General theory of critical phenomena in continuous transitions

I. Concepts of

(a). Order parameter.

Order parameter is something which is zero above $T_c$, non-zero below $T_c$.

E.g. spontaneous magnetization in Ising model $M$

or in Heisenberg model

Other types of phase transitions
liquid-vapor phase transition

[Diagram]

Order parameter is $\nu - \nu_c$ elsewhere (others possible).
Other concepts:
Dimensionality $d$ of space
\[ (d = 1, 2, 3, \ldots) \]
Dimensionality $n$ of order parameter
\[ n = 1, 2, 3, \ldots \]
E.g. Ising model $n=1$
Heisenberg model $n=3$
because $O, P$ in $\mathbb{R}^n$ and $\vec{M}$ is a 3-component vector.
Anisotropic Ising model $J_{||} > J_{\perp}$
\[ n = 2 \]
\[ J_{||} < J_{\perp} \quad n = 2 \quad O, P \text{ is } M_{xy} \text{ which is a 2-component vector} \]
\[ (d = 2, n = 2 \text{ is a special case}) \]

Other examples:

- Antiferromagnet $n=1$
  $O, P = \text{sublattice magn.}$

- Order-disorder:
  Unit of Cu rich side
  $X_{\text{Cu}} = 0.5$ on sublattice $1$

- Superconductor:
  $O, P$ is a wave function $\Psi$
  $n_5 = |\Psi|^2$
  $\Psi = f(n=2)$
Superfluid: $\Psi = \text{wave function of superfluid}$

$m = 2$ also.

More concepts:

Phase separation: Order parameter $\xi \propto |x_2 - x_c|$ or $|x_1 - x_c|$ (or $|x_2 - x_1|$ for $T < T_c$)

Critical exponents: $x_2$ and $x_1$ are coexisting compositions

Think of Ising model: $x_2$ and $x_1$ are coexisting compositions

Conjugate field: (thermodynamically conjugate field to $M$ is $H$)

$M \leftrightarrow H \leftrightarrow$ magnetic field

$\nu \leftrightarrow p \leftrightarrow$ pressure.

(sometimes not obvious) (sometimes not experimentally easy to access)

Critical exponents (for Ising model):

Near $T = T_c$

$$H \at \left( T_c, H_c \right)$$

$$T$$

(a1). Near $T_c$, $C_V \propto (T - T_c)^{\alpha'}$ for $T > T_c$

$$\propto (T_c - T)^{\alpha'} \quad T < T_c$$

(b). For $T < T_c$ $M \propto (T_c - T)^\beta$
(c). For $T \geq T_c$, \[ \max X = \left( \frac{\partial M}{\partial H} \right)_{H=0} \]

$\sim (T-T_c)^{-\gamma}$ \quad $T>T_c$

$\sim (T_c-T)^{-\delta'}$ \quad $T<T_c$

(usually, $\delta = \delta'$)

(d). For $T=T_c$

$\max M \approx H^{1/\delta}$

"Universality": $\alpha, \beta, \gamma, \delta$ depend only on $d$ and $\eta$. (hypothesis)

Analogs: analog of $X$ for ln $g$ - vapor $\therefore$

$\max \delta h = -\left( \frac{\partial v}{\partial p} \right) \propto K_T$

For $T<T_c$ must consider $K_T$ along

coexistence curve.

Correlation functions (canonical ensemble)

e.g. Ising model

Define $P_{S_iS_j}(R_{ij}) \equiv \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle$

For fluid

$g(R) = g(k) - 1$ \quad where we defined

$g(R) \approx \frac{\langle n/2 \rangle n(R) \langle R \rangle}{n^2}$
At large distances, we assume

\[ \phi(R) \approx \frac{1}{R^{\beta}} \frac{e^{-R/\xi(T)}}{\xi(R)} \]

\( \xi(T, H=0) \approx \left( \frac{T-T_c}{T_c} \right)^{-\eta} \quad T > T_c \)

\( \approx \left( \frac{T_c-T}{T_c} \right)^{-\eta} \quad T < T_c \)

and at \( T = T_c \)

\[ h(R) \approx \frac{1}{R^{d-2+n}} \]

\( d = \text{Dimensionality} \)

\( \eta = \text{another "critical exponent"} \).
Mean-field models:

(i). For Ising model

\[ F = A(T-T_c)M^2 + BM^4 - MH \]

H=0

\[ T \geq T_c \quad M = 0 \]

\[ T < T_c \quad 2MA(T-T_c) + 4BM^3 = 0 \]

\[ M = \pm \sqrt{\frac{A}{2B}(T_c-T)} \quad \Rightarrow (\beta = \frac{1}{2}) \]

\[ F = -\frac{A^2}{2B}(T_c-T)^2 \quad \Rightarrow C_V \text{ has discontinuity} \]

\[ (T < T_c) \quad (\kappa = 0) \]

\[ T > T_c \]

\[ 2A(T-T_c)M = H \]

\[ M = \frac{H}{2A(T-T_c)} = \chi H \quad \chi \propto \frac{1}{(T-T_c)} \quad \delta = 1 \]

(ii). At \( T = T_c \)

\[ 4BM^3 = H \quad M \propto H^{\frac{1}{3}} \quad \delta = 3 \]

\[ \alpha + 2\beta + \gamma = 2 \]

Other scaling law \( \omega \):

\[ \gamma = \beta(5-1) \quad (\text{Widom relation}) \]

\[ 1 = \frac{1}{2}(3-1) = 1 \]
Van der Waals equation as a mean-field theory

\[ (P + \frac{a}{v^2})(v-b) = k_BT \]

\[ P = \frac{k_BT}{av-b} - \frac{a}{v^2} \]

Critical pt.:

\[ \left( \frac{\partial P}{\partial v} \right)_T = 0 = -\frac{k_BT}{(v-b)^2} + \frac{2a}{v^3} \quad (1) \]

\[ \left( \frac{\partial^2 P}{\partial v^2} \right)_T = 0 = \frac{2k_BT}{(v-b)^3} - \frac{6a}{v^4} \quad (2) \]

\[ \frac{k_BT}{(v-b)^2} = \frac{2a}{v^3} \]

So

\[ 0 = \frac{2}{v-b} \left( \frac{2a}{v^3} \right) - \frac{6a}{v^4} \]

\[ \frac{2}{v-b} = \frac{3a}{v} \quad ; \quad 2v = 3(v-b) \]

\[ v = \frac{3b}{v_c - 3b} \]

\[ \frac{k_BT_c}{(2b)^2} = \frac{2a}{(3b)^3} \quad k_BT_c = \frac{84a}{27b} \]

\[ P_c = \frac{48a}{27b^2} - \frac{a}{9b^2} = \frac{a}{27b^2} \]
Susceptibility near $T_c$:

Since $P$ is field and $\nu$ is order parameter

then \[ -\left( \frac{\partial P}{\partial \nu} \right)_T = \left( \frac{\partial P}{\partial \nu} \right)^{-1}_T \]

is like susceptibility

\[ \left( \frac{\partial P}{\partial \nu} \right)_\nu = \frac{k_B T}{4b^2} + \frac{2a}{27b^3} \]

\[ = -\frac{k_B T}{4b^2} + \frac{k_B T_c}{4b^2} = -\frac{k_B}{4b^2} (T - T_c) \]

\[ -\left( \frac{\partial P}{\partial \nu} \right)_T \sim \frac{4b^2}{k_B} \frac{1}{(T - T_c)} \approx \frac{1}{T - T_c} \]

(analog of Curie-Weiss Law)

Similarly, \[ \nu_f - \nu_c = \Delta \nu(T) \propto (T_c - T)^{\frac{1}{2}} \] (exercise)

in Van der Waals eq. of state

Finally, right at $T = T_c$,

\[ \left( P + \frac{a}{\nu^2} \right) (\nu - b) = k_B T_c \]

\[ P = \frac{k_B T_c}{\nu - \nu} - \frac{a}{\nu^2} = \frac{\delta}{27b} \frac{a}{b^{\nu} - \nu} - \frac{a}{\nu^2} \]

