Statistical Physics (PHY831): Part 3 - Interacting systems

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Part 3: (H, PB) Interacting systems, phase transitions and critical phenomena (9 lectures)
Interacting spin systems, Ising model. Interacting classical gas, cluster expansion, van der Waals equation of state, Virial Expansion, phase equilibrium, chemical equilibrium. Interacting quantum gas, thermodynamic perturbation theory, gases with internal degrees of freedom. Superfluidity and superconductivity, phonons, rotons, vortices, BCS theory.

Homework 3.1 and Quiz 3.1, Wednesday Nov. 2
Homework 3.2 and Quiz 3.2, Friday Nov. 11

Midterm 3, Lecture 32 (Monday Nov. 14)

I. INTRODUCTION

There are many methods for interacting systems, which may be broadly classified as follows: (i) Decoupling schemes based on expansions in the fluctuations (e.g. mean field theory), equation of motion methods, integral equations etc.; (ii) Perturbation theory. High temperature expansions, low temperature expansions, expansions away from solvable models, diagrammatic methods; (iii) Computational approaches, MC, MD, Transfer matrix; (iv) Coarse grained models, field theory, Landau-Ginzburg and Landau-Ginzburg-Wilson theory. Each method has its strengths and weaknesses. We first analyse three problems using the mean field/decoupling scheme approach.

The key new phenomena that interactions bring are new phases and phase transitions between them. Understanding phase transitions and in particular continuous phase transitions is challenging but has lead to many new insights into physics. The modern understanding of phase transitions centers around the order parameter and order parameter fluctuations. The fluctuations are particularly important and are characterized through the pair correlation function. For a ferromagnet this is defined as,

$$C_{ij} =< (S_i - < S_i >)(S_j - < S_j >) >=< S_i S_j > - m_i m_j \tag{1}$$

The asymptotic behavior of C_{ij} near a continuous critical point is found to be of the form,

$$C_{ij} \to C(r) \sim \frac{1}{r^{d-2+\eta}} e^{-r/\xi} \tag{2}$$

$\xi \approx |T - T_c|^{-\nu}$ is the correlation length. Discontinous or first order transitions do not have a diverging correlation length while continuous transitions do. When the correlation length diverges, fluctuations on all length scales occur, so that special techniques such as the renormalization group are required to integrate over all of them. Fundamental concepts and methods developed for phase transitions with a diverging correlation length have contributed to developments throughout physics, including fractals, self-organized criticality, power law networks, percolation phenomena and many others. We begin our discussion of phase transitions with the mean field theory for the Ferromagnetic Ising model. This theory does a suprisingly good job of indentifying different phases and the topology of the phase diagram. However the critical behavior that it predictions is not correct. Nevertheless, mean field theory or similar approaches are the first method to try in a new interacting system.

II. MEAN FIELD THEORY OF THE ISING MODELS

A. General spin half mean field theory

The Hamiltonian we consider is,

$$H = -\frac{1}{2}\sum_{ij} J_{ij} S_i S_j - \sum_i h_i S_i \tag{3}$$

and the mean field approximation is the make an expansion in the fluctuations, so that,

$$S_i S_j = [m_i + (S_i - m_i)][m_j + (S_j - m_j)] \tag{4}$$

so that

$$S_iS_j = m_im_j + m_i(S_j - m_j) + m_j(S_i - m_i) + (S_j - m_j)(S_i - m_i) \tag{5}$$

where we defined $m_i =< S_i >$ to be the local magnetization. The mean field approximation drops the term $(S_j - m_j)(S_i - m_i)$ which is quadratic in the fluctuations, so that,

$$S_iS_j \approx m_iS_j + m_jS_i - m_im_j \tag{6}$$

The mean field Hamiltonian is then,

$$H_{MF} = -\frac{1}{2}\sum_{ij} J_{ij}(m_iS_j + m_jS_i - m_im_j) - \sum_i h_iS_i \tag{7}$$

The canonical partition function is then,

$$Z_{MF} = 2^N e^{-\frac{1}{2}\beta\sum_{ij} J_{ij}m_im_j} \prod_{i=1}^{N}(Cosh(\beta\sum_j J_{ij}m_j + \beta h_i)). \tag{8}$$

This is the general mean field theory for Ising spin 1/2 systems. For other spin possibilities (e.g. $S_i = 0, \pm 1$), the Hamiltonian is the same, but the spin sum changes so the partition function is different. The mean field equations are found by taking the average $< S_i >= m_i$,

$$m_i =< S_i >= \frac{1}{Z}\sum_{S_j=\pm 1} S_ie^{-\beta H_{MF}} = Tanh(\beta(\sum_{ij} J_{ij}m_j + h_i)) \tag{9}$$

Alternatively we can consider the free energy derived from Z_{MF} to be an energy landscape with the free energy that is observed being a minimum on this landscape. We therefore write,

$$ln(Z) = -\beta F_{MF} = Nln2 - \frac{1}{2}\beta\sum_{ij} J_{ij}m_im_j + \sum_{i=1}^{N} ln(Cosh[\beta(\sum_j J_{ij}m_j + h_i)]) \tag{10}$$

and minimize with respect to m_i (assuming $J_{ii} = 0$)

$$\frac{\delta(-\beta F_{MF})}{\delta m_i} = 0 = -\beta\sum_j J_{ij}m_j + \sum_i \beta J_{ij}Tanh[\beta(\sum_j J_{ij}m_j + h_i)] \tag{11}$$

which is satisfied provided the mean field equation () is true. The mean field theory above may then be considered to be a variational theory as we have chosen an approximate free energy and we have minimized this free energy with respect to the magnetizations m_i. Then according to the variational principle, $F_{exact} \leq F_{MFT}$, so the mean field free energy always lies above the true free energy of the problem.

B. Mean field theory for spin half ferromagnet

Now we explore the predictions of mean field theory for the case of an Ising ferromagnet. In that case the $m_i = m$ is the same everywhere, so the mean field equation reduces to,

$$H_{MF} = -\sum_{<i>} S_i(Jzm + h) + J\frac{z}{2}Nm^2 \tag{12}$$

where $\sum_j J_{ij} \to Jz$ is also assumed to be the same everywhere, and z is the co-ordination number of the lattice. This is true for ferromagnets on translationally invariant lattices. In cases where that is not the case the local mangetization m_i varies throughout the lattice and a numerical solution to the N non-linear MF equations is required. The partition function for a ferromagnet is,

$$Z_{MF} = e^{-\frac{1}{2}\beta JzNm^2}[2Cosh(\beta Jzm + \beta h)]^N \tag{13}$$

and the mean field Helmholtz free energy is,

$$F_{MF} = N[\frac{1}{2}Jzm^2 - k_BTln(2) - k_BTln(Cosh(\beta Jzm + \beta h))] \tag{14}$$

and the mean field equation are,

$$m = Tanh(\beta Jzm + \beta h) \tag{15}$$

Notice that this is the same form as the infinite range model that we solved exactly in Part II (we solved the zero field case only).

