1. Derive the $T = 0$ relations shown in the lectures

$$\Omega_0 - \Omega_0(\Delta = 0) = -\frac{1}{2} \sum_{\mathbf{k}} \frac{\Delta^4}{E_k(E_k + |\xi_k|)^2},$$

and

$$\Omega_0 - \Omega_0(\Delta = 0) = -\frac{1}{2} L^3 N(0) \Delta^2.$$

(Hint: Apply the gap equation and use $\int_{-\infty}^{\infty} \frac{dx}{\sqrt{x^2+1}(\sqrt{x^2+1}+|x|)^2} = 1$.)

Solution:

Let's first study the energy functional in superconducting state at zero temeperature, where the contribution due to excitations is absent:

$$\Omega_{s,0} = 2 \sum_{\mathbf{k}} (\xi_k v_k^2 - \Delta v_k u_k) + \frac{L^3}{g} \Delta^2 = 2 \sum_{\mathbf{k}} \xi_k v_k^2 - \Delta (2 \sum_{\mathbf{k}} v_k u_k - \frac{L^3}{g} \Delta)$$

$$= 2 \sum_{\mathbf{k}} \xi_k v_k^2 - \Delta \{ 2 \sum_{\mathbf{k}} v_k u_k - \frac{L^3}{g} \frac{g}{L^3} \sum_{\mathbf{k}} u_k v_k [1 - 2n(E_k)] \}$$

Here we used the gap equation $\Delta = \frac{g}{L^3} \sum_{\mathbf{k}} u_k v_k [1 - 2n(E_k)]$. Now since $E_k > 0$ at $T < T_c$, at $T = 0$ we have $n(E_k) = \frac{1}{e^{E_k/kT}+1} = 0$ and so

$$\Omega_{s,0} = 2 \sum_{\mathbf{k}} \xi_k v_k^2 - \Delta \{ 2 \sum_{\mathbf{k}} v_k u_k - \sum_{\mathbf{k}} u_k v_k \}$$

$$= 2 \sum_{\mathbf{k}} \xi_k v_k^2 - \Delta \sum_{\mathbf{k}} u_k v_k = \sum_{\mathbf{k}} (\xi_k - \frac{\xi_k^2}{E_k} - \frac{\Delta^2}{2E_k})$$

Here we used $v_k^2 = \frac{1}{2}(1 - \frac{\xi_k}{E_k})$ and $u_k v_k = \frac{1}{2} \frac{\Delta}{E_k}$. (The same result would obviously follow by starting from the other form we've seen before, $\Omega_{s,0} = \sum_{\mathbf{k}} (\xi_k - E_k) + \frac{L^3}{g} \Delta^2$, and then applying the gap equation in the form $\Delta = \frac{g}{2L^3} \sum_{\mathbf{k}} \frac{\Delta}{E_k} \tanh \frac{E_k}{2k_B T} = \frac{g}{2L^3} \sum_{\mathbf{k}} \frac{\Delta}{E_k}$.)

Next the energy functional in normal state at zero temperature. This is obtained from the above by setting $\Delta = 0$:

$$\Omega_{n,0} = \sum_{\mathbf{k}} (\xi_k - |\xi_k|)$$

Then the difference of these:

$$
\begin{aligned}
\Omega_{s,0} - \Omega_{n,0} &= \sum_{\mathbf{k}}(\xi_k - \frac{\xi_k^2}{E_k} - \frac{\Delta^2}{2E_k}) - \sum_{\mathbf{k}}(\xi_k - |\xi_k|) = \sum_{\mathbf{k}}(|\xi_k| - \frac{\xi_k^2}{E_k} - \frac{\Delta^2}{2E_k}) \\
&= \sum_{\mathbf{k}} \frac{2E_k|\xi_k| - 2\xi_k^2 - (E_k^2 - \xi_k^2)}{2E_k} = \sum_{\mathbf{k}} \frac{2E_k|\xi_k| - \xi_k^2 - E_k^2}{2E_k} \\
&= -\frac{1}{2}\sum_{\mathbf{k}} \frac{E_k^2 - 2E_k|\xi_k| + \xi_k^2}{E_k} = -\frac{1}{2}\sum_{\mathbf{k}} \frac{(E_k - |\xi_k|)^2}{E_k} \\
&= -\frac{1}{2}\sum_{\mathbf{k}} \frac{(E_k - |\xi_k|)^2 (E_k + |\xi_k|)^2}{E_k(E_k + |\xi_k|)^2} = -\frac{1}{2}\sum_{\mathbf{k}} \frac{(E_k^2 - \xi_k^2)^2}{E_k(E_k + |\xi_k|)^2} \\
&= -\frac{1}{2}\sum_{\mathbf{k}} \frac{\Delta^4}{E_k(E_k + |\xi_k|)^2}
\end{aligned}
$$

