CHAPTER III

PHASE TRANSITIONS AND CRITICAL PHENOMENA

Contents

Before going into the actual subject of the thesis we summarize the theoretical background of the phase transitions, crtical phenomena and the development of this field.

3.1 Introduction (Huang 1987, Binney 1992, Yeomans 1992, Robertson 1993)

The thermodynamic properties of a matter in equilibrium can be considered to fall into two groups. Those which vary smoothly and those which have sharp discontinuities. As an example of the first group we may cite the properties of ideal or nearly ideal gas (energy, entropy, specific heat, equation of state), of ideal or nearly ideal solids, of ideal or nearly ideal mixtures of gases or solids; paramagnetism and diamagnetism; and of electrons and phonons in normal metals.

The second group is usually associated with phase transitions of various types; liquid-vapor equilibrium and the critical point, order-disorder transition in alloys, ferromagnetism, antiferromagnitism, superconductivity, etc.

Standard statistical mechanics can handle the first group with relative ease; for example, treatment of an ideal system when the interactions between gas molecules or between phonons are ignored. Equilibrium in the first-order phase transition, between the crystal and vapor phases, and the form of the vapor pressure curve can then be determined by thermodynamics.

For a slightly non-ideal gas, interaction between molecules can be taken into account by perturbation theory; a chosen thermodynamic property is expressed as a series of ascending powers of a parameter which measures the strength of the interaction. As long as only a finite number of terms are considered the continuity of thermodynamic properties connot be destroyed. Discontinuous behavior can be introduced only by taking the perturbation series to infinity. In fact the problem dealing with phase transitions is the strong interaction problem in which the interactions can no longer be treated as a small perturbation but play a dominant role in the calculations and in the resulting physical properties.

3.2 Critical Point and Order Parameter (Yeomans 1992, Ma 1967)

A phase diagram of a typical fluid is shown in Figure. 3.1. As the temperature and pressure vary, water can exist as solid, liquid, or gas. Well defined phase boundaries separate the regions in which each state is stable. Crossing the phase boundaries, there is a jump in the density and laten heat.

Consider moving along the line of liquid-gas coexistence. As the temperature increases, the difference in density between liquid and gas decreases

continuously to zero as shown in Figure. 3.2. It becomes zero at the critical point beyond which it is possible to move continuously from liquid-like to a gas-like fluid. The difference in density, which becomes non-zero below the critical temperature, is called the *order parameter* of the liquid-gas transition.

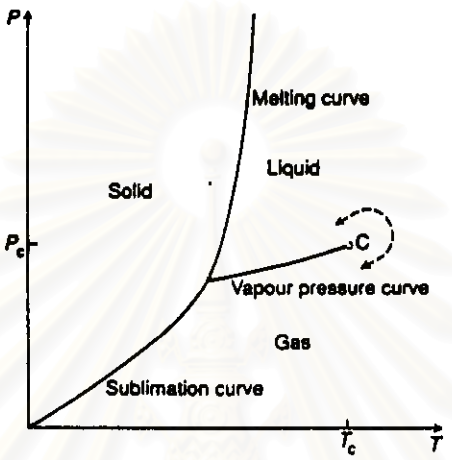

Figure 3.1 Phase diagram of a fluid

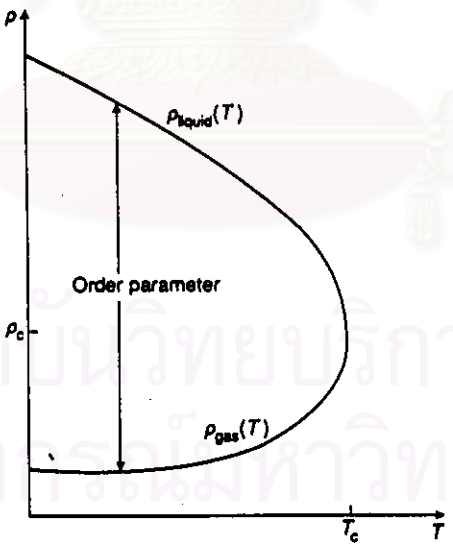

Figure 3.2 Value of the densities of the coexisting liquid and gas along the vapor pressure curve

Analogous behavior is seen in the magnetic phase transitions. The phase diagram of a simple ferromagnet is shown in Fig. 3.3. The transition occurs at zero magnetic field, H=0. Crossing the phase boundaries at temperature less than the critical temperature, there is a jump in magnetization. Above the critical temperature, it is possible to move continuously from a stability of negative magnetization to one of positive magnetization. The critical point itself, separates these two behaviors. The magnetization is continuous but its derivatives are discontinuous.

