Chapter 3

LANDAU THEORY OF PHASE TRANSITIONS

1. Second order phase transitions

The typical behavior of the order parameter $\eta(P, T)$ at a phase transition is shown in Fig. 3.1. For a second order phase transition –also

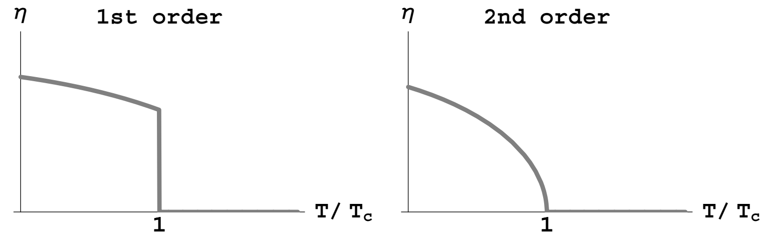

Figure 3.1. Typical behavior of the order parameter η as a function of temperature. Below the critical temperature T_c there is a finite value of the order parameter, which vanishes for $T > T_c$

refereed to as a continuous phase transition, η is small close to T_c. We assume that here the Gibbs free energy $G(P, T, \eta)$ can be expanded in terms of η:

$$G = G_0 + \alpha\eta + A\eta^2 + C\eta^3 + B\eta^4 + \ldots \, . \tag{3.1}$$

The coefficients in the Landau[1] expansion α, A, C, and B are function of P and T. G_0 is a function of P and T, but by definition independent of

[1] Lev Davidovich Landau, (Baku 1908 - Moscow 1968). Landau's work covers all branches of theoretical physics, ranging from fluid mechanics to quantum field theory. To many topics he made seminal contributions and his importance for the development of Russian physics cannot be underestimated. He received the 1962 Nobel Prize in Physics "for his pioneering theories for condensed matter, especially liquid helium".
Landau made a very strong impression on his contemporaries thanks to his brilliant intellect and great outspokenness. The story goes that Landau had a logarithmic scale with which he ranked theoretical physicists, with Einstein on top. After working out Landau-Ginzburg theory he moved himself up by half a notch.
During a period of vast repression in he former Soviet Union, in 1938, Landau was imprisoned for a year. Lev D. Landau, as well as Vladimir A. Fock, were saved from death in Stalin's

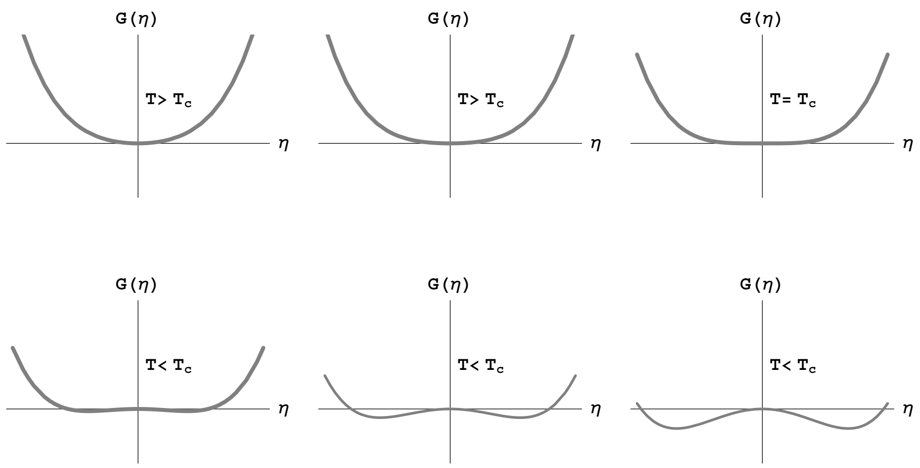

Figure 3.2. Second order phase transition: dependence of the Landau free energy on the orderparameter η above and below the phase transition temperature T_c.

η. We know that above T_c, η is vanishing and below T_c, η has some finite value. The minimum of the free energy below T_c should therefore occur at $\eta \neq 0$ and above T_c at $\eta = 0$. From this we conclude immediately that $\alpha = 0$ (for systems without external fields), because otherwise $\eta \neq 0$ at all temperatures. Also the coefficient A in front of the quadratic term in the free energy should be *positive* for $T > T_c$ (minimum at $\eta = 0$) and negative at $T < T_c$ (minimum of G at $\eta \neq 0$). The simplest choice is

$$A(P,T) = a(T - T_c), \tag{3.2}$$

which is valid close to T_c. The condition that η be finite below T_c requires $B(P,T) > 0$, so that the free energy can be expanded as $G = G_0 + a(T - T_c)\eta^2 + B\eta^4$ (setting $C = 0$ for the moment). The behavior of η can be found by minimizing the Gibbs free energy: $\frac{\partial G}{\partial \eta} = 0 \Rightarrow$

$$\begin{aligned} &2a(T - T_c)\eta = -4B\eta^3 \Leftrightarrow \\ &\eta^2 = \frac{a(T_c - T)}{2B} \qquad (T < T_c) \\ &\eta = 0 \qquad\qquad\quad\; (T > T_c) \end{aligned} \tag{3.3}$$

prisons by the eminent experimental physicist Pyotr L. Kapitza. Kapitza wrote a letter to the Great Teacher and Friend of the Soviet People Joseph Stalin in which he declared to stop his scientific work unless Landau was released. Kapitza was greatly respected for his courage.

