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

$$P(m(\vec{r})) \propto e^{-BA(m(\vec{r}))} \tag{1}$$

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

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

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, lets work with the expression

$$f(\delta m) = a_1 \delta m^2 + \gamma \left(\vec{\nabla}\delta m\right)^2 . \tag{3}$$

It is useful to go to Fourier notation:

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

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

and then

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

$$= V \sum_{\vec{q}} m_{\vec{q}} m_{-\vec{q}} = V \sum_{\vec{q}} \left|m_{\vec{q}}\right|^2 \tag{5b}$$

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

This gives for the free energy for a magnetization configuration

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

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_q, yielding for the ensemble average of the fluctuations:

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

The quantity $\left\langle |m_{\vec{q}}|^2 \right\rangle$ 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

$$G(\vec{r}) = \langle m(\vec{r})m(0)\rangle - \bar{m}^2 \tag{8a}$$
$$= \langle \delta m(\vec{r})\delta m(0)\rangle \,. \tag{8b}$$

Now introducing the Fourier transform

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

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.
>
> $$\delta m_q = R_q + i I_q \tag{10a}$$
> $$\delta m_{-q} = R_q - i I_q \tag{10b}$$
>
> 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
>
> $$A = A(\bar{m}) + 2V \sum_{\vec{q}>0} (a_1 + \gamma q^2)(R_q^2 + I_q^2). \tag{11}$$
>
> 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
>
> $$\langle R_q^2 \rangle = \langle I_q^2 \rangle = \frac{k_B T}{4V(a_1 + \gamma q^2)}. \tag{12}$$
>
> It is easy to see $\langle m_q m_{q'}\rangle = 0$ if $|\vec{q}| \neq |\vec{q}'|$ and
>
> $$\langle m_q m_q \rangle = \langle R_q^2 - I_q^2 \rangle = 0 \tag{13}$$
>
> since $\langle R_{\vec{q}} I_{\vec{q}'}\rangle = 0$ for any $\vec{q}, \vec{q}'$, and
>
> $$\langle m_q m_{-q}\rangle = \langle m_q m_q^* \rangle = \langle R_q^2 + I_q^2 \rangle = \frac{k_B T}{2V(a_1 + \gamma q^2)}, \tag{14}$$
>
> as surmised in Eq. (7).

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

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

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

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

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

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

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

$$\left\langle \left| m_{\vec{q}\simeq 0} \right|^2 \right\rangle = \frac{k_B T}{2 V a_1}. \tag{18}$$

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

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

which gives

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

or since $T_c - T_G$ will usually be small

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

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.

$$\delta f\, \xi^3 \gtrsim k_B T_c \tag{22a}$$

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

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.