**LECTURE 19**

First and Second Order Phase Transitions

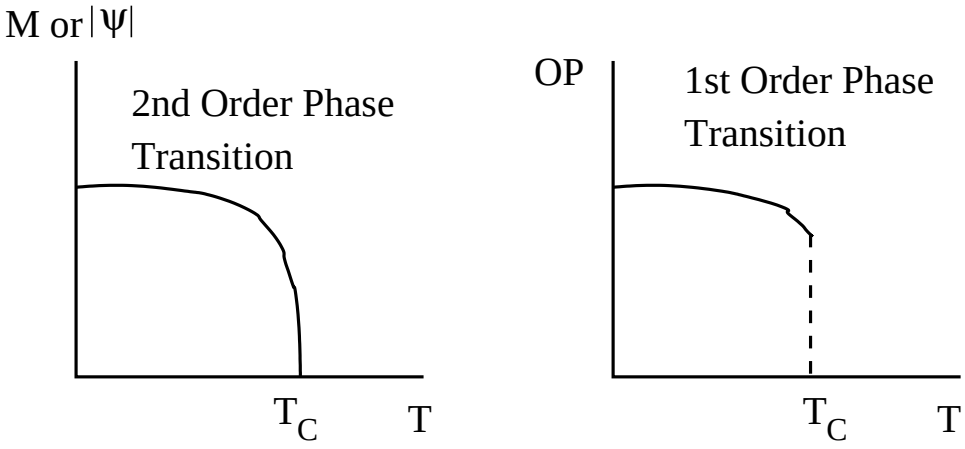
Phase transitions are often associated with ordering. For example the molecules in water are disordered whereas they are ordered in ice. This is a special case of a liquid–to–solid phase transition. Bose condensation is another example of a phase transition; the bosons are not coherent above $T_C$ but a macroscopic fraction of them can be described by a coherent wavefunction $\psi$ below $T_C$. There are 2 basic types of phase transitions: first order and second order. Water–to–ice (or liquid–to–crystalline solid) is an example of a first order phase transition. Typically a first order phase transition is associated with a discontinuity $\Delta S$ in the entropy. The entropy of the liquid $S_\ell$ is greater than the entropy of the solid $S_s$ and $\Delta S = S_\ell - S_s$. The latent heat $L$ is given by