Now we extract the critical exponents, defined by,

$$m \approx t_e^{\beta}; \quad \chi \approx t^{-\gamma}; \quad C_v \approx t^{-\alpha}; \quad m(T_c) \approx h^{1/\delta} \tag{16}$$

and $t = |T - T_c|$. To find these critical exponents, we only need to consider small values of m and h so we will use the expansions,

$$Tanh(y) = y - \frac{1}{3}y^3 + O(y^5); \qquad ln(Cosh(y)) = \frac{1}{2}y^2 - \frac{1}{12}y^4 + O(y^6). \tag{17}$$

so that,

$$-f_R = \frac{-\beta F_{MF}}{N} + ln(2) = -\frac{1}{2}Jzm^2 + ln(Cosh(\beta Jzm + \beta h))] \approx -\frac{1}{2}\beta Jzm^2 + \frac{1}{2}(\beta Jzm)^2 - \frac{1}{12}(\beta Jzm)^4 + O(m^6) \tag{18}$$

and,

$$m = \beta Jzm + \beta h - \frac{1}{3}(\beta Jzm + \beta h)^3 + ... \tag{19}$$

First, consider the case $h = 0$, where the magnetization approaches zero continuously as $T \to T_c$ from below, so we find,

$$m \approx \beta Jzm - \frac{1}{3}(\beta Jzm)^3 + O(m^5) \tag{20}$$

with solutions,

$$m = 0, \quad m = \pm\left(3\frac{(\beta Jz - 1)}{(\beta Jz)^3}\right)^{1/2} \approx (T_c - T)^{\beta} \tag{21}$$

where $k_BT_c = Jz$, and $\beta_e = 1/2$ is the mean field order parameter critical exponent for the ferromagnetic Ising model. The behavior as a function of field at the critical point is found by including the field in the leading order term only.

$$m = \beta Jzm + \beta h - \frac{1}{3}(\beta Jzm)^3; \quad \text{so at } \mathrm{T_c} \quad m = \frac{(3\beta h)^{1/3}}{\beta Jz} \approx h^{1/3} \tag{22}$$

so the exponent δ for the mean field Ising model is 1/3. To find the behavior of the zero field susceptibility in the limit $h \to 0$, we include the h in the leading order term in the expansion of the mean field equation, so that,

$$m = \beta Jzm + \beta h - \frac{1}{3}(\beta Jzm)^3 \tag{23}$$

A derivative with respect to h yields,

$$\chi = \beta Jz\chi + \beta - (\beta Jz)^3 m^2 \chi \quad \text{where} \quad \chi = \frac{\partial m}{\partial h} \tag{24}$$

Solving for χ and using $\beta Jz = T_c/T$ gives,

$$\chi = \frac{\beta}{1 - \frac{T_c}{T} + m^2(\frac{T_c}{T})^3} \approx |T - T_c|^{-\gamma} \tag{25}$$

which demonstrates that the mean field susceptibility exponent is $\gamma = 1$. To find the specific heat exponent, we expand the free energy and find C_V from it. From (), we find,

$$C_V = \frac{\partial U}{\partial T} = -T\frac{\partial^2 F}{\partial T^2} \approx |T - T_c|^{-\alpha} \tag{26}$$

where $\alpha = 0$. Calculation of the pair correlation function is more technical and is deferred to the first problem set. The results are that within mean field theory the exponents for the Ising model are $\nu = 1/2$ and $\eta = 0$.

It is useful to summarize MFT exponents for the the Ising model are to compare them with the exponents that are found in two and three dimensions: The critical exponents found by more accurate methods, and confirmed in many experiments are,

$$\alpha = 0; \quad \beta_e = 1/8; \quad \gamma = 7/4; \quad \delta = 15; \quad \nu = 1; \quad \eta = 1/4; \quad 2-\text{D Ising} \tag{27}$$

$$\alpha = 0.110; \quad \beta_e = .327; \quad \gamma = 1.237; \quad \delta = 4.789; \quad \nu = 0.630; \quad \eta = 0.036 \quad 3-\text{D Ising} \tag{28}$$

$$\alpha = 0; \quad \beta_e = 1/2; \quad \gamma = 1; \quad \delta = 3; \quad \nu = 1/2; \quad \eta = 0; \quad \text{Ising MFT} \tag{29}$$

Clearly there is a dependence of the critical behavior on the spatial dimension that is not captured in the mean field theory. We know that in one dimension there is no finite temperature phase transition in the Ising model, as seen in the exact solution. We therefore introduce the concept of the "lower critical dimension", d_l. In dimensions $d < d_l$ there is no phase transition at finite temperature. For dimensions $d > d_l$ there is a phase transition at finite temperature. As we shall see later there is also an upper critical dimension d_u. In dimensions $d > d_u$ mean field critical exponents are correct. The dimension dependence in the critical exponents only occurs in the regime $d_l < d < d_u$. Nevertheless, mean field theory provides a surprisingly good method for predicting stable phases in many problems in three dimensions. It fails as it does not treat fluctuations correctly, and the modern theory of phase transitions addresses this issue in much more detail.

The field theory approach to treating fluctuations starts with the expansion of the free energy near the critical point leading to the free energy,

$$F_L \approx f_R \approx a(T - T_c)m^2 + bm^4 - hm \tag{30}$$

as found from the mean field expansion above. This expansion and its generalizations form the foundation of Landau theory. To add fluctuations, the leading order correction (added by Ginzburg) is, $|\nabla m|^2$, which takes into account local variations in the magnetization. We then have the G-L free energy for the Ising model,

$$F_{GL} \approx a(T - T_c)m^2 + bm^4 - hm + c|\nabla m|^2 \tag{31}$$

where a, b, c are positive constants. This is considered to be a coarse-grained model and the behavior of the system is found by integration over all possible fluctuations in $m(\vec{r})$, which leads to the functional integral,

$$Z_{GL} = \int Dm e^{-\beta F_{GL}} \tag{32}$$

which is now a classical field theory.