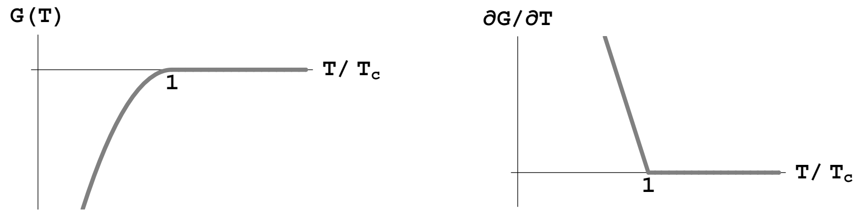

Figure 3.3. A phase transition is of nth order when there is a discontinuity in the nth derivative of the free energy with respect to temperature at $T = T_c$. In this example the first derivative has a kink at T_c. This corresponds to a 2^{nd} order phase transition, as the second derivative is discontinuous.

The minimum of the Gibbs free energy itself is

$$G_{\min} = A\eta^2 + B\eta^4 = -\frac{a^2}{4B}(T_c - T)^2 \tag{3.4}$$

plus some constant. Thus G is continuous at the phase transition (and so is e.g. the Helmholtz free energy F, when we work at fixed volume V). The higher derivatives of the the free energy, however, are not all continuous. $\frac{\partial G}{\partial T}$ has a kink at $T = T_c$ This defines a *second order* phase transition: in the classification scheme of Ehrenfest a n^{th} order phase transition has a discontinuity in the n^{th} derivative of the free energy with respect to temperature $\frac{\partial^n G}{\partial T^n}$. In principle a, B and T_c depend on pressure. Normally $T_c(P)$ is the most important, while a and B can be taken pressure independent.

2. Weakly first order phase transitions

Symmetry considerations reveal which terms appear in the Landau free energy expansion. For instance, if the order parameter is a vector η but the Hamiltonian does not depend on the direction of η, then the lowest order invariants that can appear in the expansion are $\eta \cdot \eta = \eta^2$, η^4, η^6 etc: symmetry dictates that in this case all odd terms of the free energy expansion are zero. However, the situation can also arise that the term η^3 is allowed by symmetry. Thus we have to take this term into account, and in the spirit of Landau, assume the most general and simple form of its coefficient C. In this case we assume C to be constant and negative; $C < 0$. The free energy as a function of order parameter at different temperatures is shown in Fig 3.4.

At $T > T^*$ there is one minimum, at $\eta = 0$. At the spinodal temperature T^* a second (local) minimum in the free energy starts to develop. At

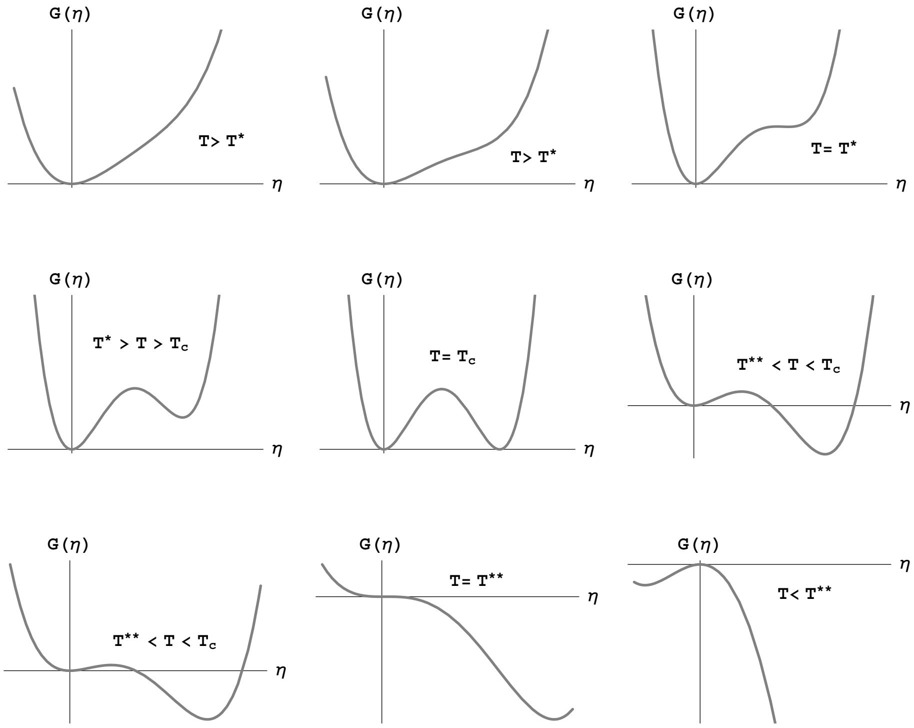

Figure 3.4. Free energy for a first order phase transition for different temperatures. The spinodal temperatures are T^* and T^{**} and T_c is the transition temperature. Note that at $T = T_c$ there is a discontinuous jump of the order parameter from zero to a finite value.

