Fluctuations and critical phenomena

Critical phenomena means the thermodynamic properties of systems near critical temperatures. In mean field theory, fluctuation were neglected. We now consider effects of fluctuation and determine the range of validity of mean field theory.

<u>Gaussian Model</u>. Consider a Landau energy defined by

$$F[\phi] = \int d^3r \left\{ a|\phi|^2 + \tfrac{1}{2} b |\phi|^4 + c|\nabla\phi|^2 \right\},$$

where $a = \alpha(T - T_c)$. The order parameter for $T < T_c$ is

$$\phi_0 = \pm\sqrt{-a/b}$$

in the absence of fluctuations.

We now calculate the partition function Z. As discussed earlier in the context of broken symmetry, it is only necessary to consider states near one solution of ϕ_0 since the other

φ_0 solution is not accessible to small fluctuation. We choose the positive solution with small deviations ψ:

$$\varphi = \varphi_0 + \psi$$

The Gaussian model retains only terms quadratic in ψ for $F(\varphi)$:

$$F(\varphi_0+\psi) \simeq \int d^3r \left\{ \varphi_0^2(a+\tfrac{1}{2}b\varphi_0^2) + 2\varphi_0\psi(a+b\varphi_0^2) \right.$$
$$\left. + (a+3b\varphi_0^2)\psi^2 + c(\nabla\psi)^2 \right\}$$
$$= \int d^3r \left\{ -\frac{a^2}{2b} - 2a\psi^2 + c(\nabla\psi)^2 \right\}$$
$$= F(\varphi_0) + \int dv \left\{ -2a\psi^2 + c(\nabla\psi)^2 \right\}$$

The partition function is a sum over all allowed values of φ:

$$Z = \int \mathcal{D}\varphi \; e^{-\beta F(\varphi)}$$

The notation is that of a functional integral and means that the sum is over all different values of $\varphi(\vec{r})$ at each point $\vec{r}$.

the equilibrium 'ground state' energy $F(\Phi_0)$ is the same at each point and factors out of the integral; leaving only a sum over the $\psi(\vec{r})$:

$$Z = e^{-\beta F(\Phi_0)} \int \mathcal{D}\psi \, \exp[-\beta \int d^3r \{-2a\psi^2 + c(\nabla\psi$$

The integral is performed using an expansion of $\psi(\vec{r})$ in terms of plane waves:

$$\psi(\vec{r}) = \frac{1}{\sqrt{V}} \sum_{\vec{q}} \psi_q \, e^{i\vec{q}\cdot\vec{r}}$$

This expansion allows the integral to be written as a product of simpler integrals:

$$Z = e^{-\beta F(\Phi_0)} \int \mathcal{D}\psi \exp\Big[-\beta \frac{\int d^3r}{V^2} \sum_q \sum_{q'} \{-2a - qq'\} \cdot \psi_q \psi_{q'} e^{i\vec{r}\cdot(q+q'}$$

$$= e^{-\beta F(\Phi_0)} \int \mathcal{D}\psi \exp\Big[-\beta \sum_q \sum_{q'} (-2a - cqq')\psi_q \psi_{q'} \cdot \delta(q+q')\Big]$$

$$= e^{-\beta F(\Phi_0)} \int \mathcal{D}\psi \exp\Big[-\beta \sum_q (-2a + q^2 c)\psi_q \psi_{-q}\Big]$$

$$= e^{-\beta F(\Phi_0)} \int \mathcal{D}\psi \exp\Big[-\beta \sum_q (-2a + cq^2)|\psi_q|^2\Big]$$

where the last step uses $\psi_q = \psi^*_{-q}$. Restricting the values of q in the sum to be positive, we include a factor of 2 in the exponent:

$$Z = e^{-\beta F(\varphi_0)} \int \mathcal{D}\psi \; e^{-2\beta \sum_{q \geq 0} (-2a + c q^2) |\psi_q|^2}$$