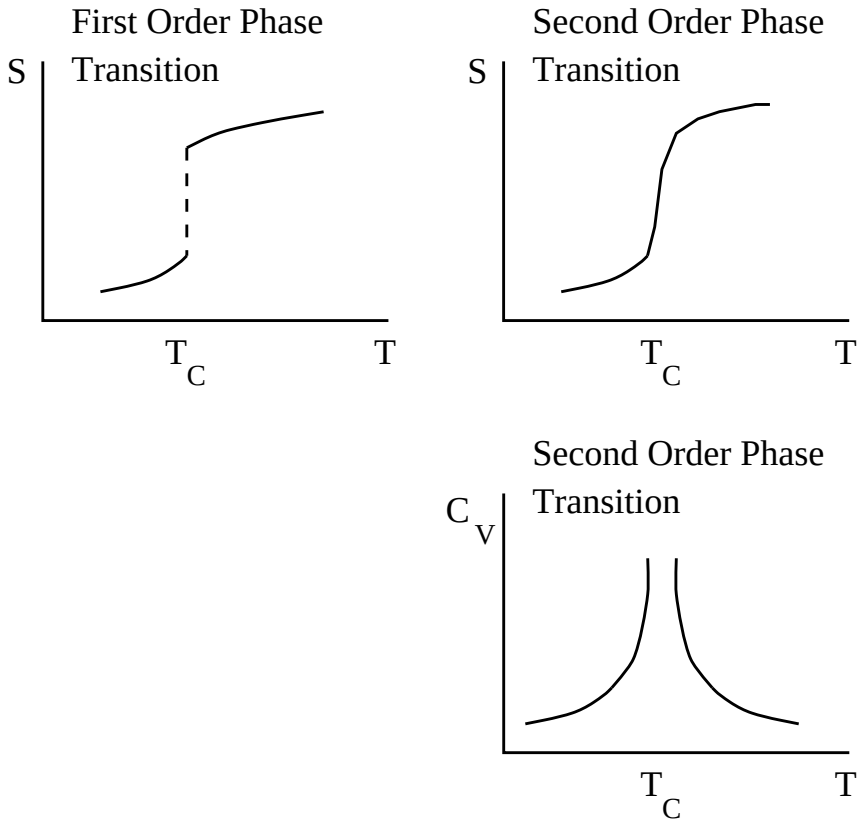
$$L = T\Delta S \tag{1}$$

To understand latent heat, suppose we add heat to a block of ice at a constant rate. Its temperature increases steadily until we reach 0 C, where the temperature stays put until the ice is all melted. All the heat we put in at 0 C goes into melting the ice; this heat is the latent heat of transformation. First order phase transitions are also often associated with sudden volume changes; ice expands relative to the water it came from. This is unusual; most solids take up less space than their liquid counterparts.

We often associate an order parameter with a phase transition. In a liquid the atoms or molecules are disordered in their arrangement, but at the transition, they suddenly become ordered. Thus a first order phase transition is associated with a discontinous jump in the order parameter.

The other type of phase transition is a second order phase transition. Bose condensation is an example of a second order phase transition. A second order phase transition does not have any latent heat associated with it; the entropy is continuous at $T_C$. In a second order phase transition the order parameter grows continuously from zero as the temperature drops below $T_C$. For Bose condensation the order parameter is $\psi$; $\psi = 0$ for $T > T_C$ and $|\psi|$ grows continuously as $T$ decreases below $T_C$.

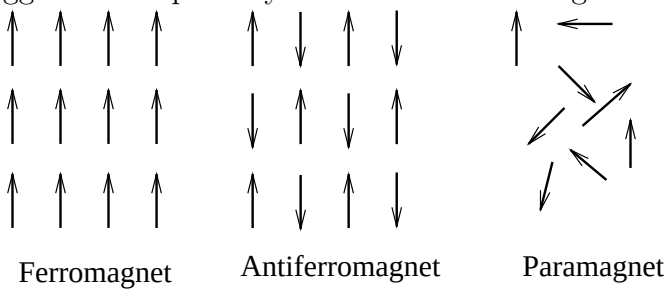





Another example of a second order phase transition is the paramagnetic to ferromagnetic phase transition. (Ferromagnets are bar magnets and can be found on refrigerator doors holding up notes.) We have discussed how the electrons in atoms have magnetic moments associated with them due to their spin and orbital angular momenta. When the atoms make up a solid, they can give the solid magnetic properties. If the magnetic moments are not pointing in any particular direction but can be aligned by an external magnetic field $H_{\rm ext}$, then the system is paramagnetic with the magnetization $M = 0$. If the magnetic moments are lined up and are pointing in the same direction even when $H_{\rm ext} = 0$, then the system is ferromagnetic with a net magnetization $M_z \neq 0$. (I'm calling $\hat{z}$ the direction of the magnetization.) A system at high temperatures can be in the paramagnetic state and can then undergo a second order phase transition into a ferromagnetic state at some temperature $T_C$. The order parameter is the magnetization $M_z$. It increases continuously from zero as $T$ drops below $T_C$. One signature of the second order phase transition is a susceptibility $\chi(T)$ which diverges at $T = T_C$. Recall that $M = \chi H$. The susceptibility tells us how easy it is for the spins to respond to a magnetic field. $\chi(T)$ diverges as one approaches $T_C$ from high or low temperatures.

As long as we're on the topic of magnetism, let me just mention one other kind of magnetic state, and that is the antiferromagnet. In an antiferromagnet the spins alternate in space: up, down, up, down, etc. The net magnetization is zero but the staggered magnetization, where we just look at every other spin, say, is not zero. This

staggered magnetization is the order parameter. Like the ferromagnet, there is a second order phase transition from a paramagnet to an antiferromagnet. If you could put on a staggered magnetic field that alternated direction from site to site, you could measure a staggered susceptibility and this would diverge at $T_C$.




Broken Symmetry

Reference: P. W. Anderson, *Basic Notions of Condensed Matter Physics*, Addison–Wesley (1984), chapter 2.

