence electrons, so n should correspond to the number of electrons ionised per atom (or per mole of atoms) in the material. In other words, it should correspond to the chemical valency if we assume that a metal consists of the ionic cores bathed in a gas of electrons. This Table shows how we get on.

Element	Valency	Apparent valency from Hall coefficient
Na	1	0.9
K	1	1.1
Cu	1 (to obtain d^{10} core)	1.3
Be	2	-0.2
Mg	2	1.5
Cd	2 (to obtain d^{10} core)	-2.2
Al	3	3.5

The agreement is at best fair and at worst (Be, Cd) disastrous. Something has gone badly wrong with at least one of the assumptions we have made.

To summarise the free electron model

Successes

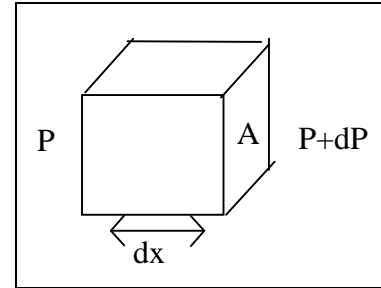
1. Metallic density of states more or less the right shape
2. Binding energies in the right range
3. Heat capacity functional form correct
4. Electrical conductivities reasonable and the Weidemann-Franz law

Failures

1. No account of the band gaps
2. No reason given why one crystal structure should be favoured rather than another
3. Hall coefficients can be seriously in error.

Electrical neutrality and screening

Although we have just considered the dynamics of an electron in a metal under the influence of electric and magnetic fields, one of the basic properties of a conductor is that it contains no internal electric field. In fact we were cheating slightly! (It doesn't alter the analysis) When an electric field is applied to a simple metal (for instance if it is put in a capacitor), then the field must somehow be *screened out*. We shall see



how the gas distorts slightly near to charges in such a way that electrons further away do not see much of the original charge. We shall derive the spatial dependence of the electron gas and the electric field that is screened. We shall consider a problem in one dimension where a metal is placed between the plates of a capacitor.

We start with Gauss's Law, $\text{div}\mathbf{E} = Q / \epsilon_0$ where Q is the charge density and \mathbf{E} the applied field. Before the field is applied, the system is electrically neutral with the electron gas charge cancelling the charges on the ions. When the field is applied, the electrons shift and this cancellation is not complete and so a charge density is induced. If the original charge density of the electron-gas (and positive lattice) separately have magnitude $|en_0|$, then the excess charge density induced by the field must be $-e(n - n_0)$ and this is Q . i.e. the positive ions do not move while the electron gas does. Then

$$\frac{dE}{dx} = -e(n - n_0) / \epsilon_0 \quad (16)$$

Next we consider particles in a small box of length dx and cross-sectional area A with pressures P and $(P+dP)$ on opposing walls. The mechanical force on the particles in the box is given by AdP down the pressure gradient. This is balanced by the electric force on the electrons $-nAdxeE$. Thus

$$\frac{dP}{dx} = -neE \quad (17)$$

We can use the degeneracy pressure for an electron gas, $P = 2nE_F/5$. We know the expression for E_F so we can differentiate the pressure equation for an electron gas.

This gives

$$\frac{dP}{dx} = \frac{2E_F}{3} \frac{dn}{dx} \quad (18)$$

Putting these three equations together gives the result:

$$\frac{d^2\mathbf{E}}{dx^2} = \frac{3e^2n_0}{2\epsilon_0E_F} \mathbf{E} = \mathbf{E} / \lambda^2 \quad (19)$$

where n has been approximated by n_0 on the right hand side. This is the screening equation, where $\lambda = \sqrt{2\epsilon_0E_F / 3e^2n_0} \approx 0.1\text{nm}$ i.e. the screening length is approximately a lattice spacing. The relevant solution to (19) is

$$\mathbf{E} = \mathbf{E}(x=0) \exp(-x / \lambda) \quad (20)$$

i.e. the electric field penetrates only to a depth of a few lattice spacings. Similarly, if we put a test charge in the electron gas, the Coulomb potential is screened, taking the

form $V(r) = \frac{e^2}{4\pi\epsilon_0 r} \exp(-r/\lambda)$. This is consistent with the idea that we can ignore the electron-electron interactions too, although there is more to it than this.

Screening is one justification for the free electron model. Another reason for the reluctance of electrons to scatter is the degenerate nature of the gas (there is nowhere for the scattered electrons to go), and there is another effect, that a periodic potential, such as is generated by a regular array of atoms, is in fact incapable, through quantum mechanics, to scatter a travelling wave electron. This is a consequence of *Bloch's Theorem*.