1. *Pair correlation function - mean field calculation*

To find the behavior of the pair correlation function within mean field theory, note that,

$$< S_i S_j >= \frac{\partial m_i}{\partial h_j} = \frac{1}{\beta^2}\frac{\partial^2 (ln(Z))}{\partial h_i h_j}. \tag{33}$$

A derivative of Eq. () yields,

$$\beta \sum_l J_{il} \frac{\partial m_l}{\partial h_j} + \beta \delta_{ij} = \frac{1}{1 + m_i^2}\frac{\partial m_i}{\partial h_j} \tag{34}$$

so that,

$$\beta \sum_l J_{il} C_{lj} + \beta \delta_{ij} = \frac{1}{1+m_i^2} C_{ij} \tag{35}$$

We define,

$$C(\vec{k}) = \sum_j C_{ij} e^{i\vec{k}\cdot\vec{r}_{ij}}; \qquad J(\vec{k}) = \sum_j J_{ij} e^{i\vec{k}\cdot\vec{r}_{ij}} \tag{36}$$

so that,

$$\sum_j e^{i\vec{k}\cdot\vec{r}_{ij}} \sum_l J_{il} C_{lj} + \beta \sum_i e^{i\vec{k}\cdot\vec{r}_{ij}} \delta_{ij} = \frac{1}{1+m_i^2} \sum_i e^{i\vec{k}\cdot\vec{r}_{ij}} C_{ij} \tag{37}$$

Noting that for translationally invariant systems $\vec{r}_{ij} = \vec{r}_{il} + \vec{r}_{lj}$, we find,

$$\beta C(\vec{k}) J(\vec{k}) + \beta = \frac{1}{1+m_i^2} C(\vec{k}); \qquad \text{or} \qquad C(\vec{k}) = \frac{1-m^2}{1-(1-m^2)\beta J(\vec{k})} \tag{38}$$

For nearest neighbor ferromagnetic interactions in a hypercubic lattice, we have,

$$J(\vec{k}) = \sum_{\alpha=1}^{d} 2J cos(k_\alpha a) \approx J(2d - k^2 a^2) \tag{39}$$

where the last expression on the RHS is correct in the long wavelength (small k) limit. The correlation function is then,

$$C(r) \approx \int d^d k C(\vec{k}) e^{-i\vec{k}\cdot\vec{r}} \approx \int d^d k \frac{e^{-i\vec{k}\cdot\vec{r}}}{1/(1-m^2) - \beta J(2d - k^2 a^2)} \tag{40}$$

we write this as

$$C(r) \approx \int d^d k \frac{e^{-i\vec{k}\cdot\vec{r}}}{1/(1-m^2) - \beta J(2d - k^2 a^2)} = \int d^d k \frac{e^{-i\vec{k}\cdot\vec{r}}}{k^2 + 1/\xi^2} \tag{41}$$

where

$$\xi^2 = \frac{1-m^2}{1-2d\beta J(1-m^2)} \approx \frac{1}{|T-T_c|^{2\nu}}; \qquad \text{with} \qquad \nu = 1/2 \tag{42}$$

To show that this is the correlation length, we need to carry out the integral (), which is assisted by using the identity,

$$\frac{1}{x} = \int_0^\infty du e^{-ux} du \tag{43}$$

so that,

$$C(r) \approx \int d^d k \frac{e^{-i\vec{k}\cdot\vec{r}}}{k^2 + 1/\xi^2} = \int_0^\infty du \int d^d k e^{-u(k^2+1/\xi^2) + i\vec{k}\cdot\vec{r}}. \tag{44}$$

The k integrals are Gaussian and can now be carried out to find,

$$C(r) \approx \int_0^\infty du e^{-u/\xi^2} (\frac{\pi}{u})^{d/2} e^{-r^2/4u} \tag{45}$$

In the limit $r >> \xi$, we can use the saddle point method to find $C(r >> \xi) \approx e^{-r/\xi}$. In the small r limit, we find $C(r) \approx r^{2-d}$. These two limiting values are combined into the approximate form,

$$C(r) \approx \frac{e^{-r/\xi}}{r^{d-2}} \tag{46}$$

which is exact in three dimensions.

C. Classification of phase transitions

The modern classification of phase transitions are based on the correlation length. If the correlation length diverges at a phase transition it is a second order or continuous transition. If the correlation length remains finite through the transition, and there are discontinuities in the free energies, the transition is considered to be discontinuous or first order. The old "Ehrenfest" classification of phase transitions, is related to the derivatives of the free energy. If the first derivative of the free energy has a discontinuity at the phase transition it is called first order. This implies for example that first order transitions have a latent heat.

The correlation length describes the length scale over which fluctuations are correlated. The correlation length diverges near a second order critical point leading to correlated fluctuations on all length scales. This concept has been generalized to many phenomena in equilibrium and non-equilibrium science. Concepts such as avalanches, fractals, self-similar networks, self-organized criticality and the physical origin of power law scaling in general rest upon the concept of the correlation length that is divergent in power law phases.

III. MEAN FIELD THEORY OF CLASSICAL GASES - VAN DER WAALS EQUATION OF STATE

A. Phenomenology

The phase behavior of a monatomic particle systems consists, in the simplest case, of solid, liquid and gas phases. However even monatomic systems can have much more interesting behavior, as occurs in the case of Helium 4, where there is the additional possibility of a superfluid phase. The case of Helium 3 is still more interesting as this monatomic systems is a Fermionic system (2 protons, one neutron, two electrons), but it still undergoes a transition to superfluidity. The BCS theory has been extended to this case and predicts not only a singlet state, but also a triplet superfluid. This has been observed experimentally. There are also more than one solid phase. Molecular systems are even more complex with for example many different solid structures for ice, with 11 confirmed crystalline phases at the time of writing this. There are also the possibility of different fluid phases, with the case of liquid crystals being heavily studied due to a variety of applications in optics.

B. 3-D Van der Waals model, a mean field theory of gas-liquid phase transitions

We consider a monatomic interacting classical gas of particles that interact through central force pair potentials, so the Hamiltonian of the system is given by,

$$H = \sum_i \frac{p_i^2}{2m} + \sum_{i>j} u(|\vec{r}_i - \vec{r}_j|) \tag{47}$$

This interaction is quite good for many systems and in particular for inert gases (Helium, Argon, Neon...) where the pair interaction is of the Lennard-Jones form,

$$u(r) = 4\epsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6] \tag{48}$$

A further simplication that works well for these systems is to assume that the pair potential may be divided into a hard core replusion and an attactive part,

$$u(r < \sigma) = \infty; \quad u(r > \sigma) = -4\epsilon(\frac{\sigma}{r})^6 \tag{49}$$

The theory below is easily extended to any pair potential that can be divided into a hard core repulsive part and an attractive part.