This is the first part of what was to be shown. Now the rest.

The function $\frac{1}{E_k(E_k+|\xi_k|)^2}$ is peaked at $\xi_k = 0$, so when converting the sum to an integral, we can use the approximation of (76). Thus

$$
\Omega_{s,0} - \Omega_{n,0} = -\frac{N(0)L^3}{2} \int_{-\infty}^{\infty} \frac{\Delta^4}{E_k(E_k + |\xi_k|)^2} d\xi_k
$$

Analyzing the integral manually is a bit tedious, but we can use Mathematica to find directly

$$
\begin{aligned}
\Omega_{s,0} - \Omega_{n,0} &= -\frac{N(0)L^3\Delta^4}{2} \int_{-\infty}^{\infty} \frac{1}{E_k(E_k + |\xi_k|)^2} d\xi_k \\
&= -\frac{N(0)L^3\Delta^4}{2} \frac{1}{\Delta^2} = -\frac{N(0)L^3\Delta^2}{2}
\end{aligned}
$$

This completes the exercise.

Note: The physical interpretation of this result is simple. The condensation energy is on the order of $L^3 N(0)\Delta^2/2$, because $L^3 N(0)\Delta$ is roughly the total number of electrons around the Fermi energy that are paired, and the energy gained in forming pairs is approximately Δ per electron.

2. Show that from the grand potential $\Omega(T, V, \mu) = \min_{v_k, \Delta}[\Omega(T, V, \mu, v_k, \Delta)]$ one obtains the specific heat

$$
C = \frac{L^3 N(0)}{2k_B T^2} \int_{-\infty}^{\infty} d\xi \frac{1}{\cosh^2 \frac{\sqrt{\xi^2+\Delta^2}}{2k_B T}} \left(\xi^2 + \Delta^2 - T\Delta \frac{d\Delta}{dT} \right).
$$

Solution:

The grand potential is given by

$$\Omega(T, V, \mu, v_k, \Delta) = 2\sum_{\mathbf{k}}(\xi_k v_k^2 - \Delta u_k v_k) + \frac{L^3}{g}\Delta^2 - 2k_BT\sum_{\mathbf{k}}\ln(1 + e^{-E_k/k_BT}),$$

where $E_k = \sqrt{\xi_k^2 + \Delta^2}$ and $u_k = \sqrt{1 - v_k^2}$. In equilibrium this is minimized with respect to v_k and Δ. (For notational simplicity, we only consider Ω to be a function of a single v_k. See note below for discussion of other notation issues.)

The specific heat is defined $C = T(dS/dT)_{V,\mu}$, where the entropy is $S = -(d\Omega/dT)_{V,\mu}$. First we calculate the entropy:

$$S = -(\frac{d\Omega}{dT})_{V,\mu} = -(\frac{\partial\Omega}{\partial T} + \underbrace{\frac{\partial\Omega}{\partial\Delta}}_{=0}\frac{\partial\Delta}{\partial T} + \underbrace{\frac{\partial\Omega}{\partial v_k}}_{=0}\frac{\partial v_k}{\partial T}) = -\frac{\partial\Omega}{\partial T}$$

where we used the stationarity (equilibrium) conditions. So it follows that only the last term in Ω contributes to the equilibrium entropy:

$$S = 2k_B\sum_{\mathbf{k}}\ln(1 + e^{-E_k/k_BT}) + 2k_BT\sum_{\mathbf{k}}\frac{e^{-E_k/k_BT}(\frac{E_k}{k_BT^2})}{1 + e^{-E_k/k_BT}}$$

$$= 2k_B\sum_{\mathbf{k}}\ln(1 + e^{-E_k/k_BT}) + \frac{2}{T}\sum_{\mathbf{k}}\frac{E_k e^{-E_k/k_BT}}{1 + e^{-E_k/k_BT}}$$

$$= 2k_B\sum_{\mathbf{k}}\ln(1 + e^{-E_k/k_BT}) + \frac{2}{T}\sum_{\mathbf{k}}\frac{E_k}{e^{E_k/k_BT} + 1}$$