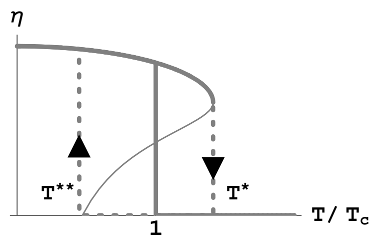

Figure 3.5. Hysteretic behavior of the order parameter signals a first order phase transition.

the phase transition temperature T_c there are two minima, separated by a hump in the free energy, but with equal G. At lower temperatures the minimum with $\eta \neq 0$ is the absolute minimum of the free energy. As a result there exists a first order (jump like) phase transition at T_c from $\eta = 0$ to some finite value η_c. At even lower temperatures there is a second spinodal point at $T = T^{**}$. The temperatures T^* and T^{**} are limits of overheating and over-cooling. Such behavior gives rise to hysteresis effects, which are indicative of first order phase transitions.

Another route to first order phase transitions. Suppose the coefficient $C = 0$ by symmetry and we have

$$G(P,T) = A(P,T)\eta^2 + B(P,T)\eta^4. \tag{3.5}$$

We assumed previously that $B(P,T_c) > 0$. But as $B(P,T_c)$ is a function of pressure, it might be that at T_c it assumes negative value: $B(P,T_c) < 0$. We then have a situation without a minimum of the free energy at any finite value of η (the free energy just decreases more and more when η becomes larger and larger). In this case, of course, we have to include higher order terms in η, as we assumed that η is a good expansion parameter (which it is if the transition is *weakly* first order). So we have $G = A\eta^2 + B\eta^4 + D\eta^6$, with $D > 0$. In this case the free energy has the form shown in Fig. 3.6.

The transition will thus be first order. We conclude that at the point where $B(P,T)$ changes sign a second order phase transition goes over to a first order phase transition. This is called the tri-critical point.

Critical points. In principle there may also exist phase transitions *without* change of symmetry. Such a phase transition is always first

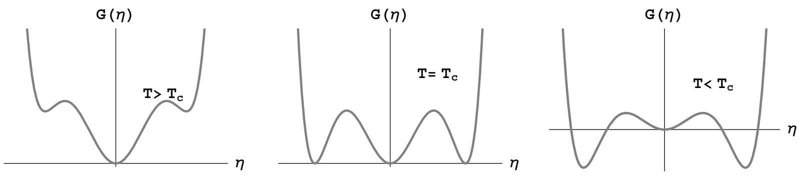

Figure 3.6. Free energy for a first order phase transition for different temperatures due to a negative quartic term in the Landau expansion. The temperature $T = T_c$ is a tri-critical point with three absolute minima in the free energy.

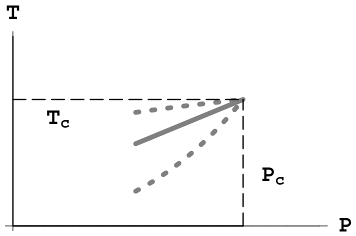

Figure 3.7. First order phase transition ending in a critical point (P_c, T_c). The transition and spinodal temperatures are indicated.

order. An example is the liquid-gas transition. Such a transition can end in a critical point (P_c, T_c). As in this case there is no change in symmetry across the 1^{st} order phase transition, one can in principle go from one phase to the other continuously by moving around the critical point. For a second order phase transition this is impossible because the symmetry of the two phases is different.

Phase transitions where the symmetry does not change are encountered not only in the liquid-gas transitions but also in many isomorphic phase transitions such as the structural and electronic γ-α phase transition in metallic Cerium, or the metal insulator transition in the transition metal oxide V_2O_3. In the latter case the experimental phase diagram is shown schematically in Fig. 3.8 and the point B is a critical point. The "Mott" transition between a non-magnetic metal and a non-magnetic insulator takes place across the line AB. Note that the phase line AB is such that with increasing temperature we go from the metallic to the high temperature insulating state. Apparently the entropy of the insulating state is higher than that of the metallic phase. The reason for this is that in the metallic state a Fermi-surface is formed. This is an ordered state in the sense that it is a unique ground state, where only fluctuation in the few states around the Fermi level contribute to the entropy at finite temperature. Most states lie deep within the Fermi sea and effectively do not contribute to the entropy. We will encounter

