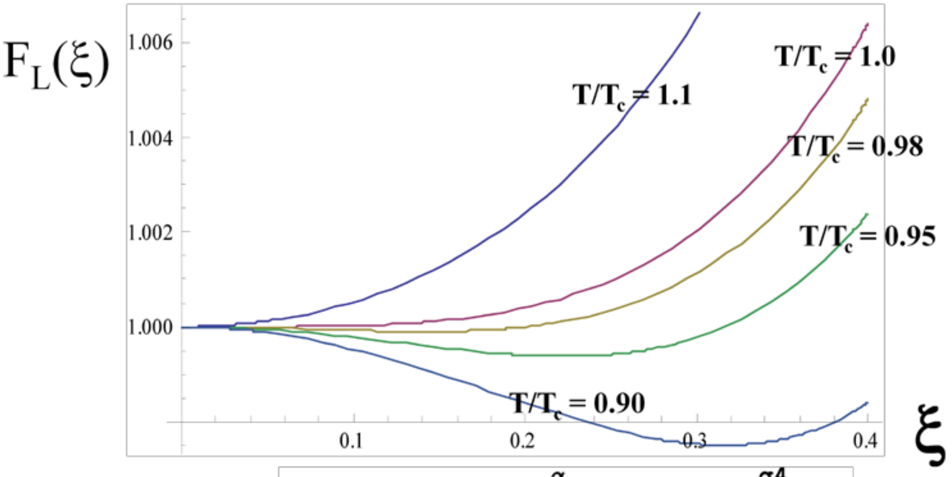
Lecture 28

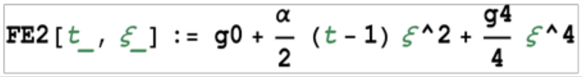
Physics 404

The Landau theory of phase transitions is a very general treatment of first and second order phase transitions. It posits the existence of an order parameter that is non-zero in the "ordered state" and zero in the "disordered state." Examples of order parameters include the magnetization (magnetic moment per unit volume) in the ferromagnetic state, superfluid density in the superconducting and superfluid states, electric polarization in the ferroelectric state, etc. Landau proposed that the free energy of such systems can be expanded as a power series in the order parameter, in the absence of an external field, and for temperatures near the transition temperature, as; $F_L(\xi,\tau) = g_0(\tau) + \frac{1}{2}g_2(\tau)\xi^2 + \frac{1}{4}g_4(\tau)\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \cdots$, where the temperature dependent coefficients will be given below. This expansion converges quickly for $|\xi| \ll 1$.

The coefficient $g_0(\tau)$ describes the free energy versus temperature for the disordered state. The question is: can the system lower its free energy by developing an ordered phase, or not? To describe a second order transition to an ordered phase, Landau proposed to simply make the factor $g_2(\tau)$ change sign at a critical temperature τ_c as $g_2(\tau) = \alpha(\tau - \tau_c)$, with $g_4(\tau) = g_4$ and α being positive constants. Now take the derivative of the Landau free energy with respect to the order parameter, and keep terms to 4th order: $\frac{\partial F_L(\xi,\tau)}{\partial \xi} = g_2(\tau)\xi + g_4\xi^3 = 0$. Setting this equal to zero leads to an equation for the equilibrium value of the order parameter that minimizes the free energy: $\xi_0(\alpha(\tau-\tau_c) + g_4\xi_0^2) = 0$. There are two solutions: $\xi_0 = 0$ and $\xi_0^2 = \frac{\alpha(\tau_c-\tau)}{g_4}$. The second solution makes sense only if $\tau < \tau_c$ since otherwise the order parameter would be an imaginary number. Below τ_c the order parameter has a non-zero equilibrium value, thus describing the ordered phase. This can be seen by going back to the free energy and substituting in the second solution: $F_L(\xi,\tau) \approx g_0(\tau) - \frac{\alpha^2}{2\,g_4}(\tau-\tau_c)^2$, valid for $\tau < \tau_c$. This shows that the free energy of the ordered phase decreases below that of the disordered phase for temperatures below τ_c. The slope of the free energy versus temperature is proportional to the entropy, and the entropy of the two phases are equal at τ_c, so there is no latent heat at the transition. The figures below show the free energy as a function of the order parameter value at various temperatures, and also show the value of the order parameter that minimizes the free energy at each temperature.

