

# G25.2651: Statistical Mechanics

## Notes for Lecture 25

### I. OVERVIEW OF CRITICAL PHENOMENA

Consider the phase diagram of a typical substance:

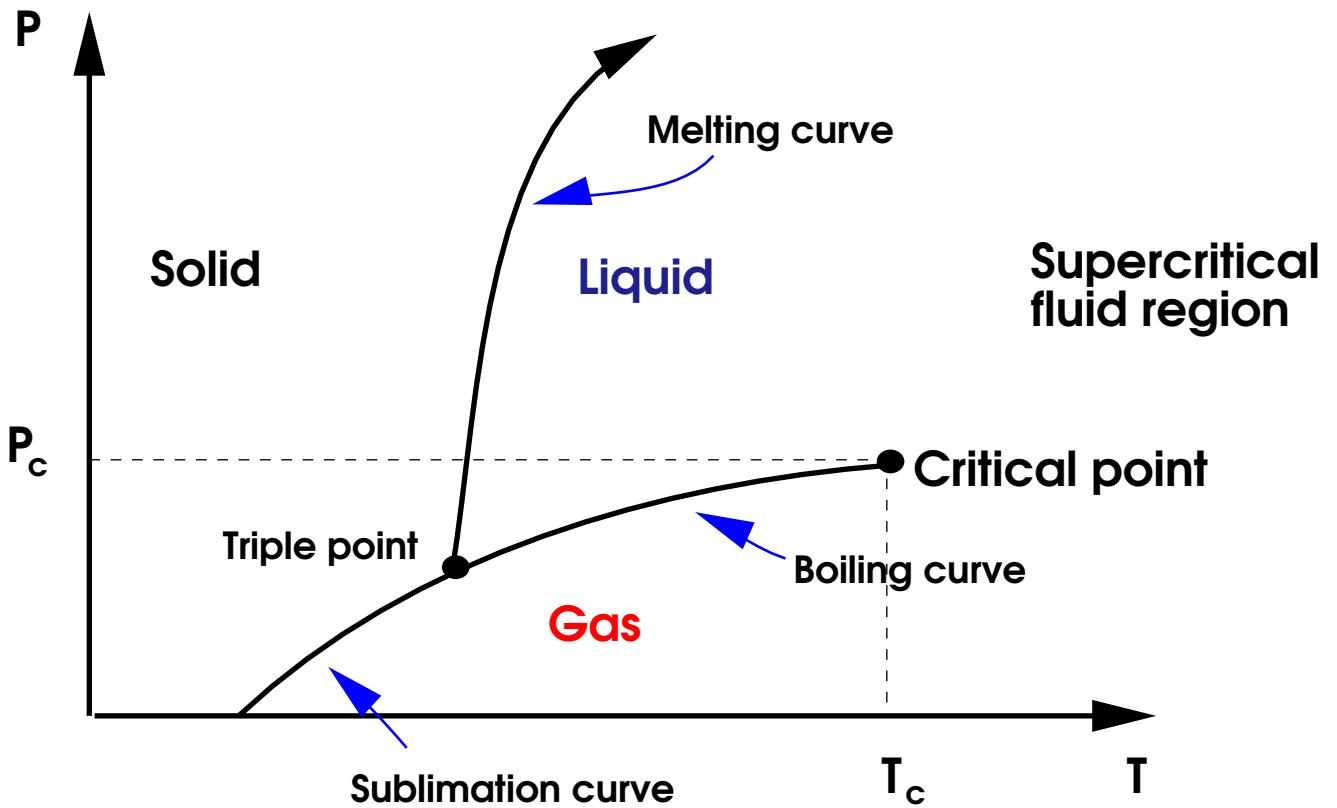


FIG. 1.

The boundary lines between phases are called the *coexistence lines*. Crossing a coexistence line leads to a *first order* phase transition, which is characterized by a discontinuous change in some thermodynamic quantity such as volume, enthalpy, magnetization.

