Properties of Phase Transitions of a Higher Order

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Abstract

The following is a thermodynamic analysis of a III order (and some aspects of a IV order) phase transition. Such a transition can occur in a superconductor if the normal state is a diamagnet. The equation for a phase boundary in an $H$–$T$ ($H$ is the magnetic field, $T$, the temperature) plane is derived. by con-
sidering two possible forms of the gradient energy, it is possible to construct a field theory which describes a III or a IV order transition and permits a study of thermal fluctuations and inhomogeneous order parameters.

I. INTRODUCTION

If the Ehrenfest classification were used to describe a third or a fourth order phase transition, the free energy and its low order derivatives, e.g., entropy and the specific heat, will be continuous, but, say for a III order transition $\square$, the specific heat will have a discontinuous temperature derivative. For a IV order transition, the temperature derivative of the specific heat will be continuous, rather, the second derivative of the specific heat will

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be discontinuous.

In fact, this is not enough. Consider a II order phase transition boundary. The phase boundary (in the $H-T$ plane, where $H$ is the mechanical variable and $T$, the temperature) is given by

$$\left(\frac{dH}{dT}\right)^2 = \frac{\Delta C}{T\Delta \chi}$$

Here, $\Delta C = C_o - C_d$ where $C_o$ and $C_d$ are respectively the ordered and disordered phase specific heat ($C = -T \frac{\partial^2 F}{\partial T^2}$) and $\Delta \chi = \chi_o - \chi_d$ is the similar discontinuity in susceptibility ($\chi = -\frac{\partial^2 F}{\partial H^2}$). Having $\Delta C = 0$ is, naturally, not enough reason to argue for a higher order transition. A horizontal second order phase boundary may have $\Delta C = 0$. A higher order transition thus necessarily requires both $\Delta C = \Delta \chi = 0$. Stated differently, near the transition temperature, $F(T) = -(T_c - T)^n$ and $F(H) = -(H_c - H)^{n'}$. The Ehrenfest classification assumes that $n = n'$. In a scaling description of a II order phase transition, $n = 2 - \alpha$, where $\alpha$, the specific heat exponent, is small. It is, however, clear that there is no limit on what $\alpha$ can be, whether positive or negative. Thus when $\alpha$ is negative and large in magnitude, the transition is probably better described as with an order corresponding to the nearest integer to $n$. Any residue in $n$ then can be viewed as a fluctuation contribution.

The well known liquid-vapor phase boundary for water is mostly I order, except when this phase line terminates at the critical point. At the critical point, the transition is second order while past the critical point, the transition is continuous without any free energy singularities. A possible scenario is that a first order line may terminate at a higher order phase transition. We encounter such a possibility in the discussion of magnetic field effects.

Recent observations in several high $T_c$ superconductors have been cited as questioning whether the order of the transition is 2. Probably the most extensive study comes for Ba$_{0.6}$K$_{0.4}$BiO$_3$ (BKBO), a cubic superconductor with a $T_c = 30$ K. Here both specific heat and susceptibility have been measured and found to be continuous at the transition. There are indications that specific heat in Bi and Tl based cuprates has features characteristic of a higher order phase transition. The issue still needs to be resolved by careful analysis.
of both the specific heat and the susceptibility. In particular, we need to know whether the transition is of order III or IV.

In the following, we consider both a III order as well as a IV order transition. Section II contains a thermodynamic analysis of a higher order phase transition. Section III contains a field theory, a Ginzburg Landau type free energy which describes such a transition. This section contains only properties associated with a uniform order parameter. A non-uniform order parameter is the subject in Section IV, whether caused by an external magnetic field or thermal fluctuations. Both are analyzed. Finally, Section V contains a summary and some outlook of future.