This could still be written in the form $S = -k_B\sum_\alpha[f_\alpha\ln f_\alpha + (1 - f_\alpha)\ln(1 - f_\alpha)]$ as in the case of an ideal fermion gas, but that is not essential here. Note, however, that the depedence on v_k and $u_k = \sqrt{1 - v_k^2}$ has dropped out and only the excitation energies E_k are left. This makes physical sense somehow: only the excitations contribute to entropy. The pair condensate does not, because there all the particles are ordered in pairs that are "in the same macroscopic quantum state".

So now we calculate the specific heat.

$$C = T(\frac{dS}{dT})_{V,\mu} = T(\frac{\partial S}{\partial T} + \frac{\partial S}{\partial\Delta}\frac{\partial\Delta}{\partial T} + \underbrace{\frac{\partial S}{\partial v_k}}_{=0}\frac{\partial v_k}{\partial T}) = T(\frac{\partial S}{\partial T} + \frac{\partial S}{\partial\Delta}\frac{\partial\Delta}{\partial T})$$

There is no reason for "stationarity" conditions on S in general, but still apparently

$\partial S/\partial v_k = 0$, as noted above. So we need

$$\frac{\partial S}{\partial T} = 2k_B \sum_{\mathbf{k}} \frac{e^{-E_k/k_BT}\frac{E_k}{k_BT^2}}{1+e^{-E_k/k_BT}} - \frac{2}{T^2}\sum_{\mathbf{k}} \frac{E_k}{e^{E_k/k_BT}+1} + \frac{2}{T}\sum_{\mathbf{k}} \frac{E_k e^{E_k/k_BT}\frac{E_k}{k_BT^2}}{(e^{E_k/k_BT}+1)^2}$$

$$= \frac{2}{k_BT^3}\sum_{\mathbf{k}} \frac{E_k^2 e^{E_k/k_BT}}{(e^{E_k/k_BT}+1)^2}$$

Now the other derivative. We will need $\frac{\partial E_k}{\partial \Delta} = \frac{\Delta}{E_k}$.

$$\frac{\partial S}{\partial \Delta} = 2k_B \sum_{\mathbf{k}} \frac{e^{-E_k/k_BT}\left(-\frac{\Delta/E_k}{k_BT}\right)}{1+e^{-E_k/k_BT}} + \frac{2}{T}\sum_{\mathbf{k}} \frac{\Delta/E_k}{e^{E_k/k_BT}+1} - \frac{2}{T}\sum_{\mathbf{k}} \frac{E_k e^{E_k/k_BT}\frac{\Delta}{E_k k_BT}}{(e^{E_k/k_BT}+1)^2}$$

$$= -\frac{2\Delta}{k_BT^2}\sum_{\mathbf{k}} \frac{e^{E_k/k_BT}}{(e^{E_k/k_BT}+1)^2}$$

So now

$$C = T\left(\frac{\partial S}{\partial T} + \frac{\partial S}{\partial \Delta}\frac{\partial \Delta}{\partial T}\right) = \frac{2}{k_BT^2}\sum_{\mathbf{k}} \frac{e^{E_k/k_BT}}{(e^{E_k/k_BT}+1)^2}\left(E_k^2 - \Delta T\frac{\partial \Delta}{\partial T}\right)$$

$$= \frac{2}{k_BT^2}\sum_{\mathbf{k}} \frac{e^{E_k/k_BT}}{(e^{E_k/k_BT}+1)^2}\left(\xi_k^2 + \Delta^2 - \Delta T\frac{\partial \Delta}{\partial T}\right)$$

$$= \frac{2}{k_BT^2}\sum_{\mathbf{k}} \frac{1}{(e^{E_k/2k_BT}+e^{-E_k/2k_BT})^2}\left(\xi_k^2 + \Delta^2 - \Delta T\frac{\partial \Delta}{\partial T}\right)$$

$$= \frac{2}{k_BT^2}\sum_{\mathbf{k}} \frac{1}{4\cosh^2 \frac{E_k}{2k_BT}}\left(\xi_k^2 + \Delta^2 - \Delta T\frac{\partial \Delta}{\partial T}\right)$$