There is one further concept that is associated with phase transitions and that is the concept of broken symmetry. Broken symmetry occurs when the ordered ground state does not have the full symmetry of the Hamiltonian. Recall that the symmetries of a Hamiltonian are associated with the operators that commute with the Hamiltonian. For example a homogeneous isotropic liquid has translational invariance; move all the atoms by the same amount and the liquid looks the same. The Hamiltonian describing this system is also invariant under translation. But once the system forms a crystal where the atoms or molecules sit on a periodic lattice, the translational invariance is broken and the ground state no longer has the full symmetry of the Hamiltonian. The Hamiltonian doesn't change; it still has translational symmetry, but the system it describes no longer has translation symmetry.

We can make this a bit more formal. Recall from that we said that if the Hamiltonian has translational symmetry, momentum is a good quantum number. States can be labelled by any value of the momentum. But in the crystal which is periodic and has discrete translational symmetry, the eigenstates are labelled by discrete values of the momentum. We saw an example of this when we solved for the eigenstates of free particle system with periodic boundary conditions and found that only discrete values of the momentum were allowed.

Notice that this broken symmetry has a certain rigidity. If you push on one corner of the crystal, all the other particles move with it in such a way as to maintain their spatial relation with the corner that you are moving. True broken symmetry is associated with some type of rigidity. P. W. Anderson calls this generalized rigidity. (Photons in a laser don't have rigidity.)

Another example is the paramagnetic to antiferromagnetic transition. The Hamiltonian describing the spins and their interactions with one another is invariant under rotations in spin space. This means that we expect its eigenstates to have good total

spin quantum numbers $S$ and $S_z$.

$$H = J \sum_{i>j} \vec{S}_i \cdot \vec{S}_j \tag{2}$$

where the exchange constant $J > 0$. The paramagnet has the symmetry of the Hamiltonian. In other words if you rotate all the spins in a paramagnet by the same amount, the paramagnet will look the same. But if you rotate an antiferromagnet by an arbitrary angle, it looks different. So the antiferromagnet is a broken symmetry state. By this same argument, a ferromagnet is a broken symmetry state and is often cited as an example of broken symmetry. But technically speaking, it is not a broken symmetry state because a ferromagnet is an eigenstate of the Hamiltonian. It can be labelled by its total spin $S$ and by $S_z$. On the other hand an antiferromagnet does not have a good spin quantum number $S$. The true ground state is a singlet with $S = 0$.

For the case of Bose condensation, the Bose condensed state is described by a wavefunction or order parameter $\psi = |\psi|e^{i\phi}$. The broken symmetry is gauge symmetry by which we mean that everywhere in the system the phase is $\phi$. This is what gives the state macroscopic phase coherence. Note that this value of $\phi$ may fluctuate in time, but at any given time, it is the same everywhere.

When a continuous symmetry such as translation or rotation is broken, low energy excitations called Goldstone modes result. These low energy excitations are collective modes that involve perturbations related to the symmetry that was broken. Collective modes involve correlated motion among a large number of atoms or spins or whatever. For example, when translational symmetry is broken and a crystal results, small translations of the atoms back and forth result in lattice vibrations. These vibrations are the Goldstone modes and the Goldstone bosons are phonons. For an antiferromagnet where rotational symmetry is broken, the Goldstone modes are spin waves and the Goldstone bosons are magnons.

Broken symmetry is a deep and far ranging concept that applies to a wide variety of phenomena. Not only does it apply to phase transitions such as those involving Bose condensation, superconductivity, magnetism, and crystallization, but it also is important in understanding the Higgs mechanism in particle physics, and the formation of matter from energy in the early stages of the universe. Phase transitions have also been proposed to describe the origin of the universe: some think the big bang was a phase transition that involved symmetry breaking.

Ginzburg–Landau Free Energy

There is a very useful way to describe second order phase transitions using the Ginzburg–Landau free energy. Let's suppose we want to describe a second order phase transition where the order parameter is denoted by $\psi$. (We could just as easily use $M$ if we were describing a magnetic transition.) We can write down a free energy in terms of $\psi$ to describe the thermodynamics of the transition. Near the transition $|\psi|$ is small, so we can expand the free energy functional $F$ in powers of $|\psi|$. We stop at fourth order. We only have even powers of $|\psi|$ because $F$ must be invariant under the transformation

