The Ginzburg-Landau Theory

A normal metal's electrical conductivity can be pictured with an electron gas with some scattering off phonons, the quanta of lattice vibrations. Thermal energy is also carried by this gas, with the result that metals of higher electrical conductivity are also metals of higher thermal conductivity.

As the metal cools, scattering of the electrons off phonons decreases, and both electrical and thermal conductivity increase. But in some metals, there is[1] a 2nd order phase transition (no latent heat) to a state where the thermal conductivity begins to decrease - and the electrical conductivity (at DC) becomes infinite. Surface currents appear that completely cancel any applied magnetic fields inside the material (the Meissner effect); one would expect $\partial\vec{B}/\partial t \propto \nabla \times \vec{E}$ to go to zero in a perfect conductor where $\vec{E}$ goes to zero, but in fact the stronger condition $\vec{B} = 0$ applies.

In some cases, the Meissner effect is not absolute; in "Type II" superconductors, magnetic flux can penetrate into the bulk of the material, but does so in discrete quantum units of $h/2e$. In "Type I" superconductors though, there is some critical field above which the entire sample goes normal-conducting.

There is no way to explain this in terms of a classical gas of electrons, which actually isn't that great a model in the first place. The atomic scale of energies is volts, so the electrons are non-relativistic. On the guess that you have some new quantum phenomena, write a complex valued function ψ and try to explain your new phenomena with it. (Ginzburg and Landau, 1950). In 1957, Bardeen, Cooper and Schrieffer will explain that ψ describes a state[2] of many bosons of overlaping spatial extent which are formed by electron-phonon interactions creating pairs of electrons called Cooper pairs. The full BCS theory is complicated and we can explain a lot with the non-microscopic GL theory.[3]

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[1] At least, when there is no externally applied magnetic field.
[2] Not really a Bose-Einstein condensate though, as the BCS treatment allows for interactions of one fermion from a (loosely bound) pair with a fermion from another overlapping pair.
[3] For some high temperature superconductors, a tensor ψ is needed. In some cases, the Cooper pairs might be spin-1 objects.

From the drop in thermal conductivity, we guess that electrons are moving into this new state described with ψ, and from the age of Shröedinger and de Broglie, we know that $|\psi|^2$ is the number density, n, for ψ. The free energy must drop or no electrons go into this new state, so there is an energy term

$$F = \int d^3\vec{x}\ \ (-\alpha)|\psi|^2.$$

Where α is positive below T_C and zero at or above T_C. But wait! That would minimize to infinitely negative energy and infinitely large field. So we add a spontaneous symmetry breaking term,

$$F = \int d^3\vec{x}\ \left[-\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4\right].$$

The parameters α and β are positive below T_C, but α is assumed to vanish linearly as $T \to T_C$. Units of α are J and β is J-m^3. This is the same sort of "Mexican Hat" potential that is used for the standard model Higgs and the equilibrium state.

There is a kinetic energy $\frac{1}{2m}\langle p^2\rangle$ with $\langle p^2\rangle$ the expectation value of p^2,

$$\langle p^2\rangle = \int d^3\vec{r}\ \ \psi^*(-i\hbar\nabla)(-i\hbar\nabla)\psi = -\hbar^2\int d^3\vec{r}\ \ \psi^*\nabla^2\psi = -\hbar^2\int d^3\vec{r}\ \ (-i\hbar\nabla\psi)^*(-i\hbar\nabla\psi)$$

where the expression on the right, sometimes written $\frac{1}{2m}|-i\hbar\nabla\psi|^2$, follows for the plane wave case anyway, give or take a minus sign. Of course, it is not clear what exactly m is. We are assuming an isotropic medium by using a single scalar m though. From the gauge invariant Dirac prescription we know to add the interaction of the magnetic field with the kinetic energy of the ψ, via $q\vec{A}$, although it is not clear what exactly q is. So now we have

$$F = \int d^3\vec{r}\ \left[-\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}\left|(-i\hbar\nabla + q\vec{A})\psi\right|^2\right]$$

which does not however include the energy of either the external magnetic field $\vec{H}_{EXT}$ or the magnetic field from the induced currents $\vec{B}_{SURF}$. The $\vec{A}$ vector is the potential for the sum of these fields, but it only appears in the energy-of-interaction term. Writing the free energy of the non-superconducting part of the metal as f_{NORM}, the total energy is

$$F = \int d^3\vec{r}\ \left[-\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}\left|\left(-i\hbar\nabla + q\vec{A}\right)\psi\right|^2 + \frac{\left|\vec{B}_{SURF}\right|^2}{2\mu_0} + \mu_0\frac{\left|\vec{H}_{EXT}\right|^2}{2} + f_{NORM} \right]$$