Let $\nu = 3\nu + \Delta \nu$

\[ \frac{1}{\nu - \nu} = \frac{1}{2\nu + \Delta \nu} = \frac{1}{2\nu} - \frac{\Delta \nu}{4b^2} + \frac{(\Delta \nu)^2}{8b^3} - \frac{(\Delta \nu)^3}{16b^4} \]
\[
\frac{a}{v^2} = \frac{a}{(3v + \Delta v)^2} = \frac{a}{9b^2} \left(1 + \frac{\Delta v}{3v}\right)^2
\]

\[
= \frac{a}{9b^2} \left[1 - \frac{2 \Delta v}{3v} + \frac{3(\Delta v)^2}{(3v)^2} - \frac{4(\Delta v)^3}{(3v)^3} + \ldots\right]
\]

So we have

\[
p = \frac{8}{27} \frac{a}{b^2} \left[1 - \frac{\Delta v}{4b^2} + \frac{(\Delta v)^2}{8b^3} - \frac{(\Delta v)^3}{16b^4} + \ldots\right]
\]

\[
- \frac{a}{9b^2} \left[1 - \frac{2 \Delta v}{3v} + \frac{3(\Delta v)^2}{(3v)^2} - \frac{4(\Delta v)^3}{(3v)^3} + \ldots\right]
\]

\[
\sqrt{p_c} = 0 + (\Delta v)^3 \frac{a}{b^5} \left(\frac{4}{243} - \frac{1}{54}\right)
\]

or

\[
P - p_c = \left(\frac{8}{27} a\right) \frac{1}{(v - v_c)^3} \frac{a}{b^5}
\]

(analogous to

or

\[
(v - v_c) = 4 C (P - p_c)^{\frac{1}{3}}
\]

\[
M \propto B^{\frac{1}{3}} \text{ in MFT}
\]
Landau theory of phase transitions

Say we have scalar order parameter
\[ M, \text{ temp } T, \text{ conjugate field } H. \text{ Conjugate field H = 0} \]

Let \( F \) be free energy at
\[ f(M, T, H=0). = \text{ free energy} \]
M determined by minimizing \( F \) at fixed \( T \)

Make argument

(i). \( F \) is a power series in \( M \)

\[ F = F_0 + \alpha_1(T) M + \alpha_2(T) M^2 + \ldots \]

(ii). Since \( F(M) = F(-M) \) we get \( \alpha_i = 0 \) for \( i \) odd

\[ F = F_0 + \beta M^2 + \ldots \]

(iii). \( \alpha, \beta \) can be anything.

but suppose smooth in \( T \).

Let \( \alpha \) go through zero at \( T = T_c \); then \( \alpha \sim \delta(T-T_c) \)

\[ F = F_0 + \alpha(T-T_c) M^2 + \beta(T) M^4 + \ldots \]
For $T > T_c$, $M = 0$

For $T < T_c$

\[ \frac{\partial F}{\partial M} = 0 \Rightarrow -2\alpha(T_0 - T_c)M + 6bM^3 = 0 \]

\[ M = \pm \sqrt{\frac{\alpha}{2b}} (T_0 - T) \]

\[ 2\alpha(T - T_c)M + 4bM^3 = 0 \]

\[ M = \pm \sqrt{\frac{\alpha}{2b}} (T_0 - T) \]

\[ F = F_0 - \frac{\alpha^2}{4b} (T_0 - T)^2 \]
Neglect T-dependence \( b \Rightarrow \)

\[ CV = -T \left( \frac{\partial^2 F}{\partial T^2} \right)_{H=0} + \frac{\alpha^2 T}{2b} \]

"classical" second order transition

\((i.3)\) add \( H \)-field

Free energy per unit volume

\[ F = F_0 + \alpha (T-T_c)M^2 + bM^4 - MH \]

given e.g. at \( T=T_c \)

\[ 4bM^3 = H \quad M = \left( \frac{H}{4b} \right)^{\frac{1}{3}} \]

Critique:

1. Valid near \( T_c \)?

2. Assumes well-behaved analytic functions (whereas critical point is mathematically a branch point)?
3D Ising system

<table>
<thead>
<tr>
<th>Expt</th>
<th>MFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0-0.14</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.32-0.39</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.3-1.4</td>
</tr>
<tr>
<td>$\delta$</td>
<td>4-5</td>
</tr>
<tr>
<td>2</td>
<td>$0.6-0.7$</td>
</tr>
</tbody>
</table>

(not proved)
(c.i.e. not proved in this class)

\[
\frac{n}{n_c} \sim (T - T_c)^\beta
\]

Perhaps mention critical opalescence?