Ginzburg-Landau theory

GL theory is a general phenomenological method for discussing the onset (or not) of various kinds of order in many-body systems. It is particularly useful for consideration of the effects of dimensionality on ordering. The approach is very general and can be applied e.g. to magnetic transitions, order-disorder phenomena in binary alloys, melting of crystals ... However, we shall be primary interested in a specific application, namely superfluidity and superconductivity.

In equilibrium and under homogeneous conditions, the superconducting state of a (3D) metal is believed to be distinguished from the normal by the existence of a finite and uniform (quasi-) expectation value of the so-called "anomalous average"

$$\Psi_{\mathrm{BCS}} \equiv \langle \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle = V^{-1}\sum_{\mathbf{k}}\langle a_{\mathbf{k}\uparrow}a_{-\mathbf{k}\downarrow}\rangle \tag{1}$$

Since Ψ_{BCS} is essentially the wave function of the two-particle state into which Bose condensation of Cooper pairs has taken place,[1] it is intrinsically a complex scalar object. This is also true for superfluid ^{4}He, where Ψ_{He} is simply (proportional to)the condensate wave function.[2] In the following I will simply write Ψ_{BCS} or Ψ_{He} as Ψ, without generally distinguishing between the two cases. Ψ is called the "order parameter" and is the fundamental object of the GL theory. In the following it will be necessary to discuss situations in which the order parameter is spatially and possibly temporally varying. Quite generally, we can define $\Psi(\mathbf{r},t)$ as the (thermal and quantum-mechanical) expectation value of some operator $\hat{\Omega}(\mathbf{r})$:

$$\Psi(\mathbf{r},t) \equiv \mathrm{Tr}\,\hat{\rho}(t)\hat{\Omega}(\mathbf{r}) \tag{2}$$

where $\hat{\rho}(t)$ is the many-body density matrix. (For example, in the BCS case $\hat{\Omega}(\mathbf{r}) \equiv \langle\hat{\psi}_\uparrow(\mathbf{r})\hat{\psi}_\downarrow(\mathbf{r})\rangle$. This definition is very general and in particular does not assume that $\hat{\rho}(t)$ is necessary the equilibrium density matrix $Z^{-1}\exp -\beta\hat{H}$.

We would now like to write the Helmholtz free energy F as a function of $\Psi(\mathbf{r})$: $F \equiv F(T, \{\Psi(\mathbf{r})\})$. Although this was originally done by Ginzburg and Landau in an intuitive fashion, and is so done in most textbooks, it is important to take a moment to discuss the *meaning* of this operation. For illustration let's start with a very simple example: a model of N spins with Ising interactions, so that not only the total magnetization M but the magnetization (spin) of each site commutes with the Hamiltonian and thus the energy eigenstates $|n\rangle$ can be chosen to be simultaneously eigenstates of the total magnetization M with eigenvalue $j\mu$, where μ is the magnetic moment per atom and j is an integer. Consider, first, the problem of determining the equilibrium density matrix of the system at temperature T subject to the condition that the total magnetization M has some prescribed value $M_0 = j\mu$. This problem can be solved by standard textbook methods, with the result that the probability of occurrence p_n of the n-th many-body state is

$$p_n = Z_r^{-1}(M_0, T)\left[\exp -\beta E_n\right]\delta_{M_n,M_0} \tag{3}$$

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[1] See AJL, Quantum Liquids, §2.4

[2] ibid. §2.2

where the restricted partition function $Z_r(M_0, T)$ is given by

$$Z_r(M_0, T) \equiv \sum_n \left[\exp -\beta E_n\right] \delta_{M_n, M_0} \tag{4}$$

The restricted Helmholtz free energy is

$$F(M_0, T) \equiv \langle \hat{H} \rangle (M_0, T) - TS(M_0, T) = -\beta^{-1} \ln Z_r(M_0, T) \tag{5}$$