II. THERMODYNAMICS

The objective in this section is to derive an equation equivalent to the Clausius-Clapeyron (C-C) equation for a higher order phase boundary and discuss its consequences. There are three quantities, \( \frac{\partial S}{\partial T}, \frac{\partial S}{\partial H} = \frac{\partial M}{\partial T} \) and \( \frac{\partial M}{\partial H} \), each continuous across the transition. The usual derivation of the phase boundary equation proceeds by equating the changes in each of the above quantities as one moves along the phase boundary. The resulting equalities are then solved for the slope of the phase boundary. Thus, the equations are (making frequent use of the Maxwell relation \( \frac{\partial S}{\partial H} = \frac{\partial M}{\partial T} \)):

\[
\frac{\partial H}{\partial T} = \frac{\Delta \partial^2 S / \partial T^2}{\Delta \partial^2 S / \partial H \partial T} = -\frac{\Delta \partial^2 M / \partial T^2}{\Delta \partial^2 M / \partial T \partial H} = \frac{\Delta \partial^2 S / \partial H^2}{\Delta \partial^2 M / \partial H^2} = -\frac{\Delta \partial^2 M / \partial T^2}{\Delta \partial^2 S / \partial H^2} \tag{2}
\]

Of all of the possible expressions (some of which can be found in Pippard \[2\]) the one below is special for two reasons: Firstly, the numerator contains thermal quantities and their derivatives, while the denominator contains mechanical expressions, similar to the C-C equation (Eq. (1)) for a second order transition. Secondly, the equation has a symmetric form, suggestive of a simple extension to higher order transitions.

\[
\left[ \frac{\partial H}{\partial T} \right]^3 = -\frac{\Delta \partial^2 S / \partial T^2}{\Delta \partial^2 M / \partial H^2} = -\frac{\Delta \partial C / \partial T}{T_c \Delta \partial \chi / \partial H} \tag{3}
\]
Eq. (3) involves the first derivative of \( \chi \) with respect to \( H \). Thus the phase boundary here is determined by the nonlinear susceptibility. If the correction to the susceptibility is quadratic in \( H (\chi(H) = \chi_0 + \chi_2 H^2) \) then assuming that specific heat field dependence is weak, the phase boundary can be integrated to show that at low fields, \( \Delta T_c \propto H^{\frac{3}{4}} \), a result which is different from a conventional superconductor where the Abrikosov result for \( \Delta T_c \) is linear in magnetic field.

Eq. (3) suggests the form of the phase boundary for a IV order phase transition. One might guess the (sometimes called “Ehrenfest equation”) phase boundary in a IV order phase transition to be

\[
\left( \frac{\partial H}{\partial T} \right)^4 = \frac{\Delta \partial^2 C/\partial T^2}{T_c \Delta \partial^2 \chi/\partial H^2}
\] (4)

Going back to III order, given that we expect \( F = -(T_c - T)^3 \), the specific heat \( C(T) \) is given by

\[
C_{\text{III}}(T) = -T \partial^2 F/\partial T^2 \approx T(T_c - T)
\] (5)

The specific heat in fact has a broad “peak” at \( T_c/2 \). A transport measurement might report a true \( T_c \) while a thermodynamic measurement will report a smaller \( T_c \). Moreover, if, as is customary, the calorimetric measurement of \( T_c \) is made by deriving \( T_c \) from a point where the entropies (of the order and disordered state) match, one will have yet another value for \( T_c \). The essential fact is that the transition is not broad, it is described by a discontinuity in higher order thermodynamic derivatives.

Looking back at Eq. (1), we note another curious thermodynamic fact. Since a typical metal is paramagnetic and a superconductor diamagnetic, it is not possible to have \( \Delta \chi = 0 \). In fact this condition is satisfied only when the normal state is a diamagnet, as is the case with all of the material examples mentioned above. A higher order transitions is possible only if the normal state is a diamagnet.