Finally, using the usual approximation for a function peaked around the Fermi energy:

$$C = \frac{N(0)L^3}{2k_BT^2}\int_{-\infty}^{\infty} d\xi_k \frac{1}{\cosh^2 \frac{E_k}{2k_BT}}\left(\xi_k^2 + \Delta^2 - \Delta T\frac{\partial \Delta}{\partial T}\right)$$

This is the desired result.

Note: You may find the notations and the logic above a bit confusing. More "precisely" you could think as follows. We define the "generalized" grand potential $\tilde{\Omega}(V,\mu,T,\{v_k\},\Delta)$ as before, just with a tilde added for clarity. In equilibrium at given T this should be minimized with respect to the extra variables $\{v_k\}$ and Δ, which means that $\partial\tilde{\Omega}/\partial v_k = 0$ and $\partial\tilde{\Omega}/\partial\Delta = 0$. These give some equilibrium values for v_k and Δ, denoted as $v_k^{eq}(T)$ and $\Delta^{eq}(T)$, which depend on T, in principle. So the equilibrium grand potential may be written as $\Omega(V,\mu,T) = \tilde{\Omega}(V,\mu,T,\{v_k^{eq}(T)\},\Delta^{eq}(T))$. Now, for example $S = -\frac{\partial\Omega}{\partial T} = -\frac{d\tilde{\Omega}}{dT}$, where the total derivative in the latter form means that you have to differentiate with respect to $v_k^{eq}(T)$ and $\Delta^{eq}(T)$ as well. It's just that the derivative of $v_k^{eq}(T)$ drops out,

because $\partial\tilde{\Omega}/\partial v_k = 0$, and so on. (On the other hand, v_k^{eq} also does not have an "explicit" temperature dependence, because it only depends on it via Δ. Is this relevant? I don't think so.)

Note 2: By the way, similarly to the equilibrium entropy calculated above, only the excitations can transport heat. (Heat and entropy are related by $dQ = TdS$.) There is no heat or entropy transfer associated with the supercurrents that are carried by the condensed electrons, and at low temperature there are only few excitations because of the energy gap. That is why a superconductor, while being a good conductor of charge, is a bad conductor of heat.

3. Show that for the specific heat of the normal state one obtains

$$C = \frac{2\pi^2}{3}L^3 N(0)k_B^2 T.$$

(Hint: Use $\int_{-\infty}^{\infty} \frac{x^2}{\cosh^2 x} dx = \frac{\pi^2}{6}$.)

Solution:

For the normal state we can use the result of the superconducting state by setting $\Delta = 0$.

$$C = \frac{N(0)L^3}{2k_BT^2}\int_{-\infty}^{\infty} d\xi_k \frac{\xi_k^2}{\cosh^2 \frac{|\xi_k|}{2k_BT}} = \frac{N(0)L^3}{2k_BT^2}\int_{-\infty}^{\infty} d\xi_k \frac{\xi_k^2}{\cosh^2 \frac{\xi_k}{2k_BT}}$$

Change to variable $x = \xi/2k_BT$:

$$C = 4N(0)L^3 k_B^2 T \underbrace{\int_{-\infty}^{\infty} dx \frac{x^2}{\cosh^2 x}}_{=\pi^2/6} = \frac{2\pi^2}{3}L^3 N(0)k_B^2 T$$

And that is the result. Note that the normal-state specific heat is linear in T.