The canonical partition function for a classical particle system is given by (see part 2, Eq. (7)),

$$Z = \frac{1}{N!h^{3N}} \int d^3q_1...d^3q_N \int d^3p_1....d^3p_n e^{-\beta H}. \tag{50}$$

Recall that the partition function of the ideal classical gas is given by,

$$Z = \frac{V^N}{N!\lambda^N}; \quad where \quad \lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \tag{51}$$

For particle systems with central force pair interactions, the partition function is,

$$Z = \frac{1}{N!\lambda^{3N}} \int d^3r_1...d^3r_N e^{-\beta \sum_{i>j} u(|\vec{r}_i - \vec{r}_j|)}. \tag{52}$$

To account for the hard core repulsion and the attractive part of the interation, we make the replacement $V \to V - Nb$, where $b = 4\pi\sigma^3/3$, which takes into account the reduction in the volume available to the particles. This is a mean field approximation as it treats the average effect of the hard core repulsions but not their fluctuations. The attractive contribution is also treated within mean field using the approximation,

$$\int d^3r_1...d^3r_N e^{-\beta \sum_{i>j} u(|\vec{r}_i - \vec{r}_j|)} \to I^N \tag{53}$$

where

$$I = Exp[-\beta \frac{N}{V} \int_\sigma u(r) 4\pi r^2 dr] = Exp[\beta a \frac{N}{V}] \tag{54}$$

where $a = -\int u(r) 4\pi r^2 dr$. The canonical partition function is then,

$$Z = \frac{q^N}{N!\lambda^N}; \quad \text{where} \quad q = (V - Nb) e^{aN/(Vk_BT)} \tag{55}$$

and the Helmholtz free energy is given by,

$$F = -k_BTln(Z) = -k_BTln\left(\frac{(V - bN)^N}{N!\lambda^{3N}}\right) - a\frac{N^2}{V} \tag{56}$$

The thermodynamics may then be calculated following the same procedures as for the classical ideal gas, to find the van der Waals equation of state,

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_BT}{V - Nb} - \frac{N^2 a}{V^2} \tag{57}$$

The entropy is,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} = k_B ln\left(\frac{(V - bN)^N}{N!\lambda^{3N}}\right) + \frac{3}{2} N k_B \tag{58}$$

and the internal energy is,

$$U = F + TS = \frac{3}{2} N k_B T - \frac{N^2 a}{V} \tag{59}$$

To find the thermodynamic state, F, S and U above need to be suplemented by the Maxwell construction for $T < T_c$. They are correct above T_c where the Helmholtz energy remains convex.

C. Critical exponents for van der Waals gas

It is convenient to work with the form,

$$P = \frac{k_BT}{v - b} - \frac{a}{v^2} \tag{60}$$

where $v = V/N$. The critical point is defined by,

$$\frac{\partial P}{\partial v}(T_c) = 0; \qquad \frac{\partial^2 P}{\partial v^2}(T_c) = 0 \tag{61}$$

which lead to the two equations,

$$\frac{-k_BT_c}{(v_c - b)^2} + \frac{2a}{v_c^3} = 0; \qquad \frac{2k_BT_c}{(v_c - b)^3} - \frac{6a}{v_c^4} = 0 \tag{62}$$

Solving gives,

$$v_c = 3b; \qquad k_B T_c = \frac{8}{27}\frac{a}{b}; \qquad P_c = \frac{a}{27b^2} \tag{63}$$

For temperatures below the critical isotherm, the van der Waals equation of state has a "wiggle" instead of a flat behavior in the co-existence region. This wiggle is not a thermodynamically stable state as if $\partial P/\partial V > 0$, the system is unstable and must compress. The question is what is the correct behavior in this regime. The Maxwell construction states that we should draw a flat line that has equal areas above and below the line, through the condition

$$P^*(v_l - v_g) = \int_{v_g}^{v_l} P dv \tag{64}$$

This is the same as the Gibb's construction for equilibrium phases. It states that when two phases co-exist they must have the same Gibb's free energy, or chemical potential. This is a condition we already saw in Part 1, as one of the fundamental conditions for equilibrium, along with equal temperature and pressure. To derive the Maxwell equal area rule, we use two constructions. The first is the tangent construction which states that if the Helmholtz free energy is not convex, then a tangent line drawn below the non-convex region is the equilibrium free energy. The composition on this "tie line" is a mixture of the compositions at the two end points of the tie line. This construction removes non-equilibrium, non-convex, parts of a Free energy surface. If we use this construction for the van der Waals free energy, we have,

$$-\frac{\partial F}{\partial V}(v_1) = -\frac{\partial F}{\partial V}(v_2) = \frac{F_1 - F_2}{V_2 - V_1} \tag{65}$$

which states that the slope at the two endpoints and on the tie line are the same. We may then write

$$-\frac{\partial F}{\partial V}(v_1)(V_2 - V_1) = F_1 - F_2 = \int_{V_1}^{V_2} P dV \tag{66}$$

dividing through by N and using the fact that the pressure $P*$ is the same at the ends and on the tie line gives the Maxwell construction (64).

We are now ready to find the critcal exponents. To define them, recall that the response functions for a particle system are defined as follows;

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N}; \quad \kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,N}; \quad \alpha_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{P,N}; \quad C_P = C_V + \frac{TV\alpha_P^2}{\kappa_T} \tag{67}$$

For any liquid-gas transition, the response functions κ_T, α_P, C_P diverge, while the response function C_V may diverge (e.g. for the Bose condensate is remains finite). We will look at the way in which these response functions behave near the critical point. The critical exponents for the liquid-gas phase transition are defined as follows;

$$C_V \approx t^{-\alpha}; \quad v_g - v_l \approx t^{\beta}; \quad \kappa_T \sim t^{-\gamma}; \quad |v - v_c| \approx |P - P_c|^{1/\delta} \tag{68}$$

Here $n = N/V = 1/v$. These expressions indicate that there is an analogy between magnetic behavior in the Ising model and the behavior near the critical point of liquid-gas systems. To be concrete, the analogies are $n_{liq} - n_{gas} \approx v_g - v_l \rightarrow 2m$, $P - P_c \rightarrow h$, $T - T_c \rightarrow T - T_c$.

The specific heat exponent is found using,

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}[\frac{3}{2}Nk_BT - \frac{Na^2}{V}] \approx |T - T_c|^{-\alpha} \quad T \geq T_c \tag{69}$$

where $\alpha = 0$. The isothermal compressibility is given by,

$$\kappa_T = -\left(V(\frac{\partial P}{\partial V})_T\right)^{-1}; \tag{70}$$

where

$$(\frac{\partial P}{\partial V})_T(V_c) == \frac{1}{Nb^2}\left[\frac{8a}{27b} - T\right] \approx |T - T_c| \quad T \geq T_c \tag{71}$$

comparing () and (), we find that $\gamma = 1$. Calculation of the order parameter behavior is more tedious. We first write,

$$\delta t = 1 - \frac{T}{T_c}; \quad \delta p = \frac{P}{P_c} - 1; \quad \delta v = \frac{V}{V_c} - 1 \tag{72}$$

In these variables, the equation of state is,

$$\delta p = \frac{8(1-\delta t)}{2+3\delta v} - \frac{3}{(1+\delta v)^2} - 1 \tag{73}$$

Expanding to third order in δv yields,

$$\delta p = -4\delta t + 6\delta t \delta v + 9\delta t(\delta v)^2 - \frac{3}{2}(\delta v)^3 \tag{74}$$

At T_c, $\delta t = 0$, so we find,

$$P - P_c \approx a(v - v_c)^3 \tag{75}$$

so that $\delta = 3$.

