

Physics 127b: Statistical Mechanics

Fluctuations at a Second Order Transition

We can use the Landau free energy to investigate *fluctuations* of the order parameter and so the validity of mean field theory, and the expansion itself.

Remember that in the canonical ensemble the probability of a macroscopic configuration is proportional to $\exp(-\beta \Delta A)$, where ΔA is the change in the Helmholtz free energy arising from the change in configuration. Thus we have for a configuration $m(\vec{r})$ of the Ising ferromagnet order parameter

$$P(m(\vec{r})) \propto e^{-\beta A(m(\vec{r}))} \quad (1)$$

with $A(m(\vec{r}))$ given by the Landau expansion.

Let's hope that fluctuations are small about the mean we calculated, i.e. $\delta m = m - \bar{m}$ is small. Then we have

$$\begin{aligned} T > T_c, \quad \bar{m} = 0, \quad f(\delta m) &= a(T - T_c)\delta m^2 + \gamma (\vec{\nabla} \delta m)^2 \\ T < T_c, \quad \bar{m} = \sqrt{a(T_c - T)/b}, \quad f(\delta m) &= 2a(T - T_c)\delta m^2 + \gamma (\vec{\nabla} \delta m)^2 \end{aligned} \quad (2)$$

Note $f(\delta m)$ provides the effective potential for small fluctuations in the quadratic minimum. Since the forms above and below T_c are basically the same, let's work with the expression

$$f(\delta m) = a_1 \delta m^2 + \gamma (\vec{\nabla} \delta m)^2 \quad (3)$$

It is useful to go to Fourier notation:

$$\delta m = \sum_{\vec{q}} m_{\vec{q}} e^{i\vec{q} \cdot \vec{r}} \quad (4a)$$

$$m_{\vec{q}} = \frac{1}{V} \int \delta m(\vec{r}) e^{-i\vec{q} \cdot \vec{r}} \quad (4b)$$

and then

$$\int (\delta m)^2 d^3 r = \int d^3 r \sum_{\vec{q}} \sum_{\vec{q}'} m_{\vec{q}} m_{\vec{q}'} e^{i(\vec{q} + \vec{q}') \cdot \vec{r}} \quad (5a)$$

$$= V \sum_{\vec{q}} m_{\vec{q}} m_{-\vec{q}} = V \sum_{\vec{q}} |m_{\vec{q}}|^2 \quad (5b)$$

where we have used $m_{-\vec{q}} = m_{\vec{q}}^*$ (δm real) in the last step.

This gives for the free energy for a magnetization configuration

$$A = A(\bar{m}) + V \sum_{\vec{q}} (a_1 + \gamma q^2) |m_{\vec{q}}|^2 \quad (6)$$

This is now used in Eq. (1) to give the probability of $m_{\vec{q}}$ and so $m(\vec{r})$. We notice that the free energy is the sum of quadratic terms, so that the probability distribution $e^{-\beta A}$ is the product of Gaussians in the $m_{\vec{q}}$, yielding for the ensemble average of the fluctuations:

$$\langle |m_{\vec{q}}|^2 \rangle = \frac{k_B T}{2V(a_1 + \gamma q^2)} \quad (7)$$

The quantity $\langle |m_{\vec{q}}|^2 \rangle$ is proportional to the static structure factor $S(\vec{q})$ that would be measured, for example, in spin dependent X-ray or neutron scattering. Fourier transforming back gives us the correlation function.

The correlation function $G(\vec{r})$ is defined by

$$G(\vec{r}) = \langle m(\vec{r})m(0) \rangle - \bar{m}^2 \quad (8a)$$

$$= \langle \delta m(\vec{r})\delta m(0) \rangle. \quad (8b)$$

Now introducing the Fourier transform

$$G(\vec{r}) = \left\langle \sum_{\vec{q}} m_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} \sum_{\vec{q}'} m_{\vec{q}'} \right\rangle \quad (9a)$$

$$= \left\langle \sum |m_{\vec{q}}|^2 e^{i\vec{q}\cdot\vec{r}} \right\rangle \quad (9b)$$

where we have used $\langle m_{\vec{q}}m_{-\vec{q}'} \rangle \propto \delta_{\vec{q}\vec{q}'}$ since fluctuations in different modes will be uncorrelated.

To see this it is best to go to real and imaginary parts—usually the best way to be really sure of fluctuations in Fourier space (are m_q and m_q^* independent or not?)—i.e.

$$\delta m_q = R_q + i I_q \quad (10a)$$

$$\delta m_{-q} = R_q - i I_q \quad (10b)$$

where we have used $\delta m(\vec{r})$ real to get $R_{-q} = R_q$ and $I_{-q} = -I_q$. Then we can write Eq. (6) as

$$A = A(\bar{m}) + 2V \sum_{\vec{q}>0} (a_1 + \gamma q^2)(R_q^2 + I_q^2). \quad (11)$$