If we now remove the constraint $M = M_0$ and allow the system to come to equilibrium at temperature T, then of course the density matrix is just $Z^{-1}(T) \exp -\beta\hat{H}$, ($Z(T) \equiv \mathrm{Tr}\, e^{-\beta\hat{H}}$), i.e. the probability of occurrence of state n is simply $Z^{-1} \exp -\beta E_n$, irrespective of its magnetization M_n. So the probability that the system has magnetization M is

$$\begin{aligned} p(M) &= Z^{-1}(T) \sum_n \exp(-\beta E_n)\, \delta_{M_n, M} \\ &\equiv Z^{-1}(T) Z_r(M, T) = \frac{\exp -\beta F(M, T)}{\sum_M \exp -\beta F(M, T)} \end{aligned} \tag{6}$$

(where in the last step we used the fact that $Z(T) \equiv \sum_M Z_r(M, T)$).

Of course, an alternative way of handling the constraint of fixed M is to introduce a Lagrange multiplier, in this case a "magnetic field" $\mathcal{H}$, so that $\hat{H} \to \hat{H} - \mathcal{H}\hat{M}$, and to replace the condition $M = M_0$ by $\langle M \rangle = M_0$. In the thermodynamic limit general theorems of statistical mechanics assure us that the fluctuations of M about M_0 are of order $N^{1/2} \propto MN^{-1/2}$, so the results are the same. However, it is not at all necessary to do this.

It is straightforward to generalize the above considerations to the problem of determining the thermal equilibrium condition subject to the set of constraints

$$M^{(\lambda)} \equiv \mu \sum_i a_{i\lambda} \sigma_{zi} = M_\lambda, \quad a_{i\lambda} = \pm 1, 0 \tag{7}$$

since the $M^{(\lambda)}$ commute with the Hamiltonian and, by virtue of the constraint on the $a_{i\lambda}$, take discrete values $n\mu$. (If we let λ denote a particular site and choose e.g. $a_{i\lambda} = +1$ for sites close to λ and 0 for others, than the physical significance of M_λ is as a "coarse-grained average" of the magnetization in the region of λ). Omitting the intermediate steps, we define the restricted free energy $F(\{M_\lambda\}, T)$ to be

$$F(\{M_\lambda\}, T) \equiv -\beta^{-1} \ln \sum_n \exp -\beta E_n \prod_\lambda \delta_{M_n^{(\lambda)}, M_\lambda} \tag{8}$$

so that the probability of occurrence of the set of values $\{M_\lambda\}$ is

$$p\{M_\lambda\} = Z^{-1} \exp -\beta F\{M_\lambda\}, \quad Z = \sum_{\{M_\lambda\}} \exp -\beta F\{M_\lambda\} \tag{9}$$

Again, it would be possible to handle the constraint $M^{(\lambda)} = M_\lambda$ by introducing a set of Lagrange-multiplier fields $\mathcal{H}_\lambda$: $\hat{H} \to \hat{H} - \sum_\lambda \mathcal{H}_\lambda \hat{M}^{(\lambda)}$. However, note that now the equivalence of this method with the above one holds only to order $k^{-1/2}$, where $k \sim \sum_i |a_{i\lambda}|^2$.

The actual problem of interest differs from the one discussed above in two respects: the order parameter $\Psi(\mathbf{r})$ is a function of a continuous variable and moreover itself takes continuous rather than discrete values, and the corresponding operator $\hat{\Omega}(\mathbf{r})$ in general fails to commute with the Hamiltonian. However, these differences lead mainly to complications of notation rather than substance. We can *very schematically* define

$$F\{\Psi(\mathbf{r}),T\} \equiv -\beta^{-1} \ln \sum_n e^{-\beta E_n} \, \tilde{\delta}\{\langle n|\hat{\Omega}(\mathbf{r})|n\rangle - \Psi(\mathbf{r})\} \tag{10}$$

where the notation $\tilde{\delta}\{\phi(\mathbf{r}) - \chi(\mathbf{r})\}$ is an appropriate generalization of $\prod_\lambda \delta_{M_n^{(\lambda)},M_\lambda}$ to the continuum limit along the lines of the functional-integral approach, which I shall assume exists but will not attempt to write out in detail. Then the probability of configuration $\Psi(\mathbf{r})$ is given by

$$p\{\Psi(\mathbf{r})\} = Z^{-1} \exp -F\{\Psi(\mathbf{r}),T\} \tag{11}$$

where the partition function is now given by the *functional integral*

$$Z \equiv \int \mathcal{D}\Psi(\mathbf{r}) \, \exp -F\{\Psi(\mathbf{r}),T\} \tag{12}$$