Notice that, while the melting curve, in principle, can be extended to infinity, the gas-liquid/boiling curve terminates at a point, beyond which the two phases cannot be distinguished. This point is called a *critical point* and beyond the critical point, the system is in a *supercritical fluid state*. The temperature at which this point occurs is called the critical temperature  $T_c$ . At a critical point, thermodynamic quantities such as given above remain continuous, but derivatives of these functions may diverge. Examples of such divergent quantities are the heat capacity, isothermal compressibility, magnetic susceptibility, etc. These divergences occur in a universal way for large classes of systems (such systems are said to belong to the same *universality class*, a concept to be defined more precisely in the next lecture).

Recall that the equation of state of a system can be expressed in the form

$$P = g(\rho, T)$$

i.e., pressure is a function of density and temperature. A set of isotherms of the equation of state for a typical substance might appear as follows:

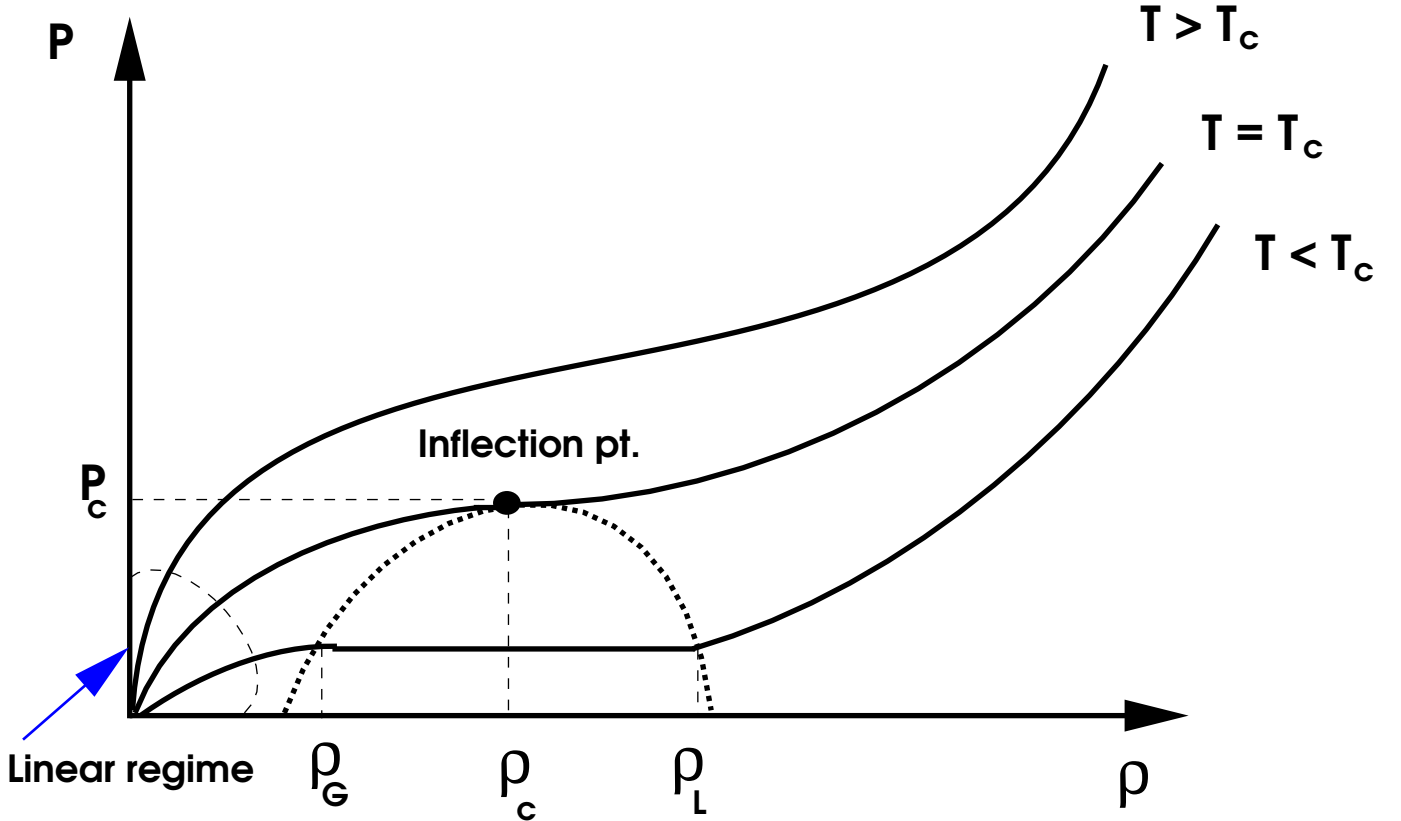


FIG. 2.

The dashed curve corresponds to the gas-liquid coexistence curve. Below the critical isotherm, the gas-liquid coexistence curve describes how large a discontinuous change in the density occurs during first-order gas-liquid phase transition. At the inflection point, which corresponds to the critical point, the discontinuity goes to 0.

As noted above, the divergences in thermodynamic derivative quantities occur in the same way for systems belonging to the same universality class. These divergences behave as power laws, and hence can be described by the exponents in the power laws. These exponents are known as the *critical exponents*. Thus, the critical exponents will be the same for all systems belonging to the same universality class. The critical exponents are defined as follows for the gas-liquid critical point:

1. The heat capacity at constant volume defined by

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_V$$

diverges with temperature as the critical temperature is approached according to

$$C_V \sim |T - T_c|^{-\alpha}$$

2. The isothermal compressibility defined by