$\psi \to \psi e^{is}$ where $s$ is a constant phase factor (or under the transformation $M_z \to -M_z$). Besides a cubic term $|\psi|^3$ would give a first order transition. So we can write

$$F = F_n + \int \left[ \frac{\hbar^2}{2m^*} |\nabla \psi|^2 + a|\psi|^2 + \frac{1}{2} b|\psi|^4 \right] dV \tag{3}$$

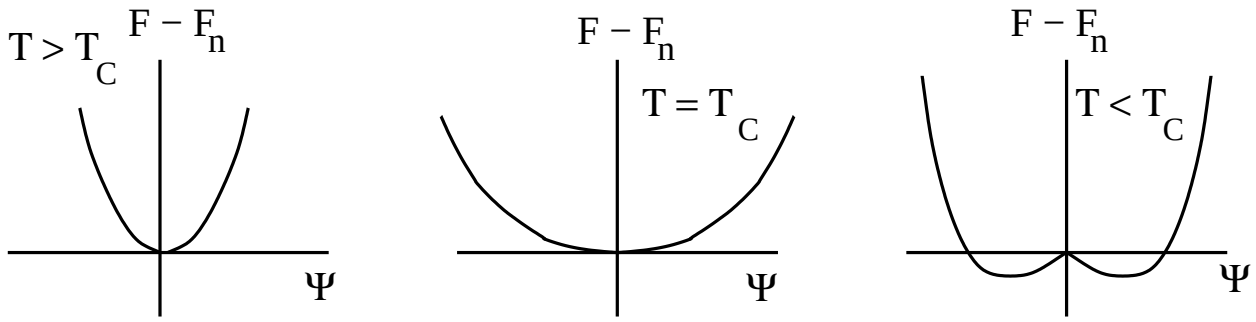
where $V$ is the volume and $F_n$ is the free energy of the normal state or high temperature state, e.g., the normal metallic state for a superconductor, the normal liquid helium state, or the paramagnetic state. $a$ and $b$ are coefficients. We have included a gradient term $|\nabla\psi|^2$. This tells us that the energy of the system increases if the order parameter varies in space. If it varies slowly so that there are only long wavelength fluctuations, then we can just keep the lowest order gradient terms. Let's assume the order parameter is uniform in space and get rid of this term entirely. This is fine for an isotropic homogeneous superconductor with no external field. The energy is lower that way and it makes life simpler. Now we just have a quartic polynomial in $|\psi|$. Because $|\psi|$ is independent of coordinates, we can pull it out of the volume integral: $\int |\psi|^2 dV = |\psi|^2 V$. Then we have

$$F = F_n + aV|\psi|^2 + \frac{1}{2} bV|\psi|^4 \tag{4}$$

The coefficient $a$ is a function of temperature

$$a = \alpha(T - T_C) \qquad \alpha > 0 \tag{5}$$

Thus $a > 0$ for $T > T_C$ and $a < 0$ for $T < T_C$.




(The $\psi$ axis should really be the complex $\psi$ plane if $\psi$ is the complex order parameter for a superfluid or a superconductor. If we had a complex $\psi$ plane, then below $T_C$, $F(\psi)$ would have the shape of a Mexican hat or the bottom of a wine bottle.) For $T > T_C$, the equilibrium value of $|\psi| = 0$. For $T < T_C$, the equilibrium value of $|\psi|^2$ is given by

$$\frac{\partial F}{\partial(|\psi|^2)} = 0 \quad \Longrightarrow \quad |\psi|^2 = -\frac{a}{b} = \frac{\alpha(T_C - T)}{b} \qquad T < T_C \tag{6}$$

For a superconductor $|\psi|^2$ represents the density of superconducting electrons; for a superfluid or Bose condensate, it represents the condensate fraction. Notice that $|\psi|^2$

goes to zero linearly as the temperature approaches $T_C$ from below. Substituting (6) back into equation (4) yields the value of the free energy $F_s$ in the ordered state. The difference in the free energies of the normal and ordered states is

$$F_s - F_n = -\frac{a^2 V}{2b} = -V\left(\frac{\alpha^2}{2b}\right)(T_C - T)^2 \tag{7}$$

Using $C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V$, we find that at $T = T_C$ there is a jump in the specific heat given by

$$C_s - C_n = V\frac{\alpha^2 T_C}{b} \tag{8}$$