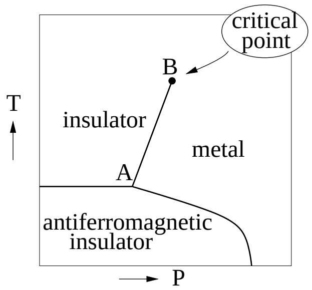

Figure 3.8. Schematic phase diagram of V_2O_3, after D.B. McWhan et al., Phys. Rev B. **7** 1920 (1973).

this consequence of the Pauli principle again when we calculate the temperature dependence of specific heat for a Fermi gas. Above the Mott transition temperature we have an insulating state with localized electrons. Localized electrons have localized spins. Disordering of these spins contributes $k_{\mathrm{B}} \ln 2$ per spin to the entropy. Therefore with increasing temperature the system goes from a state with lower, to a state with higher entropy, as one would expect from the free energy $F = E - TS$, that favors disordered (high entropy) states at high temperatures.

Exercise 3.1.
3.1.0. Find the behavior of the specific heat at fixed pressure C_p at a second order phase transition, for $T > T_c$ and $T < T_c$. Remember that G_0 depends on temperature. Show that $\partial G_0(T, P)/\partial T$ has to be finite because the entropy has to vanish at $T = 0$ (Nernst theorem) $\partial^2 G_0(T, P)/\partial T^2$ can be taken as zero.
3.1.1. Show that the total entropy connected with the ordering

$$S_{\mathrm{ord}} = \int_0^{T_c} dT C_p(T)/T.$$

Exercise 3.2.
The *susceptibility* χ is a measure for the sensitivity of the order parameter η to an infinitesimal (externally applied) conjugate field h:

$$\chi \equiv \left.\frac{\partial \eta}{\partial h}\right|_{h \to 0}.$$

The contribution to the free energy of the external field is $-\eta h V$, where V is the volume of the system. Calculate the temperature dependence of the the susceptibility close to the second order phase transition; show that

$$\chi(T) = \frac{V}{2a(T-T_c)}, \quad (T > T_c) \quad \text{and} \quad \chi(T) = \frac{V}{4a(T_c-T)}, \quad (T < T_c).$$

Note that at the phase transition the susceptibility actually diverges: the system becomes infinitely sensitive to external perturbations.

End 2nd half lecture 3

3. Inhomogeneous situation

Up to now we only considered order parameters that are homogeneous: we assumed that e.g. the magnetization is the same in the whole system, so independent of the position $\mathbf{r}$. Sometimes we also need to consider inhomogeneous situations. For instance, close to a surface the order parameter will, by definition, be inhomogeneous. Then the order parameter $\eta = \eta(\mathbf{r})$ and the total free energy is

$$G = \int d^3\mathbf{r}\{ \text{ free energy density } G(\mathbf{r})\}. \tag{3.6}$$

Again G can be expanded in terms that are quadratic, cubic, etc., in $\eta(\mathbf{r})$, just as before depending in the symmetry of the system.

However, now the order parameter can also be varying over distance. In general the energy cost of a *slow* variation of the order parameter $\eta(\mathbf{r})$ is proportional to $\frac{\partial \eta}{\partial \mathbf{r}} = \vec{\nabla}\eta$. For instance for a ferromagnet the spins tends to be aligned parallel: $\uparrow\ \uparrow\ \uparrow\ \uparrow\ \uparrow$ and a slow variation in space means $\uparrow\ \nearrow\ \rightarrow\ \searrow\ \downarrow\ \swarrow\ \leftarrow\ \nwarrow\ \uparrow$, which costs an energy that is proportional to the rate of variation. A variation is slow when its wavelength is much larger than the typical spacing between the spins (the lattice spacing). The only *invariant* (i.e. the only quantity independent of spatial orientation) containing $\vec{\nabla}\eta(\mathbf{r})$ is $|\vec{\nabla}\eta(\mathbf{r})|^2$. Thus

$$G = \int d^3\mathbf{r}\{A(P,T)\eta^2(\mathbf{r}) + B\eta^4(\mathbf{r}) + D|\vec{\nabla}\eta(\mathbf{r})|^2\}. \tag{3.7}$$

This is the Ginzburg-Landau functional (a functional of the function $\eta(\mathbf{r})$), which is widely used in the theory of superconductivity and in the discussion of domain walls in ferromagnets. When we allow for the possibility that η is a complex quantity, we have to substitute in the equations above the squared terms with absolute values squared. A straightforward variational calculation gives the following condition for minimization of the free energy:

$$A\eta + 2B\eta|\eta|^2 - D\vec{\nabla}^2\eta = 0 \tag{3.8}$$

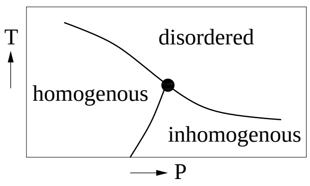

Figure 3.9. Typical phase diagram for systems with a transition from a homogenous to an inhomogeneous order parameter.

which, due to the presence of the gradient term, is now a differential equation, not unlike the Schrodinger equation, but with a non-linear term $\sim \eta^3$. Close to T_c when $\eta \to 0$ the equation can be linearized and corresponds exactly to the Schrödinger equation.