Finally, we can estimate the thermodynamic critical fields. Thus, in the standard way

\[
\frac{B_c^2}{2\mu_0} = (T_c - T)^n
\] (6)
i.e., \( B_c \sim (T_c - T)^{n/2} \), a result that is reasonable in the well known II order case but entirely unexpected for the higher order phase transitions. In the following we construct specific models to better understand the possible microscopic origins of these results.

III. GINZBURG-LANDAU THEORY

For a III order phase transition, a Ginzburg-Landau theory contains some surprises even though it is relatively straightforward to obtain the characteristic form of the free energy \( F_h(\Delta, T) \), here \( \Delta \) is the order parameter. \( F_h \) refers to the free energy with a homogeneous order parameter and \( F_0 \) is the normal state free energy.

\[
F_n = F_0 + a\Delta^4 + b\Delta^6
\]  

(7)

Here \( a = a_0\left(\frac{T}{T_c} - 1\right) \) and \( b \geq 0 \) a constant. Searching for the minimum of the free energy as a function of \( \Delta \), we find

\[
\Delta_0^2 = \frac{2|a|}{3b} = \frac{2a_0}{3b}(1 - \frac{T}{T_c}) \quad T < T_c
\]

\[= 0 \quad T > T_c \]

(8)

The various thermodynamic quantities (all of the quantities refer only to the condensing degree of freedom) are given by

\[
\langle F \rangle = \frac{4}{27} \cdot \frac{|a|^3}{b^2} = \frac{4}{27} \cdot \frac{a_0^3}{b^2} \left(1 - \frac{T}{T_c}\right)^3
\]

(9)

\[
S = \frac{\partial \langle F \rangle}{\partial T} = -\frac{4}{9} \cdot \frac{a_0^3}{b^2T_c} \left(1 - \frac{T}{T_c}\right)^2
\]

(10)

\[
C = \frac{\partial^2 \langle F \rangle}{\partial T^2} = \frac{8}{9} \cdot \frac{a_0^3}{b^2T_c^2T} \left(1 - \frac{T}{T_c}\right)
\]

(11)

We see that the specific heat has a characteristic temperature dependence. It shouldn’t be taken for a broad discontinuity of a II order transition since \( \frac{\Delta T}{T_c} \sim \frac{1}{2} \), where \( \Delta T \) is some measure of the transition width.

We should also recall now that there is no quadratic term in the order parameter in Eq. (7). In the presence of a quadratic term, the transition becomes a I or a II order.
This is a rather important and subtle point. For example, the magnetic transition in solid $^3$He involves interaction energies that do not have a quadratic term, they have only a quartic term. However, there is always a quadratic contribution from the entropy. Thus the transition is usually a I order one. A third order transition requires vanishing quadratic term in the free energy. One possible interpretation of Eq. (7) can be that the density of states at the Fermi surface (if Eq. (7) is the free energy for a superconductor) which appears as an energy scale determining factor, is in fact proportional to $\Delta^2$. Thus, we could imagine a transition between an insulator and a superconductor. The Fermi surface density of states is zero in the normal state indicating an insulator. It is finite in a metal/superconductor and the transition would be a curious but a profound feedback phenomena. As far as I am aware, there are several quadratic terms in a real insulator-superconductor transition and the real transition is a robust II order one. The above analogy is only an illustration.

What happens if the transition is a IV order? A possible free energy can be written

$$F_h = F_0 + a|\Delta|^6 + b|\Delta|^8$$

$$a = a_0(T/T_c - 1)$$

Here, one might imagine that the prefactor density of states at the Fermi surface is driven by superconductivity to be quartic in the order parameter. The results corresponding to Eqs (8–11) are

$$\Delta_0^2 = \frac{3a_0}{4b}(1 - T/T_c) \quad a < 0$$

$$\langle F' \rangle = -\frac{27}{256} \frac{|a|^4}{b^3}$$

$$C_{IV}(T) = \frac{27}{64 \, b^2 T_c^2} \frac{T}{(1 - T/T_c)^2}$$

**IV. SPATIALLY INHOMOGENEOUS ORDER PARAMETER**

Here we consider two effects, first the effect of magnetic field and then the effect of thermal fluctuations. To do either, we need to supplement the free energy Eq. (7) with
terms that involve a spatially varying order parameter. Again there are many choices and it is less obvious how they could be eliminated. The following contains consequences of one selection, we will comment on another selection, briefly, at the end of this section.