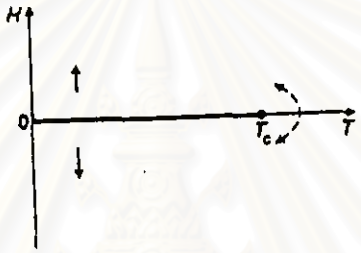

Figure 3.3 Phase diagram of a ferromagnet

The order parameter for the ferromagnetic phase transition is the magnetization. Its variation with temperature along the coexistence curve, H=0, is shown in Fig. 3.4. The order parameter of other systems are listed in Table 3.1

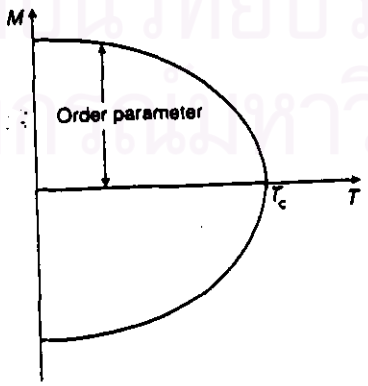

Figure 3.4 Zero field magnetization of a ferromagnet

Table 3.1 Example of diversity of phase transition

Transition	Example	Order Parameter
Liquid-Gas	H_2O	density
Ferromagnetism	Fe	magnetism
Antiferromagnetism	MnO	sublattice magnetism
Ferrimagnetism	Fe_3O_4	sublattice magnetism
Structural	$SrTiO_3$	atomic displacement
Ferroelectric	$BaTiO_3$	electric polarization
Order- disorder	CuZn	Sublattice atomic concentration
Phase separation	CCl_4+C_7F_{16}	concentration difference
Superfluid	liquid ^4He	condensate wavefunction
Superconductivity	Al, No_3Sn	ground state wavefunction
Liquid crystalline	Rod molecules	various

3.3 Critical Exponents (Binney 1992, Huang 1987)

Let us review briefly some phenomena of ferromagnetic critical point. It is found from experiments that the magnetization, the susceptibility, the critical isotherm, and the specific heat all obey *power laws* near $T = T_c$. We defined the *critical exponents* α, β, γ, δ as

$$\begin{aligned} C &\propto |T - T_c|^{-\alpha} \\ M &\propto (T_c - T)^{\beta} \\ \chi &\propto |T - T_c|^{-\gamma} \\ B &\propto M^{\delta} \end{aligned} \qquad (3.1)$$

Sometimes, people introduce exponent α', γ' for $T<T_c$. For instance $\chi \propto (T-T_c)^{-\gamma} : T>T_c.$, $\chi \propto (T-T_c)^{-\gamma'} : T<T_c.$. But it seems (and theory confirms) that one always has $\alpha=\alpha'$, $\gamma=\gamma'$, and these primed exponents have fallen into disuse.

3.4 Correlation Function (Binney 1992)

Much of knowledge about phase transition is derived from experiments in which particles are scattered by a nearly critical system. The correlation function is an example. Scattering experiments show that, for $T\neq 0$, correlation function ($G(r)$) is small at both large and small T/T_c. Furthermore when $T=T_c$ one finds the asymptotic form of correlation function when the distance (r) is large compared to the inter-molecular distance.

$$G(r) \propto \frac{1}{r^{d-2+\eta}} \tag{3.2}$$

when d is the dimensionality of the system and η is a further critical exponent. In fact, for small $|T-T_c|/T_c$ approximately

$$G(r) \propto \frac{e^{-r/\xi}}{r^{d-2+\eta}} \tag{3.3}$$

where the length ξ is called the correlation length. As the system approaches the critical point, this quantity grows without limit. One finds that

$$\xi \propto |T-T_c|^{-\nu} \tag{3.4}$$

where ν is the sixth and final critical exponent.

Before the end of this of section, I summarize some the linear combination of the critical exponents. Only two of the six critical exponents defined above are independent, because of the following " scaling law";

Fisher:	γ	=	$\nu(2-\eta)$
Rushbrooke	$\alpha+2\beta+\gamma$	=	2
Widom	γ	=	$\beta(\delta-1)$
Josephson	νd	=	$2-\alpha$

where, in the last relation, d is the dimensionality of space.

3.5 **Universality**(Yeomans 1992, Bellac 1991)

We need to justify why the critical exponents are more interesting than the critical temperature T_c itself. It turns out that, while as T_c sensitive depends on the details of the interatomic interaction, the critical exponents depend on only a few fundamental parameters. For a short range interaction model these are the dimensionality of space, d and the symmetry of the order parameter.

