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Ginzburg-Landau Theory of Phase Transitions

1 Phase Transitions

A phase transition is said to happen when a system changes its phase. The physical property that characterizes the difference between two phases is known as an order parameter. Two familiar examples of phase transitions are transitions from ice to water and paramagnet to ferromagnet. There are two types of phase transitions: first order and second order. The first order phase transitions are characterized by a discontinuous change in thermodynamic variables. An example of this would be transition from solid to liquid in crystals. In this case, the order parameter would be the Fourier component of charge density.

In the second order phase transitions, the thermodynamic variables change continuously, but a kink occurs at the transition point. The absence of discontinuity in the order parameter implies that two phases can coexist at the point of transition. In the phase diagram, this point is called a critical point. A second order liquid-gas transition occurs in water at around 647 K and 22 MPa.

Another example of second order phase transition is given by ferromagnets. At low temperature, the system has some magnetisation M along some axis even at zero external field. The direction of the magnetization can be changed discontinuously by applying some non-zero external field in the direction opposite to the magnetization. If the temperature is increased, the fluctuation of spins will increase and the magnitude of magnetization decreases. As the temperature is further increased to some critical temperature T_C , the magnetization vanishes and the second-order transition occurs. This temperature is called the critical point of the system in $H - T$ plane.

When a system undergoes a phase transition, it usually loses some symmetry. For

example, in the cases of paramagnet-ferromagnet and liquid-solid transitions, the systems lose rotational symmetry. We know from our recent discussions in class that spontaneous symmetry breaking requires existence of massless boson. The bosons are magnons in ferromagnets and phonons in crystals.

2 Critical Exponents

It is experimentally found that for temperature below T_C the magnetization $|M| \propto (T_C - T)^\beta$ with $\beta \approx 0.37$ for three dimensional ferromagnets. Similar behaviour is found in other thermodynamic quantities near T_C . The magnetization goes to zero with the relation $M \propto H^{-\delta}$ as $H \rightarrow 0$. The susceptibility diverges as $\chi \propto (T - T_C)^\gamma$ at the critical point.

3 Ginzburg-Landau Theory

In general, to study various properties of a system, we need to calculate the partition function $Z = \text{tr} \exp(-\mathcal{H}/kT)$, where \mathcal{H} , k and T are the Hamiltonian, Boltzmann constant and temperature, respectively. With the partition function we can calculate other thermodynamic quantities; for example, magnetization at constant volume and magnetic field $M = kT \frac{\partial Z}{\partial B}$. Computing the infinite sum in calculating the trace is a formidable task for a non-trivial system, but an approximation by a finite sum also brings a subtle but devastating problem. The term $\exp(-\mathcal{H}/kT)$ is assumed to be a smooth function of its variables, except possibly at the extreme values of its variables. Then finite sum of such terms would also be a smooth function. Hence, such an approximation cannot describe phase transitions and critical phenomena. Obviously, infinite sums of smooth functions in some variables need not be analytic in those variables and if we could calculate the infinite sum, we could calculate various properties of the system easily.

Ginzburg and Landau got around the problem of having to calculate the infinite sum with a brilliant insight. They argued that the form of the free energy of a system in terms of its order parameter could be guessed from the symmetries the system obeyed. Let ψ be the

order parameter, which is in general a complex field. Then, for a homogenous system, the free energy can be written as

$$F(T) = F_0 + a(T)|\psi|^2 + \frac{1}{2}b(T)|\psi|^4 + \dots,$$

where F_0 is a constant and a , b are parameters that depend on temperature T . If the system is inhomogenous, we need to also include the term $\frac{\hbar^2}{2m}|\nabla\psi|^2$, where m is the effective mass of the particle comprising the system. In the case of electrons in a magnetic field, we need to include the term $\frac{\hbar^2}{2m}|\left(\frac{1}{i}\nabla + 2eA\right)\psi|^2$, where e is the charge of an electron.

Usually, we truncate the series after the term $|\psi|^4$. Then $b(T)$ must always be positive since, otherwise, there would be no minimum of the free energy. When we plot $F(T) - F_0$, we see that there are two possible possibilities. In the case of $a(T) > 0$, the curve has one minimum at $\psi = 0$. However, if $a(T) < 0$, there are minima whenever $|\psi|^2 = -a(T)/b(T)$. Ginzburg and Landau assumed that $a(T) > 0$ above the transition temperature T_c . In this case there is a minimum when the order parameter vanishes. But if $a(T)$ decreases as T decreases and becomes negative below T_c , then minimum of the free energy is at $\psi \neq 0$. Thus, this theory describes systems that undergo phase transitions.

4 Ginzburg-Landau Theory of Ferromagnetism

In the case of a ferromagnet, the order parameter is the magnetization M . As the direction of magnetization “up” or “down” does not make any difference to the free energy, we can write down free energy as prescribed by Ginzburg and Landau:

$$F = F_0 + a(T)M^2 + \frac{1}{2}b(T)M^4.$$

Let b be a constant. To facilitate the change of sign in $a(T)$ at T_c , let us assume $a(T) = a_0(T - T_c)$, where a_0 is a positive constant. To find the ground state, we need to minimize the free energy with respect to M . This gives us the condition

$$2M[a_0(T - T_c) + bM^2] = 0.$$

This implies either $M = 0$ or $M = \pm[\frac{a_0(T_c - T)}{b}]^{\frac{1}{2}}$. However, the second condition is valid only when $T < T_c$, since we cannot take the square root of a negative number. Thus, magnetization is zero for $T \geq 0$ and it is non-zero for $T < T_c$ and is proportional to $(T_c - T)^{\frac{1}{2}}$.