To find the order parameter behavior below T_c, we use the Maxwell construction, and we note that,

$$\delta p_l = \delta p_g; \quad \delta v_l = -\delta v_g \tag{76}$$

Writing Eq. (74) for both the gas and liquid, and using the above relations, leads to,

$$12t\delta v_g = 3(\delta v_g)^3; \qquad \text{so that} \qquad \delta v_g = 0, \delta v_g = \pm 2(\delta t)^{1/2} \tag{77}$$

The order parameter exponent is then $\beta_e = 1/2$. The order parameter in this problem is the density, so the correlation function that we use to characterize the critical fluctuations is the density-density correlation function,

$$C(\vec{r}) = \sum_{ij} \delta(|\vec{r}_i - \vec{r}_j| - r)[< n(\vec{r}_i)n(\vec{r}_j) > - < n(\vec{r}_i) >< n(\vec{r}_j) >] \tag{78}$$

and we expect that

$$C(r) \approx \frac{Exp[-r/\xi]}{r^{d-2+\eta}} \tag{79}$$

From the analysis above it is evident that the critical behavior of the van der Waals gas is essentially the same as that of the Ferromagnetic Ising model. It is remarkable that two systems that are so different exhibit the same critical behavior, indicating that "long-wavelength" properties are the most important in determining the behavior near critical points. The question then arises "what is important in determining the value of critical exponents". We already have a partial answer, the spatial dimension is important. A second related answer is that the range of the interactions is important, as we have seen that the infinite range Ising model behaves like a mean field problem and is independent of dimension, whereas a short range problem depends on dimension. A more complete answer to our question depends on more developments. But first we explore probably the most important interacting quantum model in physics, the BCS theory of superconductivity.

IV. MICROSCOPIC THEORY OF SUPERCONDUCTIVITY - BCS THEORY

A. Second quantization

First quantization is the transition from the classical momentum to the quantum momentum, i.e. $p \rightarrow -i\hbar\nabla$. A many body Hamiltonian is written in terms of these operators, and we solve for a many body wavefunction that has a specific number of particles. In second quantization we allow the possibility of any number of particles, as we did in the ideal Fermi and Bose gases. Moreover we work in the "number representation" rather than working with the many body wavefunctions. Before going to the many particle case it may be useful to remember the use of raising an lowering operators in the Harmonic oscillator.

1. Second quantization of a harmonic oscillator

Creation and annihilation operators are the same as raising and lowering operators, and for a harmonic oscillator they are defined by,

$$a = \alpha(x + i\frac{p}{m\omega}); a^\dagger = \alpha(x - i\frac{p}{m\omega}); \quad \alpha = (\frac{m\omega}{2\hbar})^{1/2} \tag{80}$$

and

$$[a, a^\dagger] = 1; \quad [a, a] = [a^\dagger, a^\dagger] = 0; \tag{81}$$

and

$$\hat{n} = a^\dagger a; \quad \hat{n}|n >= n|n >; \quad H = (\hat{n} + \frac{1}{2})\hbar\omega \tag{82}$$

with

$$a^\dagger|n >= (n+1)^{1/2}|n+1 >; \quad a|n >= (n)^{1/2}|n-1 > . \tag{83}$$

2. Second quantization of many-body Boson systems

This formulation can be extended to treat a many body system composed of many harmonic oscillators that interact. In that case, if there are N harmonic oscillators, and the number representation of a state gives the number of bosons in each state, that is $|n_1, n_2....n_M >$ for a system with M single particle energy levels. The creation and annihilation operators obey the relations,

$$[a_i, a_j^\dagger] = \delta_{ij}; \quad [a_i, a_j] = 0; \quad [a_i^\dagger, a_j^\dagger] = 0 \tag{84}$$

and,

$$\hat{n}_i = a_i^\dagger a_i; \quad \hat{n}_i|n_1...n_i + 1...n_M >= n_i|n_1...n_i + 1...n_M >; \tag{85}$$

and

$$a_i^\dagger|n_1...n_i...n_m >= (n_i+1)^{1/2}|n_1...n_i + 1...n_M >; \tag{86}$$

$$a_i|n_1...n_i...n_M >= (n_i)^{1/2}|n_1...n_i - 1...n_M > \tag{87}$$

These operators act in the state space of many body wavefunctions constructed from single particle states, for example for a set of Harmonic oscillators, we need to construct a correctly symmetrized N harmonic oscillator wavefunction basis set. A state of this type is written in second quantized form as,

$$|n_1....n_i...n_M >= (a_M^\dagger)^{n_M}..(a_i^\dagger)^{n_i}...(a_1^\dagger)^{n_1}|0 > \tag{88}$$

In field theory, the interactions are often written in real space where they are called field operators. Creation and annihilation then occurs at a point in space. Nevertheless Boson second quantized field operators obey the similar commutation relations,

$$[\psi(x), \psi^\dagger(x')] = \delta(x - x'); \quad [\psi(x), \psi(x')] = [\psi(x)^\dagger, \psi^\dagger(x')] = 0; \quad \hat{n}(x) = \psi(x)^\dagger\psi(x) \tag{89}$$

3. Second quantization of many-body Fermion systems

In the case of Fermions, there are two differences: (i) each state can only have one or zero particles, (ii) the commutators change to anticommutators, so that,

$$\{a_i, a_j^\dagger\} = \delta_{ij}; \quad \{a_i, a_j\} = 0; \quad \{a_i^\dagger, a_j^\dagger\} = 0 \tag{90}$$

and,

$$\hat{n}_i = a_i^\dagger a_i; \quad \hat{n}_i|n_1...n_i+1...n_M>= n_i|n_1...n_i+1...n_M>; \tag{91}$$

and

$$a_i^\dagger|n_1...n_i...n_m>= (-1)^{S_k}\delta(n_i)|n_1...n_i+1...n_M>; \tag{92}$$

and

$$a_i|n_1...n_i...n_M>= (-1)^{S_k}\delta(n_i-1)|n_1...n_i-1...n_M> \tag{93}$$

where $S_k = \sum_{j=1}^{i-1} n_j$. These operators act in the state space of many body wavefunctions constructed from single particle states. In the case of Fermions, the correct wave functions are Slater determinants, which have the form,