The simpler integrals are gaussian:

$$Z = e^{-\beta F(\varphi_0)} \prod_{q \geq 0} \int d^2\psi_q \; e^{-2\beta(-2a + c q^2)|\psi_q|^2}$$

The measure is two dimensional since ψ_q is in general complex:

$$\psi_q = u_q + i v_q$$

Then

$$\int d^2\psi_q \; e^{-2\beta(-2a + c q^2)|\psi_q|^2} = \int du_q \, dv_q \; e^{-A(u_q^2 + v_q^2)}$$

$$= \frac{\pi}{A} = \frac{\pi}{2\beta(-2a + c q^2)}$$

Hence

$$\boxed{Z = e^{-\beta F(\varphi_0)} \prod_{q \geq 0} \frac{\pi}{2\beta(-2a + c q^2)}}$$

The corresponding free energy is

$$\mathcal{F} = -k_B T \ln Z$$
$$= F(\varphi_0) - k_B T \sum_{q \geq 0} \ln \left\{ \frac{\pi}{2\beta} \left(\frac{1}{-2a + cq^2} \right) \right\}$$

Fluctuation introduce a correction to the mean field Landau - Ginzburg theory result.

The correction is given by the second term, and it is drastic. Away from T_c, the sum diverges as $q \to \infty$, but is well behaved for small q. Near T_c, "a" is small, and the small q cause problems.

<u>Ginzburg criterion</u>. The small q behaviour for $T \sim T_c$ can be understood best by studying some of the thermodynamic functions. The heat capacity is particularly useful. Then

$$C_V = -\frac{\partial}{\partial T} U \quad \text{and} \quad U = -\frac{\partial}{\partial \beta} \ln Z$$

give

$$C_v = -\frac{\alpha^2 T}{b} - \sum_{q \geq 0} \left\{ \frac{4\alpha^2 k_B T^2}{(cq^2 - 2\alpha(T-T_c))^2} + \frac{4\alpha k_B T}{cq^2 - 2\alpha(T-T_c)} \right\}$$

(where we've used $a = \alpha(T-T_c)$.)

As $T \to T_c$, the most important term in the sum is the first. Therefore near T_c,

$$C_v \approx -\frac{\alpha^2 T_c}{b} - 4\alpha^2 k_B T_c^2 \sum_{q \geq 0} \frac{1}{[cq^2 - 2\alpha(T-T_c)]^2}$$

$$\sim -\alpha^2 T_c \left\{ \frac{1}{b} + 4k_B T_c \left(\frac{L}{2\pi}\right)^3 \int d^3q \, \frac{1}{[-2a + cq^2]^2} \right\}$$

where a conversion to an integral was made using $\sum_q \to \left(\frac{L}{2\pi}\right)^3 \int d^3q$ for a 3-dimensional sum.

Define $s = \sqrt{\frac{c}{2a}}\, q$. Then

$$C_v \sim \frac{1}{b} + 4k_B T_c \left(\frac{L}{2\pi}\right)^3 \frac{1}{(2ac^3)^{1/2}} \int d^3s \, \frac{1}{(s^2-1)^2}$$

The ratio of the second term to the first is

$$\frac{2^{nd}}{1^{st}} \sim \frac{k_B T_c b}{(ac^3)^{1/2}} = \frac{k_B T_c \, b}{\sqrt{\alpha(T-T_c)\, c^3}}$$

Fluctuation are as impotant as the mean field term when this ratio ~ 1 :

$$\frac{2^{nd}}{1^{st}} \sim \frac{\text{fluctuation energy}}{\text{mean field energy}} \sim k_B T_c \frac{b}{\sqrt{\alpha c^3 (T-T_c)}}$$

This means that fluctuations begin to dominate the critical behavior as $T \to T_c$, and mean field theory fails.