We could have derived this result also independently of the result for the superconducting state by starting from the expression of Ω for the free electron gas: $\Omega = -\frac{2}{\beta}\sum_\mathbf{k} \ln(1 + e^{-\beta(\epsilon_k - \mu)})$ and using $C = -T(\frac{\partial^2\Omega}{\partial T^2})$. However, it is perhaps simpler to start from the internal energy E and use $C = \frac{\partial E}{\partial T}$. (This intuitive result follows formally from $\Omega = E - TS - \mu N$ by applying $\frac{\partial}{\partial T}$ and then using $\frac{\partial\Omega}{\partial T} = -S$ and $T\frac{\partial S}{\partial T} = C$.) The internal energy for a free fermion gas is

$$E = 2\sum_\mathbf{k} \epsilon_k f(\epsilon_k, T), \quad \text{where} \quad f(\epsilon_k, T) = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

Noting that $\frac{d}{dx}\frac{1}{e^x+1} = -\frac{1}{4\cosh^2(x/2)}$ we have

$$\frac{\partial}{\partial T}f(\epsilon_k, T) = \frac{\epsilon_k - \mu}{k_BT^2}\frac{1}{\cosh^2[\beta(\epsilon_k - \mu)]}$$

This decays rapidly away from the energy $\epsilon_k = \mu$, so we may use the usual approximation to write

$$C = \frac{\partial E}{\partial T} = 2L^3 N(0) \int d\epsilon \epsilon \frac{\epsilon - \mu}{k_B T^2} \frac{1}{4 \cosh^2[\beta(\epsilon - \mu)/2]}$$

and since $\int d\epsilon \frac{\epsilon - \mu}{\cosh^2[\beta(\epsilon - \mu)]} = 0$, we may subtract a zero term to write this as

$$C = 2L^3 N(0) \int d\epsilon \frac{(\epsilon - \mu)^2}{k_B T^2} \frac{1}{4 \cosh^2[\beta(\epsilon - \mu)/2]}$$
$$= 2L^3 N(0) \int d\xi \frac{\xi^2}{k_B T^2} \frac{1}{4 \cosh^2(\beta\xi/2)}$$
$$= 4L^3 N(0) k_B^2 T \int_{-\infty}^{\infty} dx \frac{x^2}{\cosh^2 x} = \frac{2\pi^2}{3} L^3 N(0) k_B^2 T$$

Here we used $\int_{-\infty}^{\infty} \frac{x^2}{\cosh^2 x} dx = \frac{\pi^2}{6}$.

Note: The physical interpretation of this result is simple. The internal energy (relative to zero temperature) is on the order of $L^3 N(0)(k_B T)^2$, because $L^3 N(0) k_B T$ is roughly the total number of electrons excited from below the Fermi energy to above it, and the average energy gained by each electron is approximately $k_B T$.

4. A variation $\psi^* \to \psi^* + \delta\psi^*$ or $\mathbf{A} \to \mathbf{A} + \delta\mathbf{A}$, for example, changes the GL energy functional according to $G \to G + \delta G$. Derive the GL differential equations and their boundary conditions by requiring $\delta G = 0$ to lowest order in arbitrary variations.

(Hint: You may first want to prove the more general result that the minimum conditions for $G[\psi^*, \mathbf{A}] = \int d^3 r g(\psi^*, \nabla\psi^*, \mathbf{A}, \nabla \times \mathbf{A})$ are $\frac{\partial g}{\partial \psi^*} - \nabla \cdot \frac{\partial g}{\partial \nabla\psi^*} = 0$, $\frac{\partial g}{\partial \mathbf{A}} + \nabla \times \frac{\partial g}{\partial \nabla \times \mathbf{A}} = 0$, $\hat{\mathbf{n}} \cdot \frac{\partial g}{\partial \nabla\psi^*} = 0$, $\hat{\mathbf{n}} \times \frac{\partial g}{\partial \nabla \times \mathbf{A}} = 0$. Use relations like $\mathbf{C} \cdot \nabla\phi = \nabla \cdot (\mathbf{C}\phi) - (\nabla \cdot \mathbf{C})\phi$.)