A. Model I

Thus, we supplement the free energy (Eq. (7)) by

$$F_G = C|\nabla \Delta|^2$$  \hspace{1cm} (16)

To be specific, we will assume that $\Delta(\mathbf{r})$ is a complex function of position in 3d. Let us first look at the temperature dependent correlation length. The Euler-Lagrange equation for the order parameter is given by

$$\frac{\delta}{\delta \Delta}(F_h + F_G) = -2|a|\Delta^3 + 3b\Delta^5 - C\nabla^2 \Delta = 0$$  \hspace{1cm} (17)

We look for small amplitude variations of $\Delta(\mathbf{r})$ by writing

$$\Delta(\mathbf{r}) = \Delta_0 + \delta(\mathbf{r})$$  \hspace{1cm} (18)

The linear equation determining $\delta(\mathbf{r})$, the final solution being dependent on boundary conditions, is

$$-C\nabla^2 \delta(\mathbf{r}) + \left\{ \frac{1}{2} \frac{\delta^2 F_h}{\delta \Delta^2} \right\}_{\Delta_0} \delta(\mathbf{r}) = 0$$  \hspace{1cm} (19)

leading to a length scale, the temperature dependent correlation length $\xi(T)$

$$\xi^2(T) = C \left[ \frac{1}{2} \frac{\delta^2 F_h}{\delta \Delta^2} \right]_{\Delta_0}^{-1} = \frac{3bC}{8|a|^2}$$  \hspace{1cm} (20)

Thus, in contrast to the familiar notion of length scale, here there is an asymmetry about $T_c$. For $T > T_c$, the correlations are non-exponential. Below $T_c$, the correlations length depends linearly on $1/|a|$, as opposed to the square root dependence in a second order phase transition.
We can also identify the superfluid density. A current can be viewed as that arising from the space gradients. In that case, the density is given by expressing the free energy due to current as $V_2 \rho_s v_s^2$ where $v_s$ is the supercurrent. With Eq. (16), we have $\rho_s \sim \Delta^2$ and the consequent temperature dependence.

A.1. Magnetic Field Dependence

The gauge invariant free energy requires that the charge interaction with magnetic field be described by a transformation of the gradient term $\nabla \rightarrow (\nabla + \frac{2\pi i}{\phi_0} A)$ here $\phi_0$ is the flux quantum $\hbar / 2e$ and $A$ is the vector potential ($B = \nabla \times A$ refers to the local field, which approaches the external field $H$ outside).

It is straightforward to show that the equation for the vector potential represents flux expulsion whenever $\Delta_0 \neq 0$. It is also true that in analogy with a conventional superconductor, $\lambda^{-2} \propto \Delta^2$. All these features are standard and are dependent on $n_s = \Delta^2$. The difference appears, not entirely unexpectedly, at the calculation of $H_{c2}(T)$. The curious result is that the transition becomes I order in the presence of a magnetic field.

To see that, we derive the criterion for the instability of the normal state. The lowest order Euler-Lagrange equation is given simply by

$$- C \left| \left( \nabla + \frac{2\pi i}{\phi_0} A \right) \right|^2 \Delta = \lambda \Delta$$

(21)

The solutions of this equation are dependent on the choice of gauge, but the eigenvalues $\lambda = (2n + 1) \frac{2\pi C}{\phi_0} H$ is independent of gauge choice, with the lowest energy level corresponding to $n = 0$. If the corresponding wave function is $\phi_n(x)$, we can write

$$\Delta(x) = \sum_{(n)} \zeta_n \phi_n(x)$$

(22)

where $n$ stands for the set of quantum numbers necessary to characterize the state. In the mean field sense, the free energy can be written as

$$F = \frac{2\pi C}{\phi_0} H \zeta_0^2 + a \zeta_0^4 + b \zeta_0^6$$

(23)