To study the superconducting phenomena, we separate f_{NORM} and the externally applied magnetic field energy from the system under study and work with a free energy density of

$$f\left(\psi,\vec{A}\right) = -\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}\left|\left(-i\hbar\nabla + q\vec{A}\right)\psi\right|^2 + \frac{\left|\vec{B}_{SURF}\right|^2}{2\mu_0}.$$

Superconductivity is –amazingly enough– a 2nd order phase transition; its appearance does not entail adding or removing heat. Therefore, there is no change to the entropy $d\Sigma = \delta Q / T$. Then the energy U is also the Helmholtz free energy $F = U - T\Sigma$. Equilibrium is at[4] the minimum of f, which is found using the Euler-Lagrange equations. First use ψ as the field to be varied

$$\frac{\partial f}{\partial \psi} - \sum_j \frac{\partial}{\partial x_j}\left(\frac{\partial f}{\partial\left(\partial\psi/\partial x_j\right)} \right) = \frac{\partial f}{\partial \psi} - \nabla\cdot\frac{\partial f}{\partial(\nabla\psi)} = 0$$

and then also use $\vec{A}$ as the field to be varied

$$\frac{\partial f}{\partial A_k} - \nabla\cdot\frac{\partial f}{\partial(\nabla A_k)} = 0.$$

The extremum in the variation with ψ gives

$$-\alpha\psi^* + \beta\left(\psi^*\psi\right)\psi^* + \frac{1}{2m}\left[-\hbar^2\nabla^2 + 2i\hbar q\vec{A}\cdot\nabla + q^2\left|\vec{A}\right|^2\right]\psi^* = 0$$

whence

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[4] Tilley & Tilley, “Superfluidity and Superconductivity” (1990), and Kittel “Introduction to Solid State Physics”, (1986) argue that one should actually minimize the Gibbs free energy, $G = F + pV = F - \vec{H}_{EXT}\cdot\vec{M}$ where the externally applied magnetic field H is akin to p and one is minimizing under conditions of fixed H and T. But actually, it does not usually make much difference.

$$\left[\beta|\psi|^2-\alpha\right]\psi+\frac{1}{2m}\left[-i\hbar\nabla+q\vec{A}\right]^2\psi=0$$

where the Coulomb gauge, $\nabla\cdot\vec{A}=0$ has been taken. This is the 1st Ginzburg-Landau equation; it is a special case of the Schröedinger equation. To get the 2nd Ginzburg-Landau equation, find the extremum in the variation with A_k. The first step is to drop the non-$\vec{A}$ dependent terms from the free energy density and to re-cast the magnetic field contributions in terms of $\vec{A}$:

$$f=\frac{1}{2m}\left|\left(-i\hbar\nabla+q\vec{A}\right)\psi\right|^2+\frac{\left|\nabla\times\vec{A}\right|^2}{2\mu_0}-\frac{\mu_0}{2}\left|\vec{H}_{EXT}\right|^2$$

The energy of the external magnetic field does not appear in any derivatives. Then

$$\frac{\partial f}{\partial A_k}=\frac{1}{2m}\left[iq\hbar\psi\left(\nabla\psi^*\right)_k-iq\hbar\psi^*\left(\nabla\psi\right)_k+2q^2|\psi|^2A_k\right]$$

is straight forward; a little more tedious but still uncomplicated is

$$\sum_j\frac{\partial}{\partial x_j}\left(\frac{\partial f}{\partial\left(\partial A_k/\partial x_j\right)}\right)=\frac{\nabla^2A_k}{\mu_0}.$$

But $\nabla^2\vec{A}=\nabla\left(\nabla\cdot\vec{A}\right)-\nabla\times\nabla\times\vec{A}=-\nabla\times\vec{B}=-\mu_0\vec{J}$ in this gauge, so

$$\frac{-iq\hbar}{2m}\left[\psi\nabla\psi^*-\psi^*\nabla\psi\right]-\frac{q^2}{m}|\psi|^2\vec{A}=\vec{J},$$

the 2nd Ginzburg-Landau equation.