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{x}_1) & \psi_2(\mathbf{x}_1) & \cdots & \psi_N(\mathbf{x}_1) \\ \psi_1(\mathbf{x}_2) & \psi_2(\mathbf{x}_2) & \cdots & \psi_N(\mathbf{x}_2) \\ \vdots & \vdots & & \vdots \\ \psi_1(\mathbf{x}_N) & \psi_2(\mathbf{x}_N) & \cdots & \psi_N(\mathbf{x}_N) \end{vmatrix}. \tag{94}$$

A state of this type is written in second quantized form as,

$$|n_1....n_i...n_M>= (a_M^\dagger)^{n_M}..(a_i^\dagger)^{n_i}...(a_1^\dagger)^{n_1}|0> \tag{95}$$

In field theory, the interactions are often written in real space where they are called field operators. Creation and annihilation then occurs at a point in space. Nevertheless Boson second quantized field operators obey the similar commutation relations,

$$\{\psi(x), \psi^\dagger(x')\} = \delta(x-x'); \quad \{\psi(x), \psi(x')\} = \{\psi(x)^\dagger, \psi^\dagger(x')\} = 0; \quad \hat{n}(x) = \psi(x)^\dagger\psi(x) \tag{96}$$

4. Hamiltonians in second quantized form, both Bosons and Fermions

To work with these operators, we need to write the quantum Hamilonians that we are interested in second quantized form. This is relatively straightforward, as we can write a single particle wavefunction as,

$$\psi(\vec{r}) = \sum_k \psi_k(\vec{r}) a_k^\dagger|0> \tag{97}$$

so the second quantized form for the kinetic energy may be written as,

$$\hat{O} = \sum_{k_1,k_2} a_{k_1} O_{k_1,k_2} a_{k_2}^\dagger, \qquad O_{k_1,k_2} = \int d^3r \psi_{k_1}^*(\vec{r}) O(\vec{r}) \psi_{k_2}(\vec{r}) \tag{98}$$

and for a pair potential we have,

$$\hat{V} = \sum_{k_1,k_2,k_3,k_4} a_{k_1}^\dagger a_{k_2}^\dagger V_{k_1,k_2,k_3,k_4} a_{k_3} a_{k_3}, \qquad V_{k_1,k_2,k_3,k_4} = \int d^3r d^3r' \psi_{k_1}^*(\vec{r}) \psi_{k_2}^*(\vec{r}') V(\vec{r},\vec{r}') \psi_{k_3}(\vec{r}) \psi_{k_4}(\vec{r}') \tag{99}$$

Note that the order of the operators must be with the destruction operators to the right so the vacuum state has zero energy. This form of the Hamiltonian applies to both Fermions and Bosons, as the commutation (Bosons) and anticommutation (Fermion) relations account for the symmetry of the particles.

B. BCS theory

The original BCS paper of 1957 solved a momentum space Hamiltonian using a variational approach. Below we solve this momentum space Hamiltonian using a mean field approach introduced by Bogoliubov and developed in real space by de Gennes. BCS theory using the real space approach is more convenient for analysis of interfaces and tunnelling. It is solved using methods similar to those described here.

The BCS pairing Hamiltonian is a simplified model in which only pairs with zero center of mass momentum are included in the analysis. In the original BCS theory a singlet state was also assumed, so that,

$$H_{pair} - \mu N = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}\sigma} - \mu)\ a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} + \sum_{\vec{k}\vec{l}} V_{\vec{k}\vec{l}}\ a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k},\downarrow} a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow}, \tag{100}$$

where $N = \sum_{\vec{k}\sigma} n_{\vec{k}\sigma}$ is the number of electrons in the Fermi sea. The creation and destruction operators in this Hamiltonian obey the Fermion anticommutator relations,

$$\{a_{\vec{k},\sigma}, a^\dagger_{\vec{k}',\sigma'}\} = \delta_{\vec{k},\vec{k}'}\delta_{\sigma,\sigma'}, \quad \{a_{\vec{k},\sigma}, a_{\vec{k}',\sigma'}\} = 0, \quad \{a^\dagger_{\vec{k},\sigma}, a^\dagger_{\vec{k}',\sigma'}\} = 0, \tag{101}$$

while the number operator $n_{\vec{k},\sigma} = a^\dagger_{\vec{k},\sigma} a_{\vec{k},\sigma}$. The 1957 Bardeen, Cooper, Schreiffer (BCS) solution to this "pairing" Hamilonian introduces the averages,

$$b_{\vec{k}} =< a_{-\vec{k}\downarrow} a_{\vec{k}\uparrow} >, \quad \text{and} \quad b^*_{\vec{k}} =< a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k}\downarrow} > . \tag{102}$$

where $b^*_{\vec{k}}$ is the average number of pairs in the system at wavevector $\vec{k}$. We carry out an expansion in the fluctuations,

$$a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow} = b_l + (a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow} - b_l); \qquad a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k}\downarrow} = b^*_k + (a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k}\downarrow} - b^*_{\vec{k}}) \tag{103}$$

The mean field Hamiltonian keeps only the leading order term in the fluctuations so that,

$$H_{MF} - \mu N = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}\sigma} - \mu)\ a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} + \sum_{\vec{k}\vec{l}} V_{\vec{k}\vec{l}}\ (a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k},\downarrow} b_{\vec{l}} + b^*_{\vec{k}} a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow} - b^*_{\vec{k}} b_{\vec{l}}) \tag{104}$$

This is the Hamiltonian that leads to the BSC solution. Suprisingly it gives excellent results that agree with the experiments except very close to the phase transition. In constrast mean field theory for the Ising model and liquid-gas transition is quite poor in quantitative terms, for example predicting a critical point that is off by over 30% in most cases. The reason that the BCS mean field theory works so well for low temperature superconductors is explained by a deeper discussion of the fluctuations. We shall return to this issue later in a more general context.

The mean field Hamiltonian can be solved using an interesting transformation called the Bogoliubov-Valatin transformation. This transformation can be tuned so that the new Hamiltonian is like that of a Free Fermion system.