$$\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\rho} \left( \frac{\partial \rho}{\partial T} \right)_T$$

diverges with temperature as the critical temperature is approached according to

$$\kappa_T \sim |T - T_c|^{-\gamma}$$

3. On the critical isotherm, the shape of the curve near the inflection point at  $(\rho_c, P_c)$  is given by

$$P - P_c \sim |\rho - \rho_c|^\delta \text{sign}(\rho - \rho_c) \quad \delta > 0$$

4. The shape of the coexistence curve in the  $\rho$ - $T$  plane near the critical point for  $T < T_c$  is given by

$$\rho_L - \rho_G \sim (T_c - T)^\beta$$

These are the primary critical exponents.

### A. Review of the Van der Waals theory

Recall that the Van der Waals equation of state was derived earlier by perturbation theory. The unperturbed Hamiltonian describes a system of hard spheres and is given by

$$H_0 = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2m} + \sum_{i<j} u_0(|\mathbf{r}_i - \mathbf{r}_j|)$$

and a perturbation of the form

$$H_1 = \sum_{i<j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)$$

where  $u_0(r)$  is the hard-sphere potential given by

$$u_0(r) = \begin{cases} 0 & r > \sigma \\ \infty & r \leq \sigma \end{cases}$$

and  $u_1(r)$  is an arbitrary attractive potential. In the low density limit, we had

$$g(r) \approx e^{-\beta u_0(r)} = \theta(r - \sigma)$$

and the free energy was determined to be

$$A(N, V, T) \approx -\frac{1}{\beta} \ln \left[ \frac{(V - Nb)^N}{N! \lambda^{3N}} \right] - \frac{aN^2}{V}$$

with

$$b = \frac{2}{3} \pi \sigma^3$$

$$a = -2\pi \int_{\sigma}^{\infty} dr r^2 u_1(r)$$

The equation of state takes the form

$$P = \frac{\rho kT}{1 - \rho b} - a\rho^2$$

The critical point is defined by the conditions:

$$\frac{\partial P}{\partial V} = 0 \quad \frac{\partial^2 P}{\partial V^2} = 0$$

which leads to the following values for the critical pressure, temperature and density:

$$P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27b} \quad \rho_c = \frac{1}{3b}$$

The critical exponents predicted by the theory are as follows:

1. The internal energy is given by

$$E = \frac{3}{2}NkT + \frac{aN^2}{V}$$

from which it can be seen that the heat capacity is

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{3}{2}Nk \sim |T - T_c|^0$$

$\Rightarrow \alpha = 0$ .