As in the previous two examples, it is again possible to treat the constraint of fixed $\Psi(\mathbf{r})$ by introducing a Lagrange multiplier *function* $\lambda(\mathbf{r})$, so that

$$\hat{H} \to \hat{H} - \int \lambda(\mathbf{r})\Psi(\mathbf{r}) \, d\mathbf{r} \tag{13}$$

However, there are two reasons why this is not usually done.The first is that, unlike the first and, to an extent, the second example above, the "field" $\lambda(\mathbf{r})$, which would violate particle number conservation, does not correspond to anything which can be applied physically. The second reason is that the equivalence of the Lagrange-multiplier method to the above one (which results inter alia in eqn. (11)) is valid only to the extent that one can neglect fluctuations of $\Psi(\mathbf{r})$ (or more realistically some weighted average of it) relative to its average ("mean-field") value, and it is precisely in these fluctuations that we are often most interested.

Let's now try to write the free energy as an explicit function of Ψ, assuming for the moment that the latter has no spatial dependence. Let's consider explicitly the BCS (or helium) case. Since in this case a phase rotation of the order parameter merely corresponds to a different choice of overall phase of the 2-particle wave function (1-particle condensate wave function for helium), and the latter has no physical significance, it follows that the free energy must be invariant under such a transformation and thus can be a function only of $\Psi^*\Psi \equiv |\Psi|^2$. If we further make, with GL, the very natural assumption that F is an analytic function[3] of $|\Psi|^2$, then it may be expanded in a power series:

$$F(\Psi, T) = F_0(T) + A(T)|\Psi|^2 + \frac{1}{2}B(T)|\Psi|^4 + \mathcal{O}(|\Psi|^6) \tag{14}$$

(where the 1/2 is introduced for subsequent convenience). Note in particular that there is no term linear (or cubic) in Ψ. Generally speaking, it is sufficient to drop the terms of order $|\Psi|^6$ and higher, and also (for most purposes) to ignore the zero-order term when considering the ordering process itself.

Let us briefly consider the result of minimizing the "uniform" free energy F (eqn. (14)) under the assumption that Ψ is indeed constant in space (the standard "mean-field" approximation). It is clear that if both $A(T)$ and $B(T)$ are positive, the value of Ψ which minimizes (14) is zero, while if $B(T) < 0$ the system is unstable (in the approximation of neglect of the higher-order terms) against formation of arbitrary large values of Ψ. The interesting case, which is believed to be the one relevant to systems which become (or would "like" to become) superconducting is $B(T) > 0$, with $A(T)$ changing sign as a function of temperature. It is usually adequate to set

$$B(T) \equiv \beta > 0 \qquad A(T) \equiv \alpha(T - T_c), \qquad \alpha > 0. \tag{15}$$

Then we have the following results for the "optimal" value of Ψ, i.e. that which minimizes the free energy (14):

$$\Psi(T) = 0, \qquad T > T_c$$
$$\Psi(T) = \big(\alpha(T - T_c)/\beta\big)^{1/2}, \qquad T < T_c$$

The first conclusion should hold rather generically, provided the neglected higher-order terms in $F(\Psi)$ do not lead to an instability. The second is an approximation resulting from the neglect of those higher-order terms and the replacement of $\alpha \equiv dA/dT$ and $B(T)$ by constants; however, microscopic calculations (e.g. that of BCS in the superconducting case) indicate that it is not a bad approximation (within the framework of mean-field-type ideas, of course) even for $T_c - T \sim T_c$.