First we define the quantity (which will turn out to be the superconducting gap),

$$\Delta_{\vec{k}} = -\sum_{\vec{l}} V_{\vec{k}\vec{l}}\ b_{\vec{l}} \tag{105}$$

which reduces (104) to,

$$H_{MF} - \mu N = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}\sigma} - \mu)\ a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} - \sum_{\vec{k}} (\Delta_{\vec{k}} a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k},\downarrow} + \Delta^*_{\vec{k}} a_{-\vec{k}\downarrow} a_{\vec{k}\uparrow} - b^*_{\vec{k}} \Delta_{\vec{k}}) \tag{106}$$

The key trick to transforming (106) to Free Fermion form is to use the following transformation (where up spin is considered to be positive ($i.e.\ \sigma = +,\ for,\ spin = \uparrow$),

$$a_{\vec{k}\sigma} = u_{\vec{k}} \gamma_{\vec{k}\sigma} + \sigma v^*_{\vec{k}} \gamma^\dagger_{-\vec{k}-\sigma}, \tag{107}$$

where $u_{\vec{k}} = u_{-\vec{k}},\ v_{\vec{k}} = v_{-\vec{k}}$. For example, we have

$$a_{\vec{k}\uparrow} = u_{\vec{k}} \gamma_{\vec{k}\uparrow} + v^*_{\vec{k}} \gamma^\dagger_{-\vec{k}\downarrow}; \quad a^\dagger_{\vec{k}\downarrow} = u^*_{\vec{k}} \gamma^\dagger_{\vec{k}\downarrow} - v_{\vec{k}} \gamma_{-\vec{k}\uparrow}$$

and

$$a^\dagger_{\vec{k}\uparrow} = u^*_{\vec{k}} \gamma^\dagger_{\vec{k}\uparrow} + v_{\vec{k}} \gamma_{-\vec{k}\downarrow}; \quad a_{\vec{k}\downarrow} = u_{\vec{k}} \gamma_{\vec{k}\downarrow} - v^*_{\vec{k}} \gamma^\dagger_{-\vec{k}\uparrow}$$

The inverse transformation is,

$$\gamma_{\vec{k}\sigma} = u^*_{\vec{k}} a_{\vec{k}\sigma} - \sigma v_{\vec{k}} a^\dagger_{-\vec{k}-\sigma} \tag{108}$$

Using the Bogoliubov-Valatin transformation, it is possible to show that u_k, v_k may be chosen so that the mean field Hamiltonian is diagonal in the quasiparticle operators $\gamma_{\vec{k},\sigma}$.

To ensure that the new operators (e.g. $\gamma_{\vec{k}\uparrow}$) obey the Fermi anticommutation relations, we must have,

$$|u_{\vec{k}}|^2 + |v_{\vec{k}}|^2 = 1 \tag{109}$$

The Hamiltonian in the new operators is,

$$H_{MF} - \mu N = \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu - E_{\vec{k}} + \Delta_{\vec{k}} b^*_{\vec{k}}) + \sum_{\vec{k}} E_{\vec{k}} (\gamma^\dagger_{\vec{k}\uparrow}\gamma_{\vec{k}\uparrow} + \gamma^\dagger_{\vec{k}\downarrow}\gamma_{\vec{k}\downarrow}), \tag{110}$$

provided we impose the condition,

$$2(\epsilon_{\vec{k}} - \mu) u_{\vec{k}} v_{\vec{k}} + \Delta_{\vec{k}} v^2_{\vec{k}} - \Delta^*_{\vec{k}} u^2_{\vec{k}} = 0, \tag{111}$$

and we define $E_{\vec{k}}$ to be,

$$E_{\vec{k}} = (\epsilon_{\vec{k}} - \mu)(|u_{\vec{k}}|^2 - |v_{\vec{k}}|^2) + \Delta_{\vec{k}} u^*_{\vec{k}} v_{\vec{k}} + \Delta^*_{\vec{k}} v^*_{\vec{k}} u_{\vec{k}}. \tag{112}$$

Equations (109)-(112) along with the definition of $\Delta_{\vec{k}}$ (Eq. (105)) are the BCS solution. Now we have to extract the physics and to give physical meaning to the quantities $E_{\vec{k}}$, $\Delta_{\vec{k}}$, $b_{\vec{k}}$, $u_{\vec{k}}$ and $v_{\vec{k}}$. Without loss of generality, we can choose one of $u_{\vec{k}}$ or $v_{\vec{k}}$ to be real. We choose $u_{\vec{k}}$ to be real. Using Eq. (109) in (111), we have,

$$2(\epsilon_{\vec{k}} - \mu)(1 - |v_{\vec{k}}|^2)^{1/2} v_{\vec{k}} + \Delta_{\vec{k}} v^2_{\vec{k}} - \Delta^*_{\vec{k}}(1 - |v_{\vec{k}}|^2) = 0, \tag{113}$$

This is simplified if we write $v_{\vec{k}}$ as,

$$v_{\vec{k}} = \frac{g_{\vec{k}}}{(1 + |g_{\vec{k}}|^2)^{1/2}} \tag{114}$$

and hence,

$$|u_{\vec{k}}|^2 = 1 - |v_{\vec{k}}|^2 = \frac{1}{1 + |g_{\vec{k}}|^2}. \tag{115}$$

so that Eq. (111) reduces to,

$$2(\epsilon_{\vec{k}} - \mu) g_{\vec{k}} + \Delta_{\vec{k}} g^2_{\vec{k}} - \Delta^*_{\vec{k}} = 0. \tag{116}$$

with solution,

$$g_{\vec{k}} = \frac{-2(\epsilon_{\vec{k}} - \mu) \pm (4(\epsilon_{\vec{k}} - \mu)^2 + 4|\Delta_{\vec{k}}|^2)^{1/2}}{2\Delta_{\vec{k}}}.$$

For positive energy excitations, we take the positive root so that,

$$g_{\vec{k}} = \frac{E_{\vec{k}} - (\epsilon_{\vec{k}} - \mu)}{\Delta_{\vec{k}}} \tag{117}$$

where we defined,

$$E_{\vec{k}} = [(\epsilon_{\vec{k}} - \mu)^2 + |\Delta_{\vec{k}}|^2]^{1/2} \tag{118}$$

From this definition, and the definition of $g_{\vec{k}}$, we have,

$$|g_{\vec{k}}|^2 = \frac{E_{\vec{k}} - (\epsilon_{\vec{k}} - \mu)}{E_{\vec{k}} + (\epsilon_{\vec{k}} - \mu)}$$

and,

$$|v_{\vec{k}}|^2 = \frac{g_{\vec{k}}}{(1 + |g_{\vec{k}}|^2)^{1/2}} \frac{g^*_{\vec{k}}}{(1 + |g_{\vec{k}}|^2)^{1/2}} = \frac{(E_{\vec{k}} - (\epsilon_{\vec{k}} - \mu))^2}{|\Delta_{\vec{k}}|^2} \frac{|\Delta_{\vec{k}}|^2}{|\Delta_{\vec{k}}|^2 + (E_{\vec{k}} - (\epsilon_{\vec{k}} - \mu))^2}. \tag{119}$$

Using (118) we also find,

$$|v_{\vec{k}}|^2 = \frac{E_{\vec{k}} - (\epsilon_{\vec{k}} - \mu)}{2E_{\vec{k}}}$$

and from Eq. (118) and the normalisation condition (109), we have,

$$|u_{\vec{k}}|^2 = \frac{1}{(1 + |g_{\vec{k}}|^2)} = \frac{E_{\vec{k}} + (\epsilon_{\vec{k}} - \mu)}{2E_{\vec{k}}}. \tag{120}$$

Combining (118) and (119) it follows that,

$$u^*_{\vec{k}} v_{\vec{k}} = \frac{g_{\vec{k}}}{1 + |g_{\vec{k}}|^2} = g_{\vec{k}} |u_{\vec{k}}|^2 = \frac{\Delta^*_{\vec{k}}}{2E_{\vec{k}}} \tag{121}$$

Using these relations it is possible to show that Eqs. (112) and (118) are the same.