Landau Theory of a Second Order Phase Transition





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FE2[t_, ξ_] := g0 + α/2 (t - 1) ξ^2 + g4/4 ξ^4
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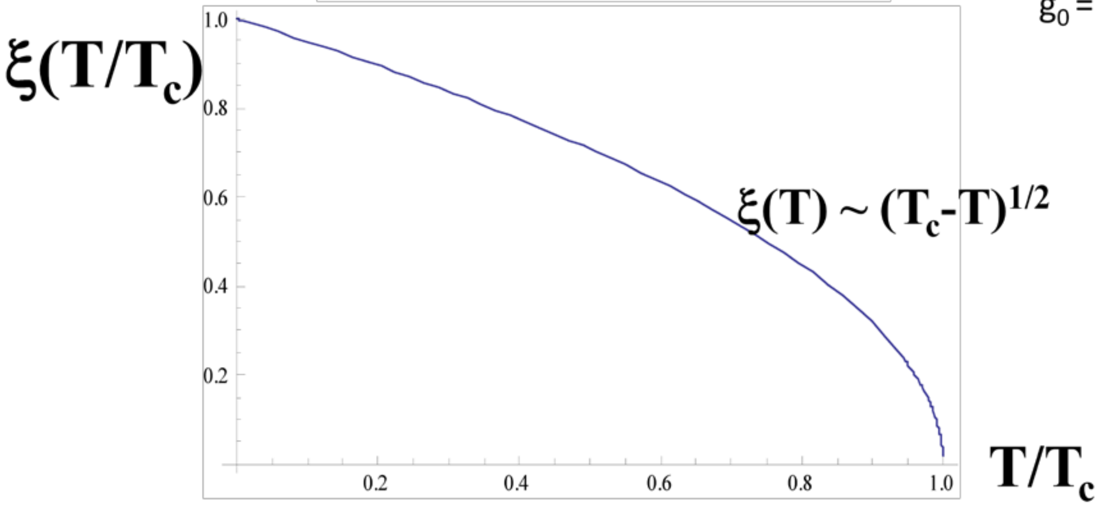
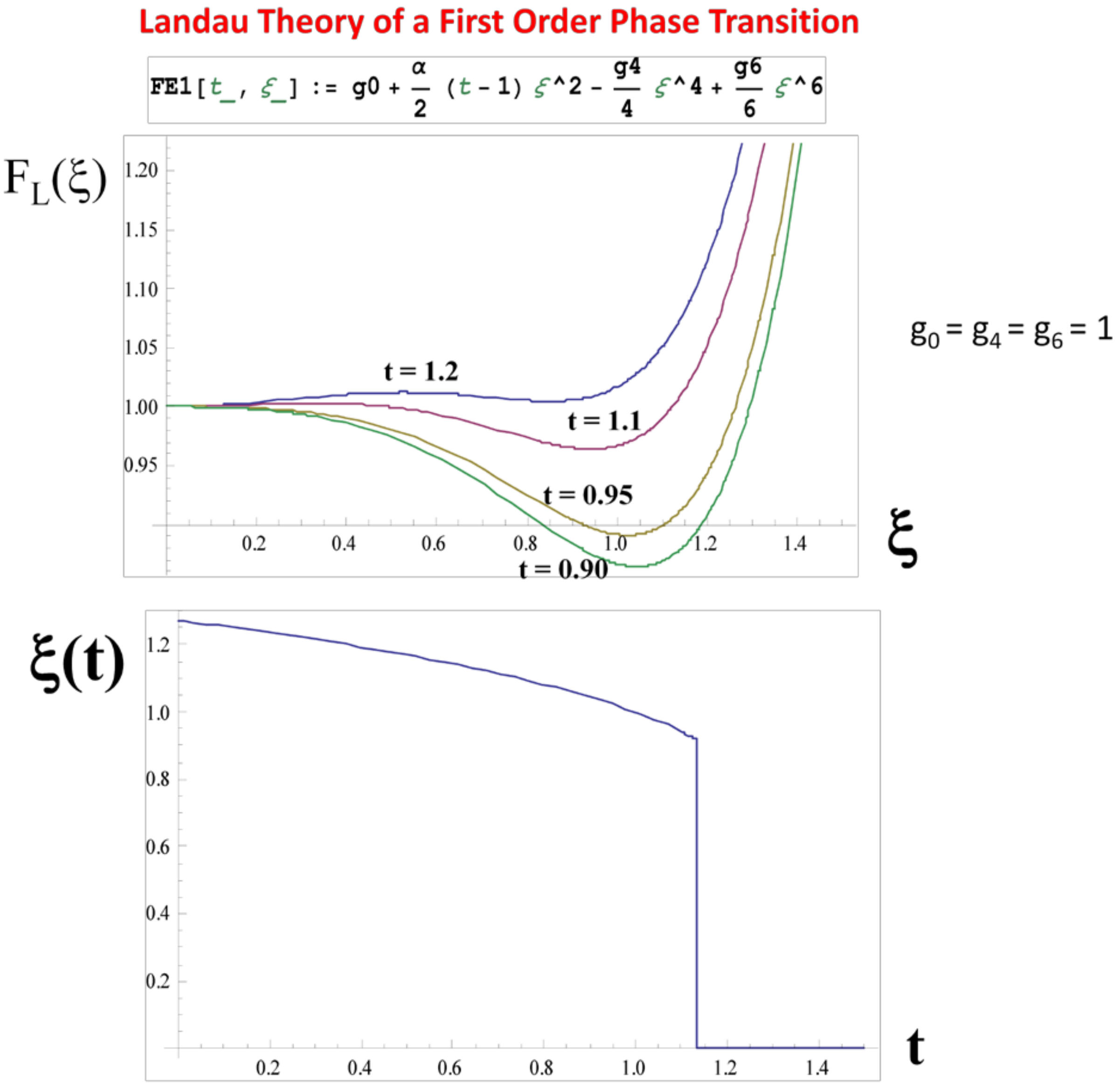
$g_0 = g_4 = 1$