What happens if $D(P,T)$ becomes negative? The system will have the internal tendency to form a non-homogeneous ordered state, i.e. it is favorable to have $\vec{\nabla}\eta(r) \neq 0$. Instead of for instance a ferromagnetic state, a spiral state,

$$\uparrow \quad \nearrow \quad \rightarrow \quad \searrow \quad \downarrow \quad \swarrow \quad \leftarrow \quad \nwarrow \quad \uparrow \quad \nearrow,$$

is more stable. Again, in order to stabilize the free energy, we have to add the next term allowed by symmetry in the free energy expansion, which in this case is $E(\vec{\nabla}^2\eta)^2$, with $E > 0$. In order to proceed with the calculation we can expand the order parameter in Fourier coefficients, without loss of generality, but paying the price of somewhat more elaborate expressions. Instead we assume that $\eta(\mathbf{r}) = \eta e^{i\mathbf{k}\cdot\mathbf{r}}$ so that $(\vec{\nabla}\eta)^2 = |\mathbf{k}|^2\eta^2$ (thus we consider only a single Fourier component of η). The wave-vector k_0 that minimizes the free energy is then given by

$$\frac{\partial}{\partial k^2}\left[Dk^2\eta^2 + Ek^4\eta^2\right] = 0 \Rightarrow k_0^2 = -\frac{D}{2E} \quad (D < 0 \text{ and } E > 0). \tag{3.9}$$

This implies that in this case a structure with wave-vector k_0 or with a period $l = 2\pi/k_0$ will be formed. Structures with a different wavevector are higher in energy, so that our assumption that η has a single Fourier component is *a posteriori* justified. In a solid the additional structure is superposed on the lattice periodicity and is therefore referred to as a *superstructure*. In general the period of this superstructure is incommensurate relative to the underlying lattice periodicity (i.e. it is not a multiple of the lattice periodicity).

The point where the coefficient D changes sign is called the Lifshits point. It signals the transition from a homogeneous ordering to an inhomogeneously ordered phase. The typical phase diagram is shown in Fig. 3.9. Such a transition occurs e.g. in the phase diagram of $CuGeO_3$ in a magnetic field (a spin-Peierls system that we will discuss later).

In general, for certain symmetry classes, in the free energy also invariants that are *linear* in the derivatives can appear, (e.g. $\mathbf{M} \cdot (\vec{\nabla} \times \mathbf{M})$ in magnetic systems). Such terms give rise to *helicoidal* structures (even in the case where $D > 0$). This is actually the situation in many rare-earth metals.

Exercise 3.3.
Consider a magnetic phase transition in a compressible lattice, where the magnetic order (η) induces a lattice deformation u. The Gibbs free energy is now

$$G = A\eta^2 + B\eta^4 + bu^2 + \gamma\eta^2 u \tag{3.10}$$

where the last term couples the two order parameters.
Show that if the coupling to the lattice is sufficiently strong the phase transition goes from being 2^{nd} to 1^{st} order. Determine the critical coupling parameter γ_c.

This illustrates a rather general rule: coupling to other degrees of freedom gives a tendency to make phase transitions first order.

4. Fluctuations

The Landau theory is essentially a mean field theory: fluctuations of the order parameter are neglected. Close to T_c however, fluctuations are important. They modify the behavior of physical quantities close to T_c (e.g. of specific heat or magnetization) and give deviations from the scaling exponents given by mean field theory (where the order parameter scales as $(\frac{T_c-T}{T_c})^{1/2}$). To determine scaling exponents for various physical (quantum) models is an important subject in present day statistical mechanics.

It is possible, however, to determine the validity of Landau theory, within the theory itself. When dealing with a 2^{nd} order phase transition we can determine how large the fluctuation region in terms of the reduced temperature $\frac{T_c-T}{T_c}$ actually is. Outside the fluctuation region, the Landau theory holds without restrictions.

In order to determine the fluctuation region we investigate fluctuations of the order parameter η in the ordered state, close to T_c. Suppose the order parameter has the value $\bar{\eta}$ in this situation. What is then the probability to find a disordered region of volume V, where the order

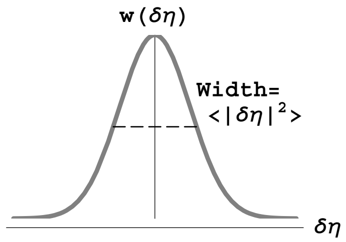

Figure 3.10. Distribution function $w(\delta\eta)$ for fluctuations of the orderparameter $\delta\eta$.