Note that we have replaced $\sum_{\vec{q}}$ by $2 \sum_{\vec{q}>0}$, i.e. a sum over some conveniently defined positive half space, since the fluctuations at \vec{q} and $-\vec{q}$ are not independent. Now Eq. (11) is truly the sum of independent quadratic terms. This means $R_{\vec{q}}$ and $I_{\vec{q}}$ (for all $\vec{q} > 0$) are independent. Gaussian, fluctuating variables, and in particular equipartition gives

$$\langle R_q^2 \rangle = \langle I_q^2 \rangle = \frac{k_B T}{4V(a_1 + \gamma q^2)}. \quad (12)$$

It is easy to see $\langle m_q m_{q'} \rangle = 0$ if $|\vec{q}| \neq |\vec{q}'|$ and

$$\langle m_q m_q \rangle = \langle R_q^2 - I_q^2 \rangle = 0 \quad (13)$$

since $\langle R_{\vec{q}} I_{\vec{q}'} \rangle = 0$ for any \vec{q}, \vec{q}' , and

$$\langle m_q m_{-q} \rangle = \langle m_q m_q^* \rangle = \langle R_q^2 + I_q^2 \rangle = \frac{k_B T}{2V(a_1 + \gamma q^2)}, \quad (14)$$

as surmised in Eq. (7).

Using the Eq. (7) and converting the \vec{q} -sum to an integral in the usual way gives

$$G(\vec{r}) = \frac{k_B T}{2V} \frac{V}{(2\pi)^3} \int d^3 q \frac{e^{i\vec{q}\cdot\vec{r}}}{a_1 + \gamma q^2}. \quad (15)$$

The integral may be done (we did a similar integral in the Thomas-Fermi model of a screened charge in an electron gas) to give

$$G(\vec{r}) = \frac{k_B T}{8\pi\gamma} \frac{e^{-r/\xi}}{r} \quad (16)$$

defining the *correlation length* $\xi = (\gamma/a_1)^{1/2}$, or explicitly

$$\xi(T) = \begin{cases} \left(\frac{\gamma}{a}\right)^{1/2} (T - T_c)^{-1/2} & \text{for } T > T_c \\ \left(\frac{\gamma}{2a}\right)^{1/2} (T_c - T)^{-1/2} & \text{for } T < T_c \end{cases} \quad (17)$$

Fluctuations occur over correlated regions of size $\xi(T)$ which *diverges* approaching the critical temperature from above or below.

These results for $S(\vec{q})$, $G(\vec{r})$, and the correlation length are known as *Ornstein-Zernike* theory.

When is mean field theory good?

The expression (7) shows that the mean square fluctuations at *long wavelengths* diverge towards T_c

$$\langle |m_{\vec{q} \approx 0}|^2 \rangle = \frac{k_B T}{2V a_1} \quad (18)$$

Close enough to T_c the fluctuations will become as important as the mean, and the simple expressions in terms of \bar{m} will break down. We estimate the temperature T_G when this happens by asking when the fluctuations over a correlation volume will be comparable to the mean, i.e. by setting

$$\langle \delta m(\xi) \delta m(0) \rangle = \bar{m}^2, \quad (19)$$

which gives

$$\frac{k_B T_G}{8\pi\gamma} \frac{e^{-1}}{\xi} = \frac{a(T_c - T_G)}{b} \quad (20)$$

or since $T_c - T_G$ will usually be small

$$\frac{T_c - T_G}{T_c} = \frac{b^2 k_B^2 T_c}{32\pi^2 e^2 a \gamma^3}. \quad (21)$$

This is known as the *Ginzburg criterion*. For temperatures closer to T_c than T_G fluctuations cannot be neglected, and mean field theory will be unreliable. A similar region above T_c is expected to be dominated by fluctuations. The region near T_c where fluctuations are important is known as the *critical region*. Outside of this range, mean field theory should be a good approximation. I have used the Ginzburg approach to calculate the range, since the numerical factors are quite large, and give a more reliable estimate of the critical region. Perhaps a better intuitive understanding is given by demanding that the free energy of the ordering over a correlation volume be greater than $k_B T_c$ for fluctuations to be small, i.e.

$$\delta f \xi^3 \gtrsim k_B T_c \quad (22a)$$

$$\frac{a^2 (T_c - T_G)^2}{2b} \left(\frac{\gamma}{2a(T_c - T_G)} \right)^{3/2} \gtrsim k_B T_c. \quad (22b)$$

We conclude that *close enough* to T_c mean field theory will *always* break down, and fluctuations become important. Since the Landau expansion itself is also only useful “near T_c ” there may in fact be no range of temperatures over which mean field theory is quantitatively accurate, although even in these cases it remains a useful qualitative guide. However the Ginzburg criterion depends on physical parameters of the

system, and some systems are accurately described by mean field theory except *very* close to T_c . One example is superconductivity, where the correlation length is long compared to atomic scales (roughly $\xi \sim \xi_0(1 - T/T_c)^{-1/2}$ where ξ_0 is larger than atomic scales by a factor $T_F/T_c \sim 10^4$). Since ξ appears cubed in the Ginzburg criterion (we are interested in fluctuations over the correlation *volume*), the critical region is unobservably small, e.g. $(1 - T_G/T_c) \sim 10^{-9} - 10^{-12}$, and mean field theory is highly accurate for practical temperature ranges.