We now turn to the question of fluctuations of Ψ around its "mean-field" value calculated above. So long as we retain the constraint that Ψ is constant in space, any fluctuations of the magnitude of Ψ will cost an energy proportional to the total volume and will hence be negligible. As to the *overall* phase of Ψ, in the BCS case this is anyway physically meaningless. Thus, to see anything interesting we have to relax the constraint that Ψ is constant in space, and this immediately raises the question of "gradient" or similar energies.

Imagine that we want to redefine the order parameter Ψ so as to take into account possible spatial variation. In any specific case the formal extension of the definition is usually straightforward; e.g. in the BCS case we would write

$$\Psi(\mathbf{r}) \equiv \langle \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r})\rangle = V^{-2}\sum_{\mathbf{k}}\sum_{\mathbf{q}} \langle a_{\mathbf{k}+\mathbf{q}/2,\uparrow} a_{-\mathbf{k}+\mathbf{q}/2,\downarrow}\rangle \exp i\mathbf{q}\mathbf{r} \tag{16}$$

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[3] If we do not make this assumption, then in general we cannot exclude terms of the form (e.g.) const $|\Psi|$ ($\equiv$ const $(|\Psi|^2)^{1/2}$).

(which, unlike the earlier definition, allows Ψ to be a function of $\mathbf{r}$). If the order parameter so defined is varying "sufficiently" slowly in space, the result will look locally much like the uniform case described above. What is "sufficiently" slowly? A *necessary* and, as it turns out, also sufficient condition is that the variation should be small on the length scale of the order of the "structure" of the object defined by Ψ. In the case of BCS theory these objects are Cooper pairs, which have a (nearly temperature-independent) radius $\sim \xi_0 \equiv \hbar v_{\mathrm{F}}/\Delta(0)$, so this criterion gives $|(d\Psi/dx)/\Psi| \ll \xi_0^{-1}$. So suppose $\Psi(x)$ is indeed bending slowly in space.[4] What is the extra free energy cost associated with the bending? It should be a function of $\partial\Psi/\partial x$ and, possibly also Ψ itself; if we assume analyticity, than the lowest order term in the gradient is of the form $|\partial\Psi/\partial x|^2 \times f(|\Psi|^2)$, where f can be expanded in Taylor series and thus, barring pathologies, tends to a constant in the limit $T \to T_c$. Thus, at least near T_c, the bending energy has the simple form

$$F_{\mathrm{bend}} = \gamma \int dx \left|\frac{\partial\Psi}{\partial x}\right|^2 \tag{17}$$

where γ is a constant (which turns out to be related to the superfluid density, see lecture 10). This is the form usually assumed in GL theory; in fact, in the BCS case it can be justified from microscopic theory in this limit (and the coefficient γ calculated). In both cases, the microscopic theory indicates that the coefficient is itself a function of $|\Psi|^2$ and hence of T, but the resulting T-dependence is fairly weak and (17) is often an adequate approximation.[5]

The "bulk" terms in the free energy (i.e. those depending on Ψ itself rather than its gradient) may be expected to have the same form, locally, as in the uniform case, so the total free energy can be expressed as a functional of the order parameter $\Psi(x)$ in the form

$$F(\{\Psi\}, T) = \int \mathcal{F}(\Psi(x), T)\, dx \tag{18}$$

where the free energy density $\mathcal{F}$ is given by

$$\boxed{\mathcal{F}(\Psi(x), T) = \alpha(T - T_c)|\Psi(x)|^2 + \frac{1}{2}\beta|\Psi(x)|^4 + \gamma|\partial\Psi(x)/\partial x|^2} \tag{19}$$

the standard form of the GL free energy function for the translationally-invariant case (in the absence of a magnetic vector potential: cf. below). It is clear from the above formula that we can define a characteristic length $\xi(T)$ by

$$\xi(T) = (\gamma/\alpha|T - T_c|)^{1/2} \tag{20}$$

This is known as the correlation length or healing length[6]: note its $(T-T_c)^{-1/2}$ divergence as $T \to T_c$. The physical significance of this length, in the condensed phase, is that it

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[4] For the moment we will consider only a strictly 1D variation, $\Psi(\mathbf{r}) \equiv \Psi(x)$.