2. The isothermal compressibility can be expressed as

$$\kappa_T = -\frac{1}{V(\partial P/\partial V)}$$

and

$$\left. \frac{\partial P}{\partial V} \right|_{V=V_c} = \frac{1}{4Nb^2} \left( \frac{8a}{27b} - kT \right) \sim (T - T_c)$$

so that

$$\kappa_T \sim (T - T_c)^{-1}$$

$\Rightarrow \gamma = 1$

3. By Taylor expanding the equation of state about the critical pressure and density, it is easy to show that

$$\frac{1}{kT}(P - P_c) \sim \text{const} + (\rho - \rho_c)^3 + \dots$$

$\Rightarrow \delta = 3$

4. The exponent  $\beta$  can be computed using the *Maxwell construction* (see problem set 11), which attempts to fix the fact that the Van der Waals equation has an unphysical region where  $\partial P/\partial V > 0$ . The Maxwell construction is illustrated below:

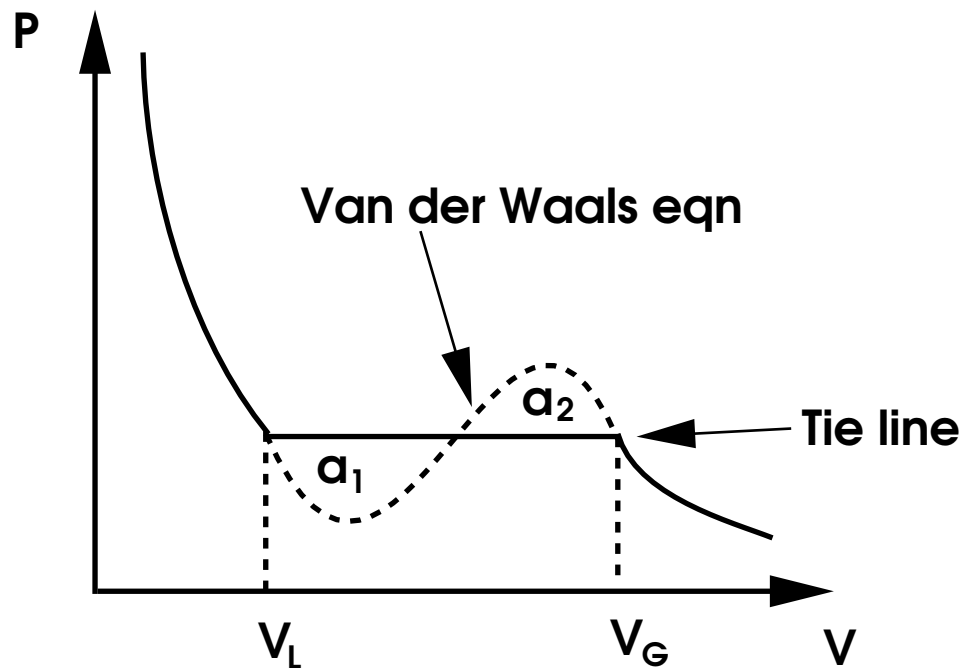


FIG. 3.

When the Maxwell construction is carried out, it can be shown that

$$\rho_L - \rho_G \sim (T_c - T)^{1/2}$$

$$\Rightarrow \beta = 1/2.$$

The following table compares the Van der Waals exponents to the experimental critical exponents:

	$\alpha$	$\beta$	$\gamma$	$\delta$
<b>VdW</b>	<b>0</b>	<b>1/2</b>	<b>1</b>	<b>3</b>
<b>Exp.</b>	<b>0.1</b>	<b>0.34</b>	<b>1.35</b>	<b>4.2</b>

FIG. 4.

Thus, one sees that the Van der Waals theory is only qualitatively correct, but not quantitatively. It is an example of a *mean field theory*.