parameter is η instead of $\bar{\eta}$?. The difference in free energy of the fluctuation with respect to the homogeneously ordered state is, in a Taylor expansion

$$\delta G = \frac{1}{2}(\eta - \bar{\eta})^2 \left.\frac{\partial^2 G}{\partial \eta^2}\right|_{\eta=\bar{\eta}} = a(T - T_c)(\eta - \bar{\eta})^2 \equiv a(T - T_c)(\delta\eta)^2, \tag{3.11}$$

where in the last line we introduced the fluctuation amplitude $\delta\eta$. The probability w for this fluctuation to occur is[2]

$$w(\delta\eta) \propto e^{-V\delta G/T} = e^{-a(T-T_c)V(\delta\eta)^2/T}. \tag{3.12}$$

The width of the fluctuation distribution determines the typical amplitude of the fluctuation

$$\langle|\delta\eta|^2\rangle = \frac{T}{aV(T - T_c)}. \tag{3.13}$$

Clearly, close to T_c the fluctuation amplitude diverges. On the other hand the energy associated with a fluctuation scales with the volume V in which the order parameter fluctuates. When the region in which the order parameter can fluctuate is small, the amplitude of the fluctuations is large. In order to proceed, we wish to determine the typical size of the fluctuations (i.e. the typical volume of a fluctuation), as our aim is to compare the amplitude of fluctuations of the order parameter with the amplitude of the order parameter itself. If we can establish that $|\delta\eta|^2 \ll \eta^2$ under some conditions, we know that under these conditions the mean field results are reliable.

[2]see, e.g., Landau and Lifshits, Statistical Physics, Part 1, §146

End 1st half lecture 4

In order to obtain spatial information on the fluctuations, we need to consider the generalized, inhomogeneous Ginzburg-Landau functional. Only in the inhomogeneous case spatial fluctuations of the order parameter are allowed for in the theory. Repeating the argument above for the inhomogeneous situation, we find

$$\langle|\delta\eta_k|^2\rangle = \frac{T/V}{a(T-T_c)+Dk^2}, \tag{3.14}$$

which is the typical amplitude of a fluctuation with wavenumber k. This is the famous Ornstein-Zernike result for fluctuations.[3] The Fourier transform of $\langle|\delta\eta_k|^2\rangle = \langle\delta\eta_k\delta\eta_{-k}\rangle$ is related to the real space correlation function $G(r) = \langle\delta\eta(0)\delta\eta(r)\rangle$. This correlation function is a measure for how quickly fluctuations of the order parameter decay in space, or equivalently, how large the volume of a typical fluctuation is. The correlation function only depends on the relative distance between the fluctuations. We establish the relationship between $G(r)$ and $\langle|\delta\eta_k|^2\rangle$ by considering

$$\begin{aligned}
\sum_k \langle|\delta\eta_k|^2\rangle e^{ikr} &= \sum_{k,\bar{k}} \delta_{k\bar{k}}\langle\delta\eta_k\delta\eta_{-\bar{k}}\rangle e^{ikr} = \sum_{k,\bar{k}} e^{i(k-\bar{k})R}\delta_{k\bar{k}}\langle\delta\eta_k\delta\eta_{-\bar{k}}\rangle e^{ikr} \\
&= \frac{1}{V}\sum_{R,k,\bar{k}} e^{i(k-\bar{k})R}\langle\delta\eta_k\delta\eta_{-\bar{k}}\rangle e^{ikr} \\
&= \frac{1}{V}\sum_{R,k,\bar{k}} \langle e^{ik(R+r)}\delta\eta_k e^{-i\bar{k}R}\delta\eta_{-\bar{k}}\rangle \qquad (3.15) \\
&= \frac{1}{V}\sum_R \langle\delta\eta(R+r)\delta\eta(R)\rangle = \langle\delta\eta(0)\delta\eta(r)\rangle = G(r).
\end{aligned}$$

[3] Frits Zernike (1888-1966) derived this result during his doctoral thesis work in Groningen (1915). Ornstein was lecturer in Groningen. Zernike was to receive the Nobel prize in 1953, not for his contributions to statistical physics, but, quoting the Nobel committee, for "his invention of the phase-contrast microscope". The committee continues by stating: "It is interesting to know that his great discovery of the phase-contrast phenomenon, which he discovered one evening in 1930 in his totally black painted optical laboratory, did not immediately receive the attention it deserved. The world famous Zeiss factories at Jena completely underestimated the value of his phase-contrast microscope. It was not until the German Wehrmacht took stock of all inventions which might serve in the war that at last (in 1941) the first phase-contrast microscopes were manufactured. The grotesque situation thus arose that the German war machinery helped to develop on an industrial scale Professor Zernike's long-neglected invention while its inventor, like his fellow-countrymen, suffered under the oppression by the same German powers during the occupation of The Netherlands. After the war, other firms also took up the production of many thousands of phase-contrast microscopes, thereby providing the service to science, and in particular to medicine, which should have been effectuated some twenty years earlier."