Solution:
The GL free energy functional is

$$G = \int d^3 r [\alpha\psi^*\psi + \frac{\beta}{2}(\psi^*)^2\psi^2 + \gamma|(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi|^2 + \frac{1}{2\mu_0}\mathbf{B}^2 - \mathbf{B} \cdot \mathbf{H}]$$
$$= \int d^3 r [\alpha\psi^*\psi + \frac{\beta}{2}(\psi^*)^2\psi^2 + \gamma(-\frac{\hbar}{i}\nabla - q\mathbf{A})\psi^* \cdot (\frac{\hbar}{i}\nabla - q\mathbf{A})\psi + \frac{1}{2\mu_0}\mathbf{B}^2 - \mathbf{B} \cdot \mathbf{H}]$$

If ψ^* corresponds to the minimum of G, then small arbitrary variations $\psi^* \to \psi^* + \delta\psi^*$ should leave G unchanged, that is $\delta G = G[\psi^* + \delta\psi^*] - G[\psi^*] = 0$, to linear order in $\delta\psi^*$. Let us differentiate

$$\delta G = \int d^3 r [\alpha\psi\delta\psi^* + \beta\psi^*\psi^2\delta\psi^* + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi \cdot (-\frac{\hbar}{i}\nabla - q\mathbf{A})\delta\psi^*]$$
$$= \int d^3 r [\alpha\psi + \beta\psi^*\psi^2 + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi \cdot (-q\mathbf{A})]\delta\psi^* + \underbrace{\int d^3 r [\gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi \cdot (-\frac{\hbar}{i}\nabla\delta\psi^*)]}_{I_2}$$

Here in the second term we should "integrate by parts", or use one of the Green formulas. Equivalently, we may use the vector identity

$$\nabla \cdot (\mathbf{C}\phi) = \mathbf{C} \cdot \nabla\phi + (\nabla \cdot \mathbf{C})\phi$$
$$\mathbf{C} \cdot \nabla\phi = \nabla \cdot (\mathbf{C}\phi) - (\nabla \cdot \mathbf{C})\phi$$

So

$$I_2 = \gamma \int d^3r \nabla \cdot [(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi(-\frac{\hbar}{i})\delta\psi^*] - \gamma \int d^3r [\nabla \cdot (\frac{\hbar}{i}\nabla - q\mathbf{A})\psi(-\frac{\hbar}{i})]\delta\psi^*$$
$$= \gamma \int d\mathbf{S} \cdot (\hbar^2\nabla\psi + q\frac{\hbar}{i}\mathbf{A}\psi)\delta\psi^* - \gamma \int d^3r [\nabla \cdot (\hbar^2\nabla + q\frac{\hbar}{i}\mathbf{A})\psi]\delta\psi^*$$
$$= -\gamma \int d^3r [\hbar^2\nabla^2\psi + q\frac{\hbar}{i}\nabla \cdot (\mathbf{A}\psi)]\delta\psi^*$$

In order for the surface integral to vanish, as we assumed above, the boundary condition $\hat{\mathbf{n}} \cdot [(\hbar/i)\nabla - q\mathbf{A}]\psi = 0$ must hold. Putting the rest of the terms together:

$$\delta G = \int d^3r \{\alpha\psi + \beta\psi^*\psi^2 - \gamma[\hbar^2\nabla^2\psi + q\frac{\hbar}{i}\nabla \cdot (\mathbf{A}\psi)] + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})\psi \cdot (-q\mathbf{A})\}\delta\psi^*$$
$$= \int d^3r [\alpha\psi + \beta\psi^*\psi^2 - \gamma\hbar^2\nabla^2\psi - \gamma q\frac{\hbar}{i}\nabla \cdot (\mathbf{A}\psi) - \gamma q\frac{\hbar}{i}\nabla\psi \cdot \mathbf{A} + \gamma q^2\psi\mathbf{A} \cdot \mathbf{A}]\delta\psi^*$$
$$= \int d^3r [\alpha\psi + \beta\psi^*\psi^2 + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A}) \cdot (\frac{\hbar}{i}\nabla\psi - q\mathbf{A}\psi)]\delta\psi^*$$
$$= \int d^3r [\alpha\psi + \beta\psi^*\psi^2 + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})^2\psi]\delta\psi^*$$

Since $\delta\psi^*$ is arbitrary, the factor in front of it must vanish identically in order for $\delta G = 0$ to be satisfied. Thus we have the first GL equation

$$\alpha\psi + \beta\psi^*\psi^2 + \gamma(\frac{\hbar}{i}\nabla - q\mathbf{A})^2\psi = 0$$

This is to be complemented by the assumed boundary condition: $\hat{\mathbf{n}} \cdot [(\hbar/i)\nabla - q\mathbf{A}]\psi = 0$. (Below we see that this boundary condition means that there is no current through the boundary.) Varying with respect to ψ would just give the complex conjugate of this equation.