From these 2 equations, we can derive much of the phenomenology of superconductors.

1). Let us start with the 2nd equation. Since the particle flow is the electric current divided by the particle charge, this tells us the equation of particle flux at least for the $\vec{A}=0$ case:

$$\frac{-i\hbar}{2m}\left[\psi\nabla\psi^*-\psi^*\nabla\psi\right]=\vec{J}/q=\vec{N}.$$

So although in the Ginzburg–Landau theory we don't in know what ψ really represents or what charge to assign to it, we can say how much of it is flowing around.

The most general form for ψ, not allowing for any time dependencies is $\psi(\vec{x}) = \sqrt{n(\vec{x})}\,\exp\left(iS(\vec{x})\right)$ which just reflects that $|\psi|^2 = n$ is, like the phase S, a function of location in the material. With this form in the 2nd Ginzburg–Landau equation,

$$\vec{J} = \frac{-qn}{m}\left(\hbar\nabla S + q\vec{A}\right)$$

showing that superconducting currents correspond to either a vector potential or a phase advance of the wavefunction.

2). Take the curl of both sides of the 2nd equation to get

$$\frac{-q^2}{m}\left[\nabla \times n\vec{A}\right] = \nabla \times \vec{J},$$

where I've used $|\psi|^2 = n$, the number density. In the center of a uniform material, n will be constant, so

$$\frac{-q^2 n}{m}\vec{B} = \nabla \times \vec{J}.$$

This is one of the London equations, proposed by Fritz and Heinz London in 1935.

3). Using the Maxwell equations with the London equation above to determine $\nabla \times \vec{J}$,

$$\nabla^2\vec{B} = \frac{nq^2\mu_0}{m}\vec{B} = \frac{1}{\lambda^2}\vec{B}.$$

where λ is the "London penetration depth", a parameter which describes how far a magnetic field can penetrate into a superconductor. Imagine a semi-infinite superconductor with $|\psi|^2 = n$ a constant positive number whenever $x > 0$, and let the $x \le 0$ half of space be filled with a constant magnetic field $\vec{B}_0$ that has of course no x component. Later we will see than an infinitely thin boundary to $|\psi|^2$ is not actually possible, but neglect that effect for now. Then there will be some exponential decay of the field inside the superconductor with characteristic scale λ,

$\vec{B}(\vec{x}) = \vec{B}_0 \exp(-x/\lambda)$. From Ampere's law, there will be surface supercurrents that also go as $exp(-x/\lambda)$.

4). A finite span is required for the wave function can go from zero to its full value. Again, let the superconductor fill the semi-infinite volume $x > 0$, and let the $x \le 0$ half of space be filled with a region of normal or no conduction, where $\psi = 0$. Allow that there might be a non-zero external field and call its direction the y direction, but let us just work with a planar boundary – nothing physical will have non-zero y or z derivatives. Then $\vec{J} = -\hat{z}\left(\frac{B_0}{\lambda\mu_0}\right)\exp\left(-x/\lambda\right)$ will be in the $-z$ direction, but we might have non-zero $\vec{A}$. In fact, with some simple sketches of loops, we can guess that an exponentially decaying $\vec{A} \propto \hat{z}$ might work, and indeed it would also satisfy the gauge condition $\nabla\cdot\vec{A} = 0$. So $\vec{A} = \hat{z}\left(\lambda B_0\right)\exp(-x/\lambda)$ and inserting this into $\vec{J} = \frac{-qn}{m}\left(\hbar\nabla S + q\vec{A}\right)$ reveals $\hbar\nabla S = 0$! We are then justified to look here for strictly real solutions to

$$\left[\beta|\psi|^2 - \alpha\right]\psi + \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi = 0$$

that is zero at $x = 0$ and rises to some constant real number at large positive x. Such a solution is

$$\psi = \sqrt{\frac{\alpha}{\beta}}\tanh\left(x/\sqrt{2}\xi\right)$$

where $\xi = \hbar/\sqrt{2m\alpha}$ is the coherence length.