Inserting in this transformation the Ornstein-Zernike expression for fluctuations leads, in three dimensions, to:

$$
\begin{aligned}
G(r) &= \frac{T}{V}\sum_{\mathbf{k}} \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{a(T-T_c)+Dk^2} = \int \frac{Te^{i\mathbf{k}\cdot\mathbf{r}}}{a(T-T_c)+Dk^2}\frac{d^3\mathbf{k}}{(2\pi)^3} \\
&= \frac{T}{D}\int \frac{e^{i\mathbf{k}\cdot\mathbf{r}}}{l^2+k^2}\frac{d^3\mathbf{k}}{(2\pi)^3} = \frac{T}{D}\frac{e^{-lr}}{4\pi r} \\
&= \frac{T}{D}\frac{e^{-r/\xi}}{4\pi r} \quad \text{with} \quad \xi = \sqrt{\frac{D}{a(T-T_c)}} \qquad (3.16)
\end{aligned}
$$

The length ξ is called the correlation length. The correlation volume is $\sim \xi^3$. Close to T_c the correlation length diverges. We thus obtained an expression for the typical volume of a fluctuation of the order parameter. Knowing the typical volume of a fluctuation, we can estimate the typical amplitude a fluctuations, using equation (3.13), where $V \sim \xi^3$. Close to T_c we obtain:

$$\langle|\delta\eta|^2\rangle = \frac{T}{\xi^3 a(T-T_c)} \simeq \frac{T_c}{\xi^3 a(T-T_c)}. \qquad (3.17)$$

The order parameter itself is $\eta^2 = \frac{a}{2B}(T_c - T)$. The fluctuations to the order parameter are therefore not important when $\langle|\delta\eta|^2\rangle \ll \eta^2 \Leftrightarrow$

$$\left[\frac{\langle|\delta\eta|^2\rangle}{\eta^2}\right]^2 \ll 1 \quad \Rightarrow \quad \frac{T-T_c}{T_c} \gg \frac{T_c B^2}{aD^3}. \qquad (3.18)$$

This is the so-called Levanyuk-Ginzburg criterion. Very close to T_c fluctuations are always dominating, but for reduced temperatures $\frac{T-T_c}{T_c}$ larger than the Ginzburg number $T_c B^2/(aD^3)$ the Landau mean field theory applies without restrictions. This is always the case if the zero-temperature correlation length $\xi_0 = \xi(T=0)$ is large enough.

This is the case in usual superconductors in which ξ_0 (called the superconducting coherence length in this context) is typically of the order of 10^4 Å, i.e. much bigger than the lattice spacing. However, for example in super-fluid ^4He, ξ_0 is of the order of the inter-atomic distance and the fluctuation region is very large. In fact the specific heat at the super-fluid transition has a shape that is completely dominated by the fluctuations. This is sometimes called the Lambda anomaly.

Exercise 3.4.
For a system in an external field h, very close to T_c, the Gibbs free energy is

$$G = \int d\mathbf{r}[B\eta^4(\mathbf{r}) - h\eta(\mathbf{r}) + D(\vec{\nabla}\eta)^2],$$

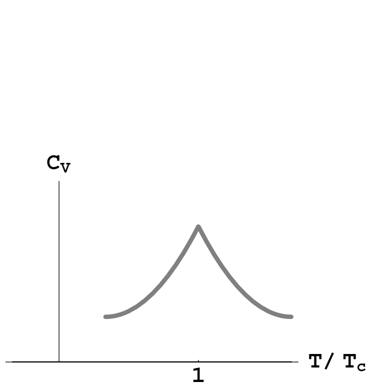

Figure 3.11. Lambda anomaly in the specific heat at the superfluidity transition of liquid ^4He.

where $B, h, D > 0$.
3.4.0. Show that in this case the orderparameter is $\left(\frac{h}{4B}\right)^{1/3}$
3.4.1. Show that the free energy cost associated with a (homogenous) fluctuation of this order parameter is

$$\delta G_0 \propto B^{1/3} h^{2/3} V,$$

where V is the volume asociated with the fluctuation.
3.4.2. For a periodic fluctuation with wavenumer k the free energy is $\delta G_k = \delta G_0 + Dk^2$. Show that this leads to a correlation length ξ that is proportional to $D^{1/2} B^{-1/6} h^{-1/3}$.
3.4.3. Obtain this same result from a dimensional analysis of the parameters B, h and D.

Exercise 3.5.
3.5.0. Show that minimization of the free energy with respect to the order parameter in the Ginzburg-Landau functional

$$G = \int d\mathbf{r}[A\eta^2(\mathbf{r}) + B\eta^4(\mathbf{r}) + D(\vec{\nabla}\eta)^2]$$

leads to the following equation for the order parameter (when η is real and T is close to T_c)

$$\vec{\nabla}^2\eta(r) - \frac{A}{D}\eta(r) - \frac{2B}{D}\eta^3(r) = 0$$

3.5.1. Show from this equation that above, but close to T_c the correlation length is $\xi = \sqrt{D/A}$.

Hint: in three dimensions the Laplacian $\vec{\nabla}^2$ has the radial part $\frac{1}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial}{\partial r})$.
Hint: Introduce $\eta(r) = \phi(r)/r$ and determine $\phi(r)$.
3.5.2. Show that after defining a dimensionless orderparameter $f(z)$, this equation reduces to