5 Ginzburg-Landau Theory of Superconductivity

Ginzburg and Landau assumed that a superconducting state is characterized by a complex order parameter $\psi = |\psi|e^{i\theta}$. Then free energy density can be written as

$$f_s(T) = f_n(T) + a_0(T - T_c)|\psi|^2 + \frac{b}{2}|\psi|^4,$$

where $f_s(T)$ and $f_n(T)$ are the superconducting and normal state free energy densities, respectively. An analysis similar to above case of ferromagnetism will show the free energy density has a minimum at $|\psi| = 0$ when $T > T_c$. Below T_c we will find the minima whenever $|\psi| = (\frac{a_0}{b})^{\frac{1}{2}}(T_c - T)^{\frac{1}{2}}$. This implies that there are infinite set of minima corresponding to all possible values of complex phase θ .

We can also find the minimum value of the free energy density, which corresponds to the condensation energy of the superconductor:

$$f_s(T) - f_n(T) = -\frac{a_0^2(T - T_c)^2}{2b} = -\mu_0 \frac{H_c^2}{2}.$$

Hence, the critical field near T_c above which superconductivity is destroyed is given by

$$H_c = \frac{a_0}{(\mu_0 b)^{\frac{1}{2}}}(T_c - T).$$

From the experiments, it turns out that electrons in the superconducting state are not distributed homogeneously inside the sample. So let us consider the expansion of the free energy density in an inhomogeneous system

$$f_s(T) = f_n(T) + \frac{\hbar^2}{2m}|\nabla\psi|^2 + a(T)|\psi|^2 + \frac{b}{2}|\psi|^4.$$

Here we have suppressed the r dependence of $\psi(r)$. To find ψ corresponding to the minimum, we must minimize the total free energy of the system

$$F_s(T) = F_n(T) + \int \left(\frac{\hbar^2}{2m}|\nabla\psi|^2 + a(T)|\psi|^2 + \frac{b}{2}|\psi|^4 \right) d^3r.$$

Minimization of F_s with respect to ψ and ψ^* yields the condition

$$-\frac{\hbar^2}{2m}\nabla^2\psi + a\psi + b\psi|\psi^2| = 0.$$

For simplicity, we consider a one dimensional interface between a normal metal and a superconductor. Let us assume the interface is along x direction, i.e. for $x < 0$ we find normal metal and for $x > 0$ we find superconductor. Then the solution of previous equation is given by

$$\psi(x) = \psi_0 \tanh\left(\frac{x}{\sqrt{2}\xi(T)}\right),$$

where ψ_0 is the value of the order parameter in the bulk far from the surface and ξ is the coherence length defined by $\xi = \left(\frac{\hbar^2}{2m|a(T)|}\right)^{\frac{1}{2}}$. Since ξ is in the denominator of the argument of the function \tanh , it is a measure of the distance from the surface over which the order parameter has recovered back to nearly its bulk value. Using the relation $a = a_0(T - T_c)$, we can rewrite $\xi(T) = \xi(0)|t|^{-\frac{1}{2}}$, where $t = \frac{T-T_c}{T_c}$ is called the reduced temperature. We can see that $\xi(T)$ diverges at the critical temperature T_c with a critical exponent of $\frac{1}{2}$.

We can study the behaviour of a superconductor in a magnetic field by considering the following expansion for free energy density

$$f_s(T) = f_n(T) + \frac{\hbar^2}{2m} \left| \left(\frac{\hbar}{i} + 2eA \right) \psi \right|^2 + a(T)|\psi| + \frac{b}{2}|\psi|^4 + \frac{1}{2\mu_0}B^2,$$

where A is the vector potential such that $B = \nabla \times A$. The total energy is given by

$$F_s(T) = F_n(T) + \int \left(\frac{\hbar^2}{2m} \left| \left(\frac{\hbar}{i} + 2eA \right) \psi \right|^2 + a(T)|\psi| + \frac{b}{2}|\psi|^4 + \frac{1}{2\mu_0}B^2 \right) d^3r$$

Minimizing the total energy with respect to A , we find

$$\nabla \times B = \mu_0 j$$

with

$$j = -\frac{2ehi}{2m} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{(2e)^2}{m} |\psi|^2 A.$$

Now consider the superconductor under a very weak field. When the field is zero we already know that $\psi \approx \psi_0$ in the bulk of the superconductor. So in the case of weak field we can keep only the leading term such that

$$j = -\frac{(2e)^2}{m} \psi_0^2 A.$$

Taking the cross product, we get,

$$\nabla \times \nabla \times B = -\frac{\mu_0(2e)^2}{m}\psi_0^2 B = -\frac{1}{\lambda^2}B,$$

where $\lambda = \left(\frac{m}{4\mu_0 e^2 \psi_0^2}\right)$ is defined as the penetration depth. The purpose of this naming becomes clear if we consider a field $B = (0, 0, B_z(x))$. Then the solution of the previous equation is $B = B_0 e^{(-x/\lambda)}$. Thus the penetration depth defines the distance inside the surface of the superconductor beyond which the external magnetic field is screened out to zero. This screening is verified experimentally.

6 Conclusions

A phase transition is said to happen when a system changes its phase. Two examples of this phenomena are transition from paramagnet to ferromagnet and normal metal to superconductor. Ginzburg and Landau had a brilliant insight to express the free energy in terms of the order parameter. We can then study various properties of the system by minimizing the free energy and solving the resulting equations. The Ginzburg-Landau theory is able to describe many macroscopic properties of systems that undergo phase transitions; however, this theory does not give a microscopic explanation.

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