[5] Note that F is actually a sum of two terms, namely $|\partial|\Psi|/\partial x|^2$ and $|\Psi|^2|\partial\phi/\partial x|^2$ where $\psi(r)$ is the phase of $\Psi(x)$; in the more general case the coefficients (γ_{ampl} and γ_{phase}) are not necessary equal.

[6] Or sometimes, rather misleadingly, as the "coherence length".

is a measure of the minimum distance over which one can "bend" the order parameter, either in magnitude or in phase, before the bending energy becomes comparable to the condensation energy (the latter is $-\frac{1}{2}\alpha^2(T-T_c)^2/\beta \sim \alpha(T_c-T)|\Psi_0|^2$, while the bending energy $= \gamma(\partial\Psi/\partial x)^2 \sim \gamma L^{-2}|\Psi_0|^2$, where Ψ_0 is the equilibrium value of the order parameter and L is the characteristic length of bending; they are equal in order of magnitude when $L \sim (\gamma/\alpha(T_c-T))^{1/2} \sim \xi(T)$, as stated). The actual magnitude of $\xi(T)$ must be determined from microscopic theory; in the BCS case it turns out to be of order $\xi_0(1-T/T_c)^{-1/2}$ where $\xi_0 \sim \hbar v_{\mathrm{F}}/\Delta(0)$ is the characteristic "scale of structure". Since $\Delta(T) \sim \Delta(0)(1-T/T_c)^{1/2}$ we can equally well say that $\xi(T)$ is of order $\hbar v_{\mathrm{F}}/\Delta(T)$. We see that our previous general criterion for applicability of the simple GL formulae, namely $|(\partial\Psi/\partial x)/\Psi| \ll \xi_0^{-1}$, is compatible with bending on the scale of $\xi(T)$ if $T \to T_c$.

So far, we considered explicitly only a strictly 1D situation. Obviously, if our system is really 2D or 3D and is *isotropic*, all we have to do is to replace the argument x in $\Psi(x)$ by $\mathbf{r}$ ($\Psi \to \Psi(\mathbf{r})$) and generalize the gradient term in $\mathcal{F}$ to $|\boldsymbol{\nabla}\Psi(\mathbf{r})|^2$. In the case (for example) of a system which is 3D but anisotropic, again we set $\Psi \to \Psi(\mathbf{r})$, but now the bending energy has the form

$$\mathcal{F}_{\mathrm{bend}} = \sum_{i=1}^{3} \gamma_i |\partial\Psi/\partial x_i|^2 \tag{21}$$

where the three γ_i are in general different. We can then define different correlation (healing) lengths for the different axis:

$$\xi_i(T) \equiv (\gamma_i/\alpha|T-T_c|)^{1/2} \tag{22}$$

Note that the more "difficult" the motion is in a given direction, the smaller γ_i and hence the *shorter* the correlation length at fixed T.[7]

A very interesting and common case is where the motion in two directions is essentially continuous, but that in the remaining direction has to be treated in discrete terms. An obvious example are the cuprates, where the 2D motion in a given CuO$_2$ plane can be treated as continuous but the different planes (or at least the different multilayers) must be treated as discrete. In such case we need a different notation: the order parameter must be treated as a function of a continuous in-plane variable $\mathbf{r}$, and a discrete variable n which labels the planes: $\Psi \to \Psi_n(\mathbf{r})$. The bulk terms are sums of continuous analogies to the above one, i.e. (neglecting the Ψ-independent term, etc.)

$$F_{\mathrm{bulk}} = \sum_n \int d\mathbf{r}_\parallel \left\{\alpha(T-T_c)|\Psi_n(\mathbf{r}_\parallel)|^2 + \frac{1}{2}\beta|\Psi_n(\mathbf{r}_\parallel)|^4\right\} \tag{23}$$

The in-plane bending energy is also a sum of terms similar to those described above:

$$F_\parallel = \sum_n \int d\mathbf{r}_\parallel\, \gamma_\parallel |\boldsymbol{\nabla}_\parallel \Psi_n(\mathbf{r}_\parallel)|^2 \tag{24}$$

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[7] E.g. in the cuprate superconductors $\gamma_\perp$ (perpendicular to CuO$_2$ planes) $\ll \gamma_\parallel$.

where the notation "$\|$" indicates the direction(s) parallel to the planes.