<u>Length scales</u>. An important insight can be obtained by considering length scales in the problem. Using the methods illustrated above, we can evaluate the averages

$$\langle \varphi_i(\vec{r}) \rangle = \frac{1}{Z} \int \mathcal{D}\varphi \; \exp[-\beta F(\varphi)] \, \varphi(\vec{r})$$

$$\langle \varphi(\vec{r}) \varphi(\vec{r}') \rangle = \frac{1}{Z} \int \mathcal{D}\varphi \; \exp[-\beta F(\varphi)] \varphi(\vec{r}) \varphi(\vec{r}')$$

and thus form a correlation function

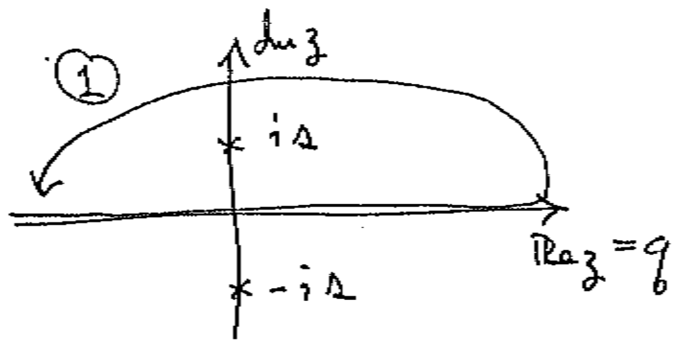
$$k_B T \chi(\vec{r}) = \langle \varphi(0) \varphi(r) \rangle - \langle \varphi \rangle \langle \varphi \rangle$$

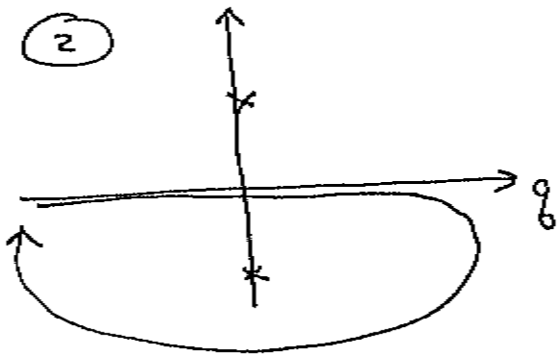
The result would be, in q transformed form, write

$$\chi(\vec{r}) = -\frac{1}{2c(2\pi)^2 ir}\int_{-\infty}^{\infty}\frac{q\sinh(iqr)\,dq}{(q+i\lambda)(q-i\lambda)}$$

$$= \frac{1}{c(2\pi)^2 ir}\left\{\int_{-\infty}^{\infty}\frac{q e^{-iqr}}{(q+i\lambda)(q-i\lambda)}dq - \int_{-\infty}^{\infty}\frac{q e^{iqr}}{(q+i\lambda)(q-i\lambda)}dq\right\}$$

Extending the integrals to the complex plane, two contours are possible:





For convergence, choose 1 for the second integral and 2 for the first. We then obtain, using calculus of residues,

$$\chi(r) = \frac{1}{c(2\pi)^2 ir}\left\{+2\pi i\left(\frac{-i\lambda e^{-\lambda r}}{-2i\lambda}\right) + 2\pi i\left(\frac{i\lambda e^{-\lambda r}}{2i\lambda}\right)\right\}$$

-1 for clockwise path

$$\chi(q) = \beta \langle \psi_q \psi_q^* \rangle$$

$$= \frac{1}{2(-2a + c\,q^2)}$$

Transforming back to real space

$$\chi(\vec{r}) = \frac{1}{(2\pi)^3} \int d^3q \, \frac{e^{i\vec{q}\cdot\vec{r}}}{2(-2a + c\,q^2)}$$