$$\xi\frac{d^2f}{dz^2} + f - f^3 = 0,$$

for a one-dimensional system. (Note that A is negative below T_c.)
3.5.3. Now consider an inhomogeneous system that is ordered, where the orderparameter is specified by the boundary condition that $f \to -1$ for $z \to -\infty$ and $f \to 1$ for $z \to \infty$. This describes, e.g., the situation where there is a domain wall in a ferromagnet around $z = 0$, where the magnetization changes sign. Inhomogenous superconductors (e.g. superconductivity near a surface) fall in this same class.
Show that in this case the order parameter f behaves as

$$f(z) = \tanh\left[\frac{z}{\xi\sqrt{2}}\right]$$

and make a sketch.
Thus the spatial variation of the orderparameter is confined to a region $|z| \approx \xi$.

Exercise 3.6.
3.6.1. Show that at $T = T_c$ for a three-dimensional system amplitude fluctuations of the orderparameter decay algebraicly, with the powerlaw: $\xi \propto r^{-1}$.
3.6.2. Show that at $T = T_c$ for a one-dimensional system the lengthscale associated with amplitude fluctuations of the orderparameter diverges (i.e. the fluctuation region becomes as large as the system itself).
Hint:

$$\frac{1}{\pi}\int_{-\infty}^{\infty}\frac{e^{ikr}}{l^2+k^2}dk = \frac{e^{-lr}}{l} \quad \text{(when } r \geq 0\text{)}.$$

Exercise 3.7.
Show that in dimension $d \geq 4$ the Levanyuk-Ginzburg criterion is always fullfilled when $T \to T_c$. In this situation meanfield theory becomes exact and therefore the dimension $d = 4$ is refered to as the "upper critical dimension".

Hint: Use that in dimension d the volume V of a typical fluctuation is proportional to ξ^d.

5. Fluctuation-Dissipation Theorem

The fluctuation-dissipation theorem states that the response of a given system to a small external perturbation is directly related to the fluctuations in the system at thermal equilibrium. For a small perturbation the response is linear. The essential point is that the fluctuation-dissipation theorem relates equilibrium fluctuations to out-of-equilibrium quantities. Therefore it is an important results in statistical mechanics.

We consider a system with orderparameter η. As in the previous section in equation 3.12 we use the Landau free energy $G(\eta)$ as Hamiltonian for the system, so that the partition function is

$$Z = \int e^{-\beta G(\eta)} d\eta. \tag{3.19}$$

The conjugate field h couples to the orderparameter so that in presence of the field the free energy G changes with $V\eta h$, where V is the volume of the system. The linear response of the system to an external field is by definition determined by its susceptibility χ, where

$$\chi = \frac{\partial \eta}{\partial h},$$

for very small h. We show now that this susceptibility is proportional to the *fluctuations* of the orderparameter. In presence of the conjugate field the partition function becomes

$$Z = \int e^{-\beta[G(\eta) - hV\eta]} d\eta, \tag{3.20}$$

so that the expectation value of the order parameter is given by

$$\langle \eta \rangle = \frac{1}{Z} \int \eta e^{-\beta[G(\eta) - hV\eta]} d\eta = \frac{T}{V} \frac{1}{Z} \frac{\partial Z}{\partial h}. \tag{3.21}$$

In a similar way we derive that the expectation value of the squared order parameter is

$$\langle \eta^2 \rangle = \left[\frac{T}{V}\right]^2 \frac{1}{Z} \frac{\partial^2 Z}{\partial h^2}, \tag{3.22}$$

so that the expectation value for the fluctuations is

$$\langle |\delta\eta|^2 \rangle = \langle \eta^2 \rangle - \langle \eta \rangle^2 = \left[\frac{T}{V}\right]^2 \frac{\partial}{\partial h} \left[\frac{1}{Z} \frac{\partial Z}{\partial h}\right] = \frac{T}{V} \frac{\partial \eta}{\partial h}, \tag{3.23}$$

and we find thus for the susceptibility per unit volume

$$\frac{\chi}{V} = \frac{1}{T} \langle |\delta\eta|^2 \rangle, \tag{3.24}$$

or, generalizing this to the the inhomogeneous situation where the amplitude of the fluctuations depends on wavenumber $\mathbf{q}$

$$\frac{\chi(\mathbf{q})}{V} = \frac{1}{T}\langle|\delta\eta_{\mathbf{q}}|^2\rangle = \frac{1}{T}\sum_{\mathbf{r}} e^{i\mathbf{q}\cdot\mathbf{r}}\langle\delta\eta(\mathbf{0})\delta\eta(\mathbf{r})\rangle, \tag{3.25}$$

which is just the Fourier transform of the real-space correlation function of fluctuations of the orderparameter $G(\mathbf{r})$.

End 2nd half lecture 4