What about the "bending" energies in the direction(s) *perpendicular* to the planes? Here we must be more careful. The most natural assumption is that only nearest-neighbor planes are coupled; if in analogy to the bulk case we content ourselves with the lowest-order term allowed by symmetry, it has the following form

$$F_\perp = -\frac{J}{2}\int\sum_{\text{n. n.}}\left(\Psi_i(\mathbf{r}_\|)\Psi_j^*(\mathbf{r}_\|) + \text{c.c.}\right)d\mathbf{r}_\| \tag{25}$$

where J is to a first approximation independent of T. To calculate J for any specific case we need a microscopic model of the interplane contact; e.g. in the BCS case this is provided by the Bardeen-Josephson tunneling model and J turns out to be an effective Josephson coupling constant. There is now an important difference from the continuous case, in the sense that the maximum energy per unit area to "dislocate" one plane relative to its neighbors is finite, namely zJ where z is the number of nearest neighbors (2 in the 2D case). The interesting question is whether or not this energy is greater or smaller than the total condensation energy per unit area of the system in question. Generally speaking, in the case of systems we think of as "quasi-2D" and at temperatures appreciably away from T_c, it will be smaller (this could in fact be taken to be the definition of a "quasi-2D" system). In that case it makes perfect sense to consider possible fluctuations involving the complete dislocation of neighboring planes (though cf. next lecture). However, close to T_c we see that $F_\perp$ scales as $|\Psi|^2$, hence as $T_c - T$, whereas the "bulk" condensation energy is proportional to $|\Psi|^4$, i.e. to $(T_c - T)^2$. Hence sufficiently close to T_c the energy necessary to dislocate neighboring planes relative to one another is large enough to take us out of the condensed phase, and such fluctuations can be neglected. Once this condition is well fulfilled, it is consistent to replace RHS of the expression for $F_\perp$ by a continuum expression, as follows: we have from our original discrete expression

$$F_\perp = -\frac{J}{2}\sum_n\int d\mathbf{r}_\|\left\{\Psi_{n+1}^*(\mathbf{r}_\|)\Psi_n(\mathbf{r}_\|) + \text{c.c.}\right\} \tag{26}$$

Now we subtract from the "bulk" free energy a term of the form

$$J\sum_n\int|\Psi_n|^2\,d\mathbf{r}_\| \equiv \frac{J}{2}\sum_n\int d\mathbf{r}_\|\left\{|\Psi_{n+1}|^2(\mathbf{r}_\|) + |\Psi_n|^2(\mathbf{r}_\|)\right\} \tag{27}$$

and compensate by adding it to $F_\perp$, which then becomes

$$F_\perp = +\frac{J}{2}\int\sum_n|\Psi_{n+1}(\mathbf{r}_\|) - \Psi_n(\mathbf{r}_\|)|^2\,d\mathbf{r}_\| \tag{28}$$

Now, provided that the variation of $\Psi(\mathbf{r}_\|)$ from one plane to the next is small compared to $\Psi(\mathbf{r}_\|)$ itself (which must be true in this limit if we are not to exceed the bulk condensation energy), we can approximate $\Psi_n(\mathbf{r}_\|)$ by a continuous function of the *3D* coordinate $\mathbf{r} \equiv (\mathbf{r}_\|, z)$ and write

$$\Psi_{n+1}(\mathbf{r}_\|) - \Psi_n(\mathbf{r}_\|) \approx a(\partial\Psi(\mathbf{r})/\partial z) \tag{29}$$

(where a is the interplane distance), and the interplane coupling term $F_\perp$ becomes

$$F_\perp = +\frac{Ja^2}{2}\int |\nabla_z \Psi(\mathbf{r})|^2 \, dz d\mathbf{r}_\| \equiv \frac{Ja^2}{2}\int |\nabla_z \Psi(\mathbf{r})|^2 d\mathbf{r} \tag{30}$$