Next we consider variations in $\mathbf{A}$, writing $\mathbf{B} = \nabla \times \mathbf{A}$, so that

$$G = \int d^3r [\alpha\psi^*\psi + \frac{\beta}{2}(\psi^*)^2\psi^2$$
$$+ \gamma\hbar^2\nabla\psi^* \cdot \nabla\psi + \gamma q\frac{\hbar}{i}\psi\nabla\psi^* \cdot \mathbf{A} - \gamma q\frac{\hbar}{i}\psi^*\nabla\psi \cdot \mathbf{A} + \gamma q^2|\psi|^2\mathbf{A} \cdot \mathbf{A}$$
$$+ \frac{1}{2\mu_0}(\nabla \times \mathbf{A}) \cdot (\nabla \times \mathbf{A}) - (\nabla \times \mathbf{A}) \cdot \mathbf{H}]$$

Then

$$\delta G = \int d^3r[-\gamma\frac{\hbar}{i}q(\psi^*\nabla\psi - \psi\nabla\psi^*) + 2\gamma q^2|\psi|^2\mathbf{A}]\cdot\delta\mathbf{A}$$

$$+ \underbrace{\int d^3r[\frac{1}{\mu_0}(\nabla\times\mathbf{A})\cdot(\nabla\times\delta\mathbf{A}) - \mathbf{H}\cdot(\nabla\times\delta\mathbf{A})]}_{I_3}$$

To develop the integral I_3 we need the following vector differential formula

$$\nabla\cdot(\mathbf{G}\times\mathbf{F}) = \mathbf{F}\cdot(\nabla\times\mathbf{G}) - \mathbf{G}\cdot(\nabla\times\mathbf{F})$$
$$\mathbf{F}\cdot(\nabla\times\mathbf{G}) = \nabla\cdot(\mathbf{G}\times\mathbf{F}) + \mathbf{G}\cdot(\nabla\times\mathbf{F})$$

Using this

$$I_3 = \frac{1}{\mu_0}\int d^3r[\mathbf{B} - \mu_0\mathbf{H}]\cdot(\nabla\times\delta\mathbf{A})$$

$$= \frac{1}{\mu_0}\int d^3r\nabla\cdot[\delta\mathbf{A}\times(\mathbf{B} - \mu_0\mathbf{H})] + \frac{1}{\mu_0}\int d^3r[\nabla\times(\mathbf{B} - \mu_0\mathbf{H})]\cdot\delta\mathbf{A}$$

$$= \frac{1}{\mu_0}\int d\mathbf{S}\cdot[\delta\mathbf{A}\times(\mathbf{B} - \mu_0\mathbf{H})] + \frac{1}{\mu_0}\int d^3r(\nabla\times\mathbf{B})\cdot\delta\mathbf{A}$$

In the latter term we assumed $\nabla\times\mathbf{H} = 0$, which is valid in the absence of free currents. (See note below.) The surface term, on the other hand, vanishes at least by assuming $\hat{\mathbf{n}}\times(\mathbf{B} - \mu_0\mathbf{H}) = 0$ on the surface.

Now, taking all terms together again

$$\delta G = \int d^3r[-\gamma\frac{\hbar}{i}q(\psi^*\nabla\psi - \psi\nabla\psi^*) + 2\gamma q^2\mathbf{A} + \frac{1}{\mu_0}\nabla\times\mathbf{B}]\cdot\delta\mathbf{A}$$

Since $\delta\mathbf{A}$ is arbitrary, $\delta G = 0$ requires

$$\frac{1}{\mu_0}\nabla\times\mathbf{B} = \frac{q\hbar\gamma}{i}(\psi^*\nabla\psi - \psi\nabla\psi^*) - 2\gamma q^2|\psi|^2\mathbf{A}$$

This is the second GL equation, and it must be solved with the boundary condition $\hat{\mathbf{n}}\times(\mathbf{B} - \mu_0\mathbf{H}) = 0$. It follows from Maxwell's equations that the right-hand side is to be interpreted as a current density.