Table 3.2 gives some numerical values for the critical exponents of several systems. The critical exponents of different transition as liquid-gas transition of xenon and the separation of a mixture of two organic chemicals are equal to each other the experimental error. This phenomena is called *universality*.

We assign each system to a universality class in such a way that any two systems in the same universality class have the same dimensionality, d, and order parameters of the same dimensionality, D. Table 3.1 shows that all systems in the same universality class have the same critical exponents.

Table 3.2 Values of critical exponents

	Xe	Binary fluid	β -brass	^{4}He	Fe	Ne
D	1	1	1	2	3	3
α	< 0.2	0.113±0.005	0.05±0.06	-0.014±0.016	-0.03±0.12	0.04±0.12
β	0.35±0.015	0.322±0.002	0.305±0.05	0.34±0.01	0.37±0.01	0.358±0.003
γ	$1.3^{+1}_{-.3}$	1.239±0.002	1.25±0.02	1.33±0.03	4.3±0.1	1.33±0.02
δ	$4.2^{+.4}_{-.3}$	4.85±0.03		3.95±0.15	1.33±0.015	4.29±0.05
η	0.1±.1	0.017±0.015	0.08±0.07	0.021±0.05	0.07±.04	0.041±0.01
ν	≈ 0.57	0.625±0.06	0.65±0.02	0.672±0.001	0.69±0.02	0.64±0.1

For more evidence, see Fig 3.5 plotted by Guggenheim (1945)(Binney 1992). The coexistence curves of eight different fluids are plotted in reduce units, T/T_c and ρ/ρ_c. When close to critical point, all data lie on the same curve and hence can be describes by the same exponent β $\left(\beta \approx \frac{1}{3}\right)$.

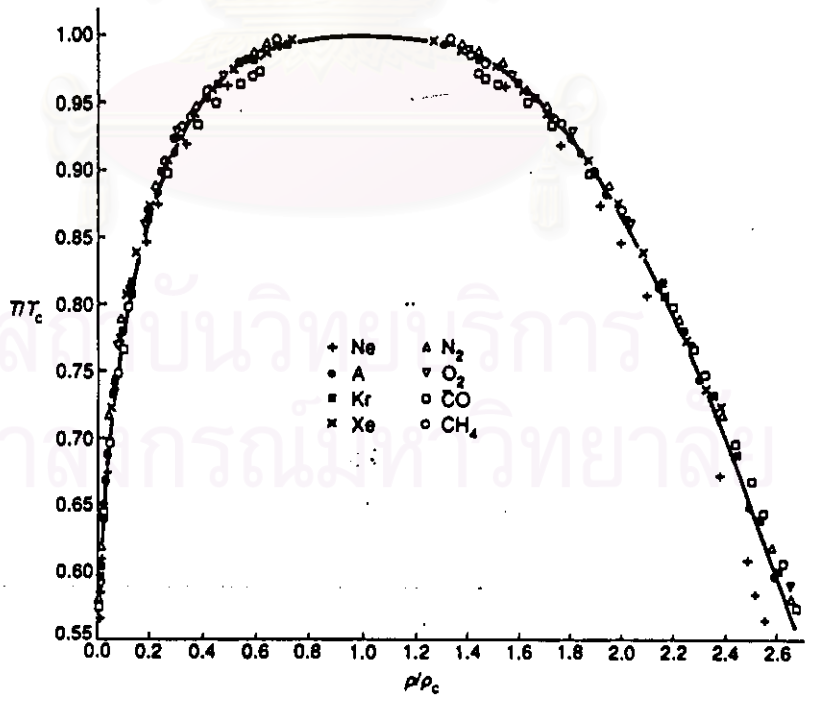

Figure 3.5 The coexistence curve of eight different fluid plotted in reduced variables. The fit assume an exponent $\beta \approx 1/3$.

3.6 Models

In this section we introduce some models that play an important role in the development of the theory of phase transition. Many important results related to phase transition have been derived from studying particular model.

We shall be concerned about models of what happens on a lattice of N sites. This lattice may be one, two or three dimensions which is denoted by d, and we shall assume that the sample is cubic, having $L = N^{\frac{1}{d}}$ sites on a side. The model's order parameter is defined at each lattice point. The order parameter may be a scalar since its value at each lattice point is a single real number, or may be a complex value ,or a vector, or even a tensor. We shall denote the real dimensionality of order parameter by D. When $D=1$ implies that the order parameter is a scalar, $D=2$ implies that order parameter is two vectors or complex values and so forth.