The transition occurs at $H_{c2}(T)$ where
\[ H_{c\Delta}(T) = \frac{\phi_0}{8\pi b C} |a|^2 \]  

(24)

However, the order parameter develops discontinuously at \( T_c \). Its value at \( T_c \), \( \Delta_\zeta_0 \) is given by

\[ \Delta_\zeta_0 = \left( \frac{2\pi C}{b\phi_0} H \right)^{\frac{1}{4}} \]  

(25)

The latent heat \( (L = T_c \Delta s) \) can also be obtained, it is given by

\[ L = T_c \Delta s = \frac{2\pi a_0 C}{b\phi_0} H / T_c \]  

(26)

All of these quantities are measurable and provide an unequivocal test of the model for the gradient energy. They represent a first order phase transition for \( H \neq 0 \) while the \( H = 0 \) transition is a III order one. We have a first order line ending in a critical point which is of higher order than the conventional second order.

At this stage, the applicability of ideas of this subsection to BKBO breaks down. As far as we can tell, the transition is \textit{not} of I order in any finite field, there is no latent heat, no discontinuity—nor any other trace. In fact, all evidence in finite field, points to a transition higher in order than II. Before proceeding with another ansatz for free energy in sec. 4.2, let us consider thermal fluctuations following Eq. (16).

A.2. Thermal Fluctuations

Let us consider a scalar order parameter \( \Delta(r) \). We consider a partition function

\[ z = \int D[\Delta(r)] \exp[-\beta(F_h + F_G)] \]  

(27)

The partition function provides the thermodynamic free energy which then leads to the other thermodynamic properties. As is customary, the integral is evaluated in a saddle point approximation. Consider \( \Delta(r) = \Delta_0 + \delta(r) \) where \( \Delta_0 \) is the minimum of \( F_h \), as in Eq. (8):

\[ e^{-\beta F} = z = e^{-\beta(F_h)} \prod_k \int d\delta_k \exp \left[ -\frac{\beta}{2} \sum_q \left\{ \frac{\delta^2 F_h}{\delta \Delta^2} \bigg|_{\Delta_0} + c q^2 \right\} \delta^2_q \right] \]  

(28)
where $\delta_q$ (or $\delta_k$) is the Fourier transform or $\delta(\tau)$, and the first term is given by $8|a|^2/3b$. Thus, the free energy becomes

$$\hat{F} = \langle F_h \rangle + F_f$$

$$F_f = -\frac{kT}{2} \sum_q \ln \left[ \frac{2\pi kT}{\left(\frac{8|a|^2}{3b} + Cq^2\right)} \right]$$

$$C_f = -T \frac{\delta^2 F}{\delta T^2} \approx |a|^{d-2}$$

In this model, the transition at $H = 0$ is quite robust. In Eq. (30), we have the temperature dependence of the fluctuation specific heat, which is well behaved for $d \geq 2$. The upper critical dimension for this model is $d = 2$. (Recall that the upper critical dimension in a II order case is $d = 4$). The fluctuations in this model, described by Eq. (16) are divergent only for $d = 1$. Thus there are no critical fluctuations and no need to go beyond mean field theory, at least not for $d \geq 2$. This also means that if the experimental exponents are not meanfield like, model I is probably not applicable.

If $\Delta(\tau)$ were a 2–d vector, then the phase fluctuations behave similar to their behavior in case of a II order phase transition. There are the usual infrared divergences in 1 and 2–d indicating the importance of topological defects $[11]$ in the phase transitions, etc.