Note: In the simplest geometry of a long narrow cylinder parallel to the externally applied field, $\mathbf{H}$ is just constant, equal to the given external field "at infinity". If we take this for granted, then $\nabla\times\mathbf{H} = 0$ trivially. However, in general also $\mathbf{H}$ must be solved by including the energy of the magnetic field outside of the superconductor into G and minimizing with respect to that as well. This should yield the equilibrium condition $\nabla\times\mathbf{H} = 0$ as a result. (Check it as an exercise, if you like.)

Note 2: The above results would follow much more compactly by applying general results along the following lines. Assume that $S[f, \mathbf{g}] = \int d^3r\, s(f, \nabla f, \mathbf{g}, \nabla \times \mathbf{g})$. Then consider arbitrary variations $f \to f + \delta f$ and $\mathbf{g} \to \mathbf{g} + \delta \mathbf{g}$. By Taylor expansion

$$\delta S = S[f + \delta f, \mathbf{g} + \delta \mathbf{g}] - S[f, \mathbf{g}]$$
$$= \int d^3r [\frac{\partial s}{\partial f}\delta f + \frac{\partial s}{\partial \nabla f} \cdot (\nabla \delta f) + \frac{\partial s}{\partial \mathbf{g}} \cdot \delta \mathbf{g} + \frac{\partial s}{\partial \nabla \times \mathbf{g}} \cdot (\nabla \times \delta \mathbf{g})]$$

Then by applying $\mathbf{C} \cdot \nabla \phi = \nabla \cdot (\mathbf{C}\phi) - (\nabla \cdot \mathbf{C})\phi$ and $\mathbf{F} \cdot (\nabla \times \mathbf{G}) = \nabla \cdot (\mathbf{G} \times \mathbf{F}) + (\nabla \times \mathbf{F}) \cdot \mathbf{G}$ we find

$$\delta S = \int d^3r [\frac{\partial s}{\partial f}\delta f + \nabla \cdot (\frac{\partial s}{\partial \nabla f}\delta f) - (\nabla \cdot \frac{\partial s}{\partial \nabla f})\delta f$$
$$+ \frac{\partial s}{\partial \mathbf{g}} \cdot \delta \mathbf{g} + \nabla \cdot (\delta \mathbf{g} \times \frac{\partial s}{\partial \nabla \times \mathbf{g}}) + (\nabla \times \frac{\partial s}{\partial \nabla \times \mathbf{g}}) \cdot \delta \mathbf{g}]$$

And by using the Gauss theorem

$$\delta S = \int d^3r [\frac{\partial s}{\partial f}\delta f - (\nabla \cdot \frac{\partial s}{\partial \nabla f})\delta f + \frac{\partial s}{\partial \mathbf{g}} \cdot \delta \mathbf{g} + (\nabla \times \frac{\partial s}{\partial \nabla \times \mathbf{g}}) \cdot \delta \mathbf{g}]$$
$$+ \int d\mathbf{a} \cdot (\frac{\partial s}{\partial \nabla f}\delta f + \delta \mathbf{g} \times \frac{\partial s}{\partial \nabla \times \mathbf{g}})$$

where $d\mathbf{a} = \hat{\mathbf{n}}\, da$ is a surface differential. Now since the variations are arbitrary, in order to have $\delta S = 0$, the following equations and boundary conditions must hold:

$$\frac{\partial s}{\partial f} - \nabla \cdot \frac{\partial s}{\partial \nabla f} = 0, \quad \hat{\mathbf{n}} \cdot \frac{\partial s}{\partial \nabla f} = 0$$
$$\frac{\partial s}{\partial \mathbf{g}} + \nabla \times \frac{\partial s}{\partial \nabla \times \mathbf{g}} = 0, \quad \hat{\mathbf{n}} \times \frac{\partial s}{\partial \nabla \times \mathbf{g}} = 0$$

Apply these with $S = G$, $s = g$, $f = \psi^*$ and $\mathbf{g} = \mathbf{A}$.