3.6.1 The Ising Model (Binney 1992)

The Ising model is a model of a ferromagnet or antiferromagnet. It was invented by W. Lenz (1888-1957) and it was first solved by E. Ising in 1925, who treated the case $d=1$ which does not have a phase transition.

In 1944 Onsager (1903-1976) solved the model for $d=2$ in the absence of an externally applied magnetic field and showed that the crtical exponents of the model were quite different from the Landau theory prediction. We still have no exact solution for $d=3$ model or for $d=2$ model in non -zero magnetic field.

We consider a lattice in d- dimension of sites $\{i\}$ labeled 1,2,...,N, which we take to be hypercubic. The order parameters are classical spin variables S_i associated with each point of the lattice, which takes only two values; (1,-1) or (spin up or down).

The system's Hamiltonian is

$$H = \frac{1}{2}\sum_{i,j} J_{i,j} S_i S_j - \mathrm{B}\sum_i S_i \qquad (3.5)$$

where B is an external field, the subscripts label lattice sites, and $J_{i,j}$ is the exchange interaction defined by

$$J_{i,j} = \begin{cases} J, & i \text{ and } j \text{ neighbouring sites} \\ 0, & otherwise \end{cases} \qquad (3.6)$$

The partition function of the model can be written

$$Z_{Ising} = \sum_{\{S_i\}} \exp\left[\beta\left(B\sum_i S_i - \frac{1}{2}\sum_{i,j} J_{i,j} S_i S_j\right)\right] \qquad (3.7)$$

where $\{S_i\}$ indicates that the sum is over all possible lattice sites.

If in equation (3.5) we set $J < 0$, neighboring spins try to align parallel to one another and parallel to B. This case is the model of a ferromagnet. If we set $J > 0$, neighboring spins try to align antiparalled to one another and (3.7) becomes the partition function of an antiferromagnet.

3.6.2 The XY and Heisenburg Models

The magnetic dipoles of the Ising model can point in only two directions. It turns out that qualitatively different phase transitions can occur in systems of spins that have greater flexibility of orientation.

The spin of XY model are unit vectors confined to rotate in a plane. The Heisenburg model consists of an array of D dimensional spin. The XY model may be considerd to be a special case of $D=2$ of the Heisenburg model. In this model neighboring spins are assumed to have exchange energy JS_iS_j so that the partition function of the system becomes

$$Z_{Heisen} = \sum_{\{S_i\}} \exp\left[\beta\left(B\sum_i S_i - \frac{1}{2}\sum_{i,j} J_{i,j}S_iS_j\right)\right]$$

Since two dimensional vectors may be represented by complex numbers, the order parameter of the XY model may be replaced by a complex order parameter ψ. The exchange energy then becomes $\frac{1}{2}J\left(\psi_i^*\psi_j + \psi_i\psi_j^*\right)$.

3.6.3 The Gaussian and Landau Ginzberg Models (Goldenfeld 1992)

The Landau-Ginzburg approach has played an important role in the theory of superconductivity and other critical phenomena. The system Hamiltonian in term of the scalar order parameter $S(x)$ is

$$-H\{S(x)\} = \int d^dx\left[\frac{1}{2}(\nabla S)^2 + \frac{1}{2}r_0S^2 + \frac{1}{4}u_0S^4 - h_0S\right] \qquad (3.8)$$

where $S^2 = S(x).S(x) = \sum_{i=1}^{n}(S_i(x))^2$

$S^4 = (S^2)^2$

$(\nabla S)^2 = \sum_i \sum_j \left(\frac{\partial S_i}{\partial x_j}\right)^2$

The coefficients r_0, u_0 are functions of temperature, and h_0 is the applied magnetic field.

The Gaussian model's Hamiltonian is similar to the Landau-Ginzburg model but without the quartic term ($u_0 = 0$).

3.7 Mean Field Theory

The mean field theory was invented by P.E. Weiss (1865-1940) as a theory of magnetism, and for a long time it was the only theory of phase transitions. Therefore it has a very important place in the development of this field and even today. It is usually the first tool applied to sort out the essential physics of a new type of phase transition.

The solution from mean field theory is an example of an approximate solution. There are many numerical solutions of various models; the mean field theory often seems to be crude, the exact solutions are too complicated. A peculiar feature of a critical phenomena is that there is just a few things one can do to improve the mean field theory substantially without solving the problem exactly. This makes the theory of critical phenomena a very difficult field.

3.8 Renormalization Group

This method allows us to simplify calculations in the critical regime to the points at which critical exponents could be extracted without ever working out the partition function of the problem. More details are discussed in the chapter.