**B. Model II**

Let us consider a different gradient energy term. If we follow the physical picture where the overall energy scale in the free energy depends on the order parameter, the gradient term perhaps looks like

$$F_G = \tilde{c}\Delta^2|\nabla\Delta|^2$$

which can also be viewed as the square of the gradient of $\Delta^2$. We see that for a scalar order parameter, the Eyler-Lagrange equation is given by

$$-2|a|\Delta^2 + 3b\Delta^4 - \tilde{c}(\nabla\Delta)^2 - \tilde{c}\Delta \nabla^2 \Delta = 0$$

$(32)$
A linearized version of this equation, about the homogeneous solution, becomes

$$4|a|\delta(r) - \tilde{c}\nabla^2\delta(r) = 0$$  \hspace{1cm} (33)

In contrast to Eq. (19), the correlations length exponent is back to being $\frac{1}{2}$. But much else has changed. The effect of magnetic field can be incorporated by replacing the derivative in Eq. (31) by a covariant term. Like sec. IV.A.1, the order parameter can be expanded in the Landau orbital wave functions which are eigen functions of the covariant Laplacian. The nonquadratic nature of the free energy introduces interactions and transitions between the Landau orbital states. However overlooking these interactions (for small fields as in sec. IV.A.1), we see that the transition in the presence of a magnetic field is III order with a phase boundary given by

$$\frac{2\pi\tilde{c}}{\phi_0}H = a_0(1 - T/T_c)$$  \hspace{1cm} (34)

If $\Delta(r)$ is a complex number, the number density of excitations is proportional to $\Delta^4_0$, a feature also shared by the penetration depth ($\lambda^{-2} \propto \Delta^4$).

The proverbial fly in this ointment comes from a study of thermal fluctuations. The thermal fluctuations contain a divergent (logarithmic) contribution to the free energy, yielding a specific heat that diverges as $|a|^{-2}$, independent of dimension. There is additional dimension dependent divergence, which for specific heat takes the form $C \propto |a|^{(d/2-2)}$. To see the details, consider Eq. (28) as worked out for model II, we have

$$e^{-\beta F} = z = e^{-\beta (F_Q)} \prod_k \int d\delta_k \exp \left[ -\beta \sum_q \Delta^2_0[4|a| + cq^2]\delta^2_q \right]$$

i.e.

$$F_f = \frac{kT}{2} \sum_q \ln \left[ \Delta^2_0(4|a| + cq^2) \right]$$

It is the $\Delta^2_0$ term that is singular in the eventual derivation of the entropy and specific heat.

At this moment, it is hard to imagine that the entire mean field analysis of model II, as described above, is meaningless. And yet, a mean field analysis depends on the validity of the saddle point evaluation of the partition function. An estimate of corrections to mean field, seen above for model II, is divergent and it is unclear if some sort of renormalization
will restore these results to a finite value. Barring that, model II remains very dubious as a valid model. These problems are equally exacerbated for a IV order phase transition.

V. SUMMARY

It appears therefore that a thermodynamic description of a III or IV order phase transition is relatively straightforward, although the consequences are almost unavoidably subtle. Once we recognize the possibility of these phase transitions, it is clear that we cannot lump them together with all of the other continuous transitions. There are subtle and interesting differences which call for a separate identification and analysis.

It is possible that a higher order transition has been observed before. Then it was attributed to an extreme case of sample inhomogeneity since the transition temperature measured from different techniques were all different. The above is an attempt to outline a systematic formalism for the analysis of higher order transitions. We have an equation for the phase boundary Eqs. (3) and (4) and furthermore, we also have a field theory which leads to a III (or IV) order phase transition. In searching for the effects of a magnetic field or thermal fluctuations, we find two models. In one case, the finite field transition is a I order transition which ends into a III order critical point. All thermodynamic quantities vanish at this critical point ($H = 0$) appropriately. In the other model, we find strong thermal fluctuations which, on the one hand appear to question the validity of a mean field theory. It is also possible that the correct model still remains elusive.

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