The order parameter is predicted to show a square-root temperature dependence near τ_c: $\xi_0 \sim \sqrt{\tau_c - \tau}$, which is consistent with experiments on many 2nd order phase transitions, including those on ferromagnets, superconductors, superfluids, etc.

The Landau theory can also describe first order phase transitions by simply changing the sign of the 4th order term and retaining a positive 6th order term: $F_L(\xi,\tau) = g_0(\tau) + \frac{\alpha}{2}(\tau - \tau_c)\xi^2 - \frac{1}{4}g_4(\tau)\xi^4 + \frac{1}{6}g_6(\tau)\xi^6 + \cdots$. Minimizing the free energy with respect to variations in the order parameter value leads to a quartic equation that yields a phase transition at a temperature τ_0. The difference from the second order case is that the order parameter does not increase continuously from zero, but in fact appears discontinuously, as shown in the figure below. There is a latent heat associated with this phase transition. An example order parameter is the difference in density of the liquid and vapor phases, $\rho_{liquid} - \rho_{vapor}$. Note that this order parameter goes to zero at the critical point in the phase diagram.



Landau Theory of a First Order Phase Transition

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FE1[t_, ξ_] := g0 + α/2 (t - 1) ξ^2 - g4/4 ξ^4 + g6/6 ξ^6
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In general order parameters do not have to be real numbers. They can be complex numbers, vectors, tensors, etc. Nature has developed many subtle types of order that are described by these more complicated order parameters, and there associated phase transitions.

We next briefly discussed kinetic theory, which is the classical approach to understanding thermodynamics starting from the dynamics of individual molecules. Following the first few pages of Chapter 14, we examined the collision of a single molecule with a wall of a container, which is the elementary process that gives rise to pressure. By proposing a distribution function for the velocities of the molecules we were able to derive the ideal gas law $PV = N\tau$, using only the concept of equipartition of energy.

The velocity distribution function was calculated by 'deconstructing' the quantum solution for the ideal gas from Chapter 6. By converting from quantum number 'n' to classical speed 'v' we were able to calculate the distribution of speeds for molecules of mass M at temperature τ as $P(v) = 4\pi\left(\frac{M}{2\pi\tau}\right)^{3/2} v^2 e^{-Mv^2/2\tau}$, which is called the Maxwell velocity distribution. There are several applets on the class web site that illustrate how quickly a gas of classical particles held in a box will adopt this speed distribution. The root-mean-square velocity is $v_{rms} = \langle v^2\rangle^{1/2} = \sqrt{\frac{3\tau}{M}}$. The rms speed of oxygen molecules at room temperature is about 460 m/s.