So we have recovered the continuum expression, with the bending coefficient $\gamma_\perp$ identified with $Ja^2/2$. It is clear that the condition for the procedure to be self-consistent is that the "perpendicular" correlation length $\xi_\perp(T)$ calculated in this way should be large compared to the interplane spacing a. The overall upshot of the analysis is that, at least within the framework of mean-field theory, an arbitrary system which undergoes a second-order phase transition always looks "3 dimensional" sufficiently close to T_c (i.e. like a highly anisotropic 3D continuum).

To conclude this lecture, let's write down the equation which determines the *average* value of $\Psi(\mathbf{r})$ in thermal equilibrium in the "mean-field" approximation. By definition, the latter is obtained by setting $\delta F\{\Psi(\mathbf{r})\}/\delta\Psi(\mathbf{r}) = 0$. If no special boundary conditions are imposed on $\Psi(\mathbf{r})$, then it is intuitively obvious that the minimum value of F is achieved by setting $\Psi(\mathbf{r}) = \text{const}$, and the condition $\partial F/\partial\Psi = 0$ then just gives back the results obtained above. If on the other hand physical conditions impose nontrivial boundary conditions on $\Psi(\mathbf{r})$ (e.g. $\Psi(\mathbf{r}) \to 0$ on the interface between the superconductor and a normal metal) then we must include the gradient terms in the minimization. Performing the standard integration by parts, we obtain in the isotropic case

$$\gamma\nabla^2\Psi(\mathbf{r}) - \alpha(T)\Psi(\mathbf{r}) + \beta|\Psi(\mathbf{r})|^2\Psi(\mathbf{r}) = 0 \tag{31}$$

which is the standard form of the GL equation (mean-field equation) for the order parameter $\Psi(\mathbf{r})$ in a neutral system.

One final note: If the system we are discussing is charged and $\Psi(\mathbf{r})$ is the relevant order parameter, as in the case of superconductivity, then it is necessary to modify eqn. (19) for F by the standard minimal-coupling replacement

$$\boldsymbol{\nabla}\Psi(\mathbf{r}) \to \big(\boldsymbol{\nabla} - (2ie/\hbar)\mathbf{A}(\mathbf{r})\big)\Psi(\mathbf{r}) \tag{32}$$

where $\mathbf{A}(\mathbf{r})$ is the electromagnetic vector potential (the factor of 2 arises because $\Psi(\mathbf{r})$ is essentially the center-of-mass wave function of the Cooper *pair*). Also, the free energy then contains an additional, purely electromagnetic term $\mu_0^{-1}\int(\boldsymbol{\nabla}\times\mathbf{A}(\mathbf{r}))^2\, d\mathbf{r}$. With these modifications, the condition $\delta F/\delta\Psi = 0$ now leads to a modified form of eqn. (31) in which

$$\nabla^2\Psi(\mathbf{r}) \to \big(\boldsymbol{\nabla} - (2ie/\hbar)\mathbf{A}(\mathbf{r})\big)^2\Psi(\mathbf{r}) \tag{33}$$

while the condition $\delta F/\delta\mathbf{A}$ leads to Maxwell's equation $\nabla^2\mathbf{A}(\mathbf{r}) = -\mu_0^{-1}\mathbf{j}(\mathbf{r})$ with the electromagnetic current $\mathbf{j}(\mathbf{r})$ given by the expression

$$\mathbf{j}(\mathbf{r}) = i\gamma\,\frac{2e}{\hbar}\,\big(\Psi^*(\mathbf{r})(\boldsymbol{\nabla} - \frac{2ie}{\hbar}\mathbf{A}(\mathbf{r}))\Psi(\mathbf{r}) - \text{c.c.}\big) \tag{34}$$

We shall mostly not need this generalization, as it turns out that in most quasi-2D situations the electromagnetic coupling is of minor importance (see lecture 13).