## II. MAGNETIC SYSTEMS AND THE ISING MODEL

Imagine a cubic lattice in which particles carrying spin  $\mathbf{S}$  are placed on the lattice sites with  $|\mathbf{S}| = \hbar/2$  as shown below:

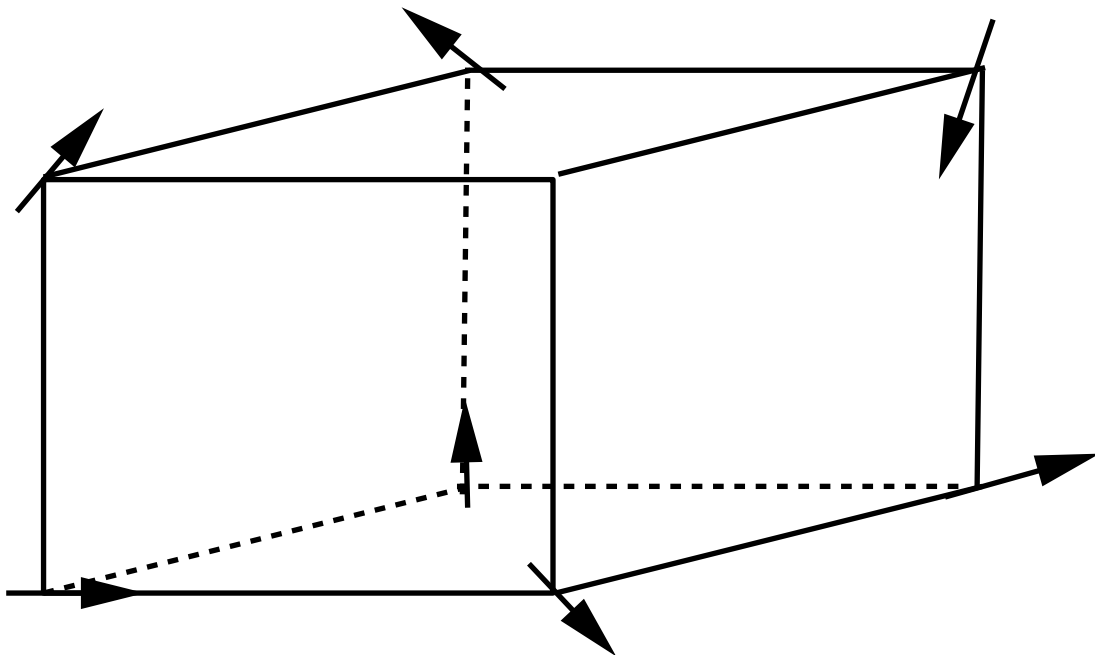


FIG. 5.

Such a model describes ferromagnetic materials, which can be magnetized by applying an external magnetic field  $h$ . In the absence of a field, the unperturbed Hamiltonian takes the form

$$H_0 = -\frac{1}{2} \sum_{i,j} \sigma_i \cdot \mathbf{J}_{ij} \cdot \sigma_j$$

where  $\mathbf{J}$  is a tensor and  $\sigma$  is a spin vector such that  $|\sigma| = 1$ . Quantum mechanically,  $\sigma$  would be the vector of Pauli matrices. In general, the spins can point in any spatial direction, a fact that makes the problem difficult to solve.

A simplification introduced by Ising was to allow the spins to point in only one of two possible directions, up or down, e.g., along the  $z$ -axis only. In addition, the summation is restricted to nearest neighbor interactions only. In this model, the Hamiltonian becomes

$$H_0 = -\frac{1}{2} \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j$$

where  $\langle i, j \rangle$  indicates restriction of the sum to nearest neighbor pairs only. The variables  $\sigma_i$  now can take on the values  $\pm 1$  only. The couplings  $J_{ij}$  are the spin-spin “ $J$ ” couplings.

In the presence of a magnetic field, the full Hamiltonian becomes

$$H = -\frac{1}{2} \sum_{\langle i,j \rangle} J_{ij} \sigma_i \sigma_j - h \sum_{i=1}^N \sigma_i$$

which describes a uniaxial ferromagnetic system in a magnetic field. The parameters  $T$  and  $h$  are experimental control parameters.