For $T < T_c$, write $a = -\alpha t$, $t = T_c - T$, and simplify into spherical coordinates:

$$\chi(\vec{r}) = \frac{-1}{2c(2\pi)^3} \int \frac{q^2\,dq\; d(\cos\theta)\; d\varphi\; e^{iqr\cos\theta}}{\Delta^2 + q^2}$$

where $\Delta^2 = \frac{2\alpha t}{c}$. Then with $\cos\theta = u$,

$$\chi(\vec{r}) = -\frac{2\pi}{2c(2\pi)^3} \int_0^\infty \int_{-1}^{1} \frac{q^2\,dq\; du\; e^{iqru}}{(q + i\Delta)(q - i\Delta)}$$

$$= -\frac{1}{2c(2\pi)^2} \int_0^\infty \frac{q^2\,dq}{(q+i\Delta)(q-i\Delta)} \cdot \frac{2\sinh(iqr)}{i\,qr}$$

Since the integrand is even in q, we can or

$$\boxed{\chi(r) = \frac{1}{2\pi c} \frac{e^{-\lambda r}}{r}}$$

The quantity

$$\frac{1}{\lambda} = \sqrt{\frac{c}{2\alpha(T_c - T)}}$$

is a length characteristic of the fluctuations. As $T \to T_c$, this length diverges. This is the correlation length, and is commonly defined by the symbol $\xi = \frac{1}{\lambda}$.

Critical Exponents

The key feature of ξ is the power law dependence on temperature:

$$\xi \sim |T - T_c|^{-1/2}$$

The exponent can be measured experimentally and calculated using a variety of methods. Example results are:

Experiment	2 dimensional Ising	3 dimensional Ising	3 dimensional Heisenberg
0.6–0.7	1	0.64	0.7

The value $1/2$ is called the 'mean field' result. It differs from experiment and differs from other theoretical results for 1, 2, 3 and 4 dimensional systems.

Several exponents can be defined, and studied as functions of reduced temperature t:

$$t = \frac{T - T_c}{T_c}$$

These include

Heat capacity $C \sim |t|^{-\alpha}$

Order parameter $\varphi \sim |t|^{\beta}$

Susceptibility $\chi \sim |t|^{-\gamma}$

Correlation length $\xi \sim |t|^{-\nu}$

General relations between these exponents have been discovered, and values are the same for systems falling in the same 'universality class'. The theory for our understanding of critical exponents is called the "renormalization group".

Exercise. Start with a free energy density for a one dimensional system with order parameter $\Phi(x)$ that undergoes an order-disorder phase transition:

$$F[\Phi(x)] = -\frac{\alpha}{2}(T_c - T)\Phi^2 + \frac{b}{4}\Phi^4 + \frac{c}{2}\left(\frac{d}{dx}\Phi\right)^2$$

a) What are the two values of Φ for a uniform phase with $T < T_c$?

Suppose the system goes toward one of these values as $x \to +\infty$, but toward the other value as $x \to -\infty$.

b) Show that the variational calculus gives the equation

$$c\frac{\partial^2}{\partial x^2}\Phi(x) = -\alpha(T_c - T)\Phi(x) + b\Phi^3(x)$$

for $\Phi(x)$ to minimise $F[\Phi]$.

c) Solve the equation in b) to obtain

$$\Phi(x) = \Phi_0 \tanh(x/l)$$

and determine l. This equation applies for $\Phi \to \pm\Phi_0$ as $x \to \pm\infty$. Hint: obtain a first integral for the differential equation in b).

<u>Exercise</u>. Calculate the temperature dependence of the quantity

$$r(T) = \beta F(\Phi_0)\,\xi$$

where

$$F(\Phi) = \frac{1}{2}\alpha(T-T_c)\,\Phi^2 + \frac{b}{4}\Phi^4$$

and $F(\Phi_0)$ is the minimal value. Do this for i) 2 dimensional systems, and ii) 4 dimensional systems.

<u>Exercise</u> Show that $\chi(q) = \beta\langle \psi_q \psi_q^* \rangle \simeq \dfrac{1}{2(-2a+cq^2)}$