5). Flux quanta are a result of ψ being a complex number. For a closed loop that remains more than a few λ_L from any normally-conducting regions, $\vec{J}$ is zero, so $\oint d\vec{\ell}\cdot\vec{J} = 0$ and

$$\hbar\oint d\vec{\ell}\cdot\nabla S = -q\oint d\vec{\ell}\cdot\vec{A} = -q\iint d\vec{a}\cdot\left(\nabla\times\vec{A}\right) = -q\iint d\vec{a}\cdot\vec{B} = -q\Phi.$$

In order for ψ to be single valued, the integral of the phase advance in such a closed loop has to be an integer times 2π, so the magnetic flux Φ is quantized in units of h/q. But be clear – we have not proven that any flux can enter at all. We have only shown that if it does enter it will do so in quantal units. The experimental fact that magnetic flux can penetrate into a Type II superconductor in units of $h/2e$ tells us what value to assign to q – it is the amount that corresponds to the dissociation of a single Cooper pair!

6). Critical field phenomena are a result of the combination of the expression for free energy and the independence of λ_L and ξ. Consider again the free energy density

$$-\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m}\left|\left(-i\hbar\nabla + q\vec{A}\right)\psi\right|^2 + \frac{\left|\vec{B}_{SURF}\right|^2}{2\mu_0}.$$

To start with, let us neglect the boundary regions where there is non-zero current flow and $\vec{A}$ and just consider the bulk of the superconductor. In that region, where $\vec{A}$ and $\vec{J}$ are zero, we can drop the 3rd term and just consider

$$f = \quad -\alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 \quad + \frac{\left|\vec{B}_{SURF}\right|^2}{2\mu_0}.$$

Below T_C, the first two terms together are negative, or there would be no superconductivity at all. Superconductivity begins to collapse when the positive term from the magnetic field that creates the Meissner effect gets large enough to make f positive. Past that point, collapse of both ψ and $\vec{B}_{SURF}$ simultaneously will reduce the free energy and superconductivity will disappear.

To write the critical field level in terms of α and β, re-derive the 1st Ginzburg-Landau (Schröedinger) equation from the above equation. It is just $\left[\beta|\psi|^2 - \alpha\right]\psi = 0$, from which $|\psi|^2 = n = \alpha/\beta$. Then $f = 0$ at $\left|\vec{B}_{SURF}\right| = \alpha\sqrt{\mu_0/\beta}$ or $H_c = \alpha\sqrt{1/\mu_0\beta}$. Since the field produced by the Meissner effect exactly cancells the externally applied field, this is also the level of externally applied critical field. I believe that this effect limits the maximum current that can be carried through the superconductor; at some point the magnetic field outside the superconductor that is created by the supercurrent exceeds H_c.

7). The thermodynamics of flux penetration –that is, what happens near the edges of the superconductor at high applied fields– provides an understanding of how Type I and Type II materials arise.

Recall that the London penetration depth λ controls how far a magnetic field can penetrate into a superconducting region from a normally conducting one. For larger values of λ, this $\left|\vec{B}\right|^2/2\mu_0$ term adds a larger positive contribution to the free energy. The coherence length ξ controls how quickly ψ gets up to its central-material value as one moves into a superconducting region from a normally conducting region; a larger ξ corresponds to a lower density of superconducting electrons just inside a normal/superconducting boundary and hence a smaller negative energy contribution from $-\alpha|\psi|^2 + \beta/2\,|\psi|^4$.

So for large ξ relative to λ, a boundary will have a net positive energy in the region where the ψ is not large and there is some penetrating magnetic flux. In such a case it is never thermodynamically advantageous to increase the size of the normal/superconducting boundary, and flux quanta never enter the material. That is a Type I superconductor.

On the other hand, if ξ is small relative to λ, there can be a layer near the boundary where the free energy is negative. Then, if the applied field is close enough to $\alpha\sqrt{\mu_0/\beta}$, the drop in free energy created by introducing a flux quantum is greater than the drop in free energy caused by having the volume of the flux quantum in a superconducting state. At such a point, ($H_{\mathrm{EXT}} = H_{\mathrm{c1}}$) magnetic flux enters the Type II superconductor. It will continue to accept flux until even an infinitesimally small ψ can not be sustained ($H_{\mathrm{EXT}} = H_{\mathrm{c2}}$). I will skip the details – turns out $H_{c2} = \sqrt{2}\,\frac{\lambda}{\xi} H_c$.

Type II superconductors will have their flux vortices move around when there is an electrical current; this dissipates energy and one technique is to create pinning points where flux vortices will for some reason be trapped. Then one can continue to superconduct fairly large amounts of current through the material.