Define the magnetization per spin as

$$m = \frac{1}{N} \sum_{i=1}^N \sigma_i$$

Then the phase diagram looks like:

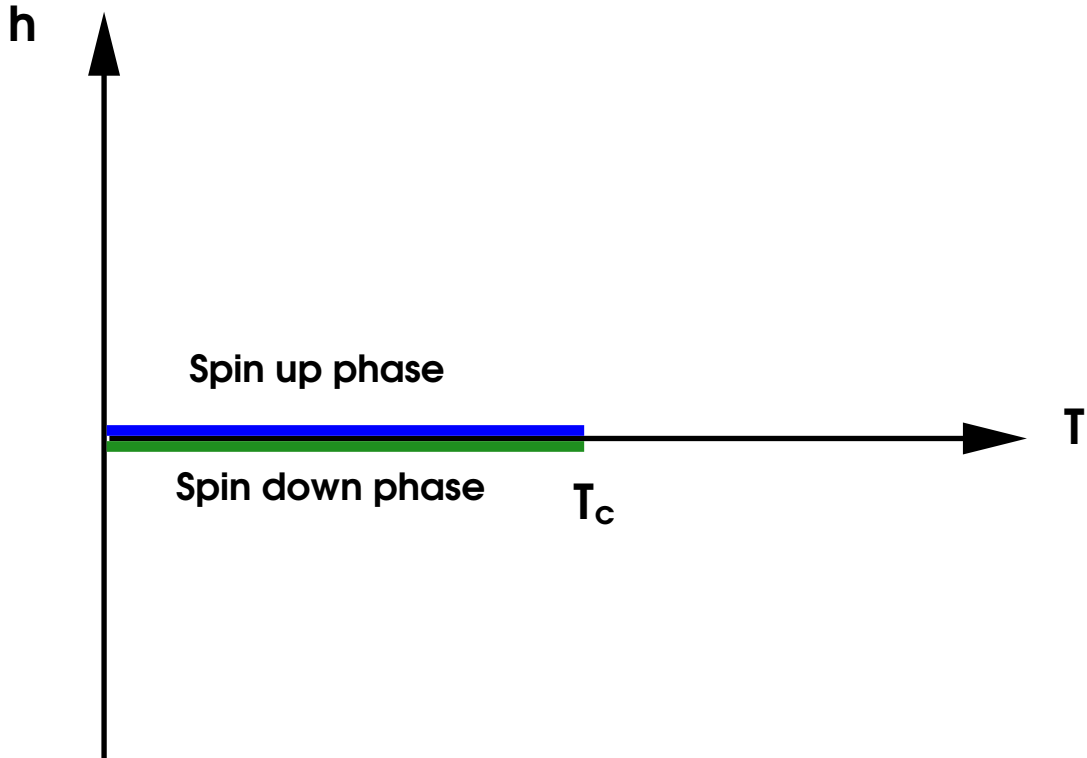


FIG. 6.

where the colored lines indicate a nonzero magnetization at  $h = 0$  below a critical temperature  $T$ . The persistence of a nonzero magnetization in ferromagnetic systems at  $h = 0$  below  $T = T_c$  indicates a transition from a *disordered* to an *ordered* phase. In the latter, the spins are aligned in the direction of the applied field before it is switched off. If  $h \rightarrow 0^+$ , then the spins will point in one direction and if  $h \rightarrow 0^-$ , it will be in the opposite direction. A plot of the isotherms of  $m$  vs.  $h$  yields:

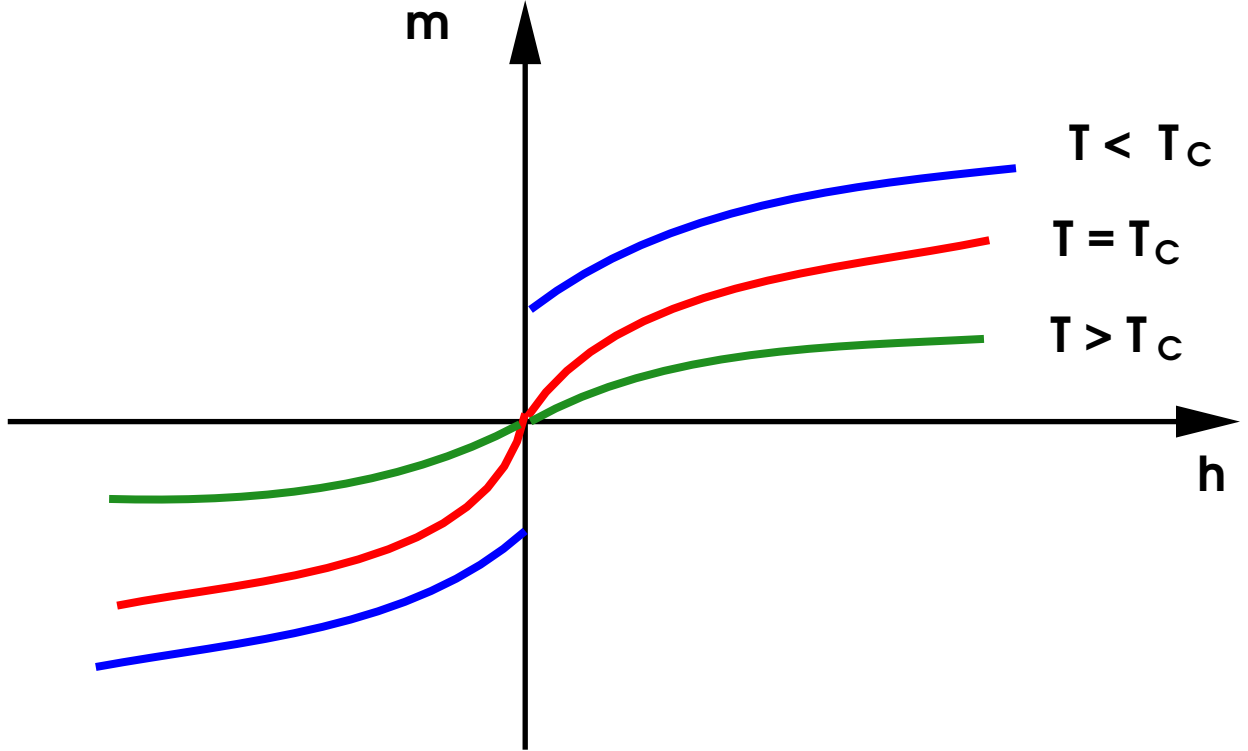


FIG. 7.

Notice an inflection point along the isotherm  $T = T_c$ , at  $h = 0$ , where  $\partial m / \partial h \rightarrow \infty$ .

The thermodynamics of the magnetic system can be defined in analogy with the liquid-gas system. The analogy is shown in the table below:

<u>Gas-Liquid</u>	<u>Magnetic</u>
$P$	$h$
$V$	$-M = -Nm$
$\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}$	$\chi = \frac{\partial m}{\partial h}$
$A = A(N, V, T)$	$A = A(N, M, T)$
$G = A + PV(P)$	$G = A - hM(h)$
$P = -\frac{\partial A}{\partial V}$	$h = \frac{\partial A}{\partial M}$
$V = \frac{\partial G}{\partial P}$	$M = -\frac{\partial G}{\partial h}$
$C_V = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_V$	$C_M = -T \left( \frac{\partial^2 A}{\partial T^2} \right)_M$

$$C_P = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_P \qquad C_h = -T \left( \frac{\partial^2 G}{\partial T^2} \right)_h$$

where  $\chi$  is the magnetic susceptibility. The magnetic exponents are then given by

$$\begin{aligned} C_h &\sim |T - T_c|^{-\alpha} & h = 0 \text{ limit} \\ \chi &\sim |T - T_c|^{-\gamma} & h = 0 \text{ limit} \\ h &\sim |m|^\delta \text{sign}(m) & \text{at } T = T_c \\ m &\sim (T_c - T)^\beta & T < T_c \end{aligned}$$