The gap at zero temperature

To proceed further, we need to evaluate the quantity $b_{\vec{k}}$ which measures the number of superconducting pairs in the condensate. Using the transformation (107), we have,

$$b_{\vec{k}} = < a_{-\vec{k}\downarrow} a_{\vec{k}\uparrow} > = < (u_{\vec{k}} \gamma_{-\vec{k}\downarrow} - v^*_{\vec{k}} \gamma^\dagger_{\vec{k}\uparrow})(u_{\vec{k}} \gamma_{\vec{k}\uparrow} + v^*_{\vec{k}} \gamma^\dagger_{-\vec{k}\downarrow}) > \tag{122}$$

The expectation value $< Operator >$ is taken over the ground state of the interacting Hamiltonian. The ground state has no quasiparticle excitations so that $< \gamma^\dagger_{\vec{k}\sigma} \gamma_{\vec{k}\sigma} >= 0$. From (122), we find that,

$$b_{\vec{k}} = u_{\vec{k}} v^*_{\vec{k}} \tag{123}$$

Combining Eqs. (105), (121) and (122), we find the famous "gap equation"

$$\Delta_{\vec{k}} = -\sum_{\vec{l}} V_{\vec{k}\vec{l}} \frac{\Delta_{\vec{l}}}{2E_{\vec{l}}} \tag{124}$$

with the quasiparticle excitations having the energy spectrum,

$$E_{\vec{k}} = ((\epsilon_{\vec{k}} - \mu)^2 + |\Delta_{\vec{k}}|^2)^{1/2} \tag{125}$$

In the special case of an angle independent gap $\Delta_{\vec{k}} = \Delta$, and assuming a constant pairing potential $-V$ in a band near the Fermi surface of width $\hbar\omega_c$, Eq. (124) reduces to,

$$1 = \frac{N(\epsilon_F)V}{2} \int_{\epsilon_F - \hbar\omega_c}^{\epsilon_F + \hbar\omega_c} \frac{d\epsilon}{((\epsilon - \epsilon_F)^2 + |\Delta|^2)^{1/2}} = N(\epsilon_F)V \int_0^{\hbar\omega_c/\Delta} \frac{dx}{(1 + x^2)^{1/2}} = N(\epsilon_F)V \; Sinh^{-1}(\frac{\hbar\omega_c}{\Delta}) \tag{126}$$

From (126), we take the weak coupling limit $\hbar\omega_c/\Delta >> 1$ to find the BCS gap *at zero temperature*,

$$\Delta = 2\hbar\omega_c Exp[\frac{-1}{N(\epsilon_F)V}] \tag{127}$$

Note that, following convention, $N(\epsilon_F)$ is the density of states *for one electron spin*, whereas the density of states quoted in most other applications is a factor of two larger. In the weak coupling limit $N(\epsilon_F)V << 1$, this expression is of the same form as the gap found in the Cooper problem, except for a factor of two in the exponential. The ground state energy is given by,

$$f_s(T = 0) - f_n(T = 0) = \sum_{\vec{k}} (\epsilon_{\vec{k}} - \mu - E_{\vec{k}} + \Delta_{\vec{k}} b^*_{\vec{k}}) = -\frac{1}{2} N(\epsilon_F) \Delta^2 \tag{128}$$

This is also called the condensation energy. As we shall show later using Landau theory, the difference in free energy between the normal and superconducting states $f_n(H = 0) - f_s(H = 0) = \frac{1}{2}\mu_0 H_c^2$. Combining these two equations we get an extimate of the critical field of type one superconductors in terms of the gap,

$$H_c^2 = N(\epsilon_F)\Delta^2/\mu_0 \tag{129}$$

The *density of states* for the excitations is very important as it is measured in tunnelling. The density of states is found from,

$$D(E)dE = N(\epsilon)d\epsilon \approx N(\epsilon_F)d\epsilon \tag{130}$$

Since,

$$dE = \frac{2(\epsilon-\mu)d\epsilon}{2((\epsilon-\mu)^2+\Delta^2))^{1/2}}, \tag{131}$$

we have,

$$D(E) = \frac{N(\epsilon_F)((\epsilon-\mu)^2+\Delta^2))^{1/2}}{\epsilon-\mu} = \frac{N(\epsilon_F)E}{(E^2-\Delta^2)^{1/2}} \tag{132}$$

This density of state applies for $E > |\Delta|$, while the density of states is zero otherwise.

The excitation or quasiparticle spectrum is also important. Recall that for a free Fermi system near the Fermi energy, we have,

$$\epsilon_k - \epsilon_F = \frac{\hbar^2 k^2}{2m} \approx \frac{\hbar^2 k_F}{m}(k-k_F) \tag{133}$$

which is found by using $k = k_F + (k - k_F)$ and expanding to leading order in $k - k_F$. In a superconductor the quasiparticle spectrum is,

$$E_k = ((\epsilon_k-\epsilon_F)^2+\Delta^2)^{1/2} \approx ((\frac{\hbar^2 k_F}{m}(k-k_F))^2+\Delta^2)^{1/2} \tag{134}$$

Finite temperature

To extend the ground state calculations to finite temperature, we only need to extend the evaluation of $b_{\vec{k}}$ to finite temperatures. From Eq. (122) we have,

$$< a_{-\vec{k}\downarrow}a_{\vec{k}\uparrow} >= u_{\vec{k}}v^*_{\vec{k}}(< 1-\gamma^\dagger_{\vec{k}\uparrow}\gamma_{\vec{k}\uparrow}-\gamma^\dagger_{-\vec{k}\downarrow}\gamma_{-\vec{k}\downarrow} >) = \frac{\Delta_{\vec{k}}}{2E_{\vec{k}}}(1-2f(E_{\vec{k}})) \tag{135}$$

where f is the Fermi function,

$$f(E_{\vec{k}}) = \frac{1}{e^{\beta E_{\vec{k}}}+1} \tag{136}$$

The *gap equation* at finite temperature (combining (105), (135) and (136)) is then,

$$\Delta_{\vec{l}} = -\sum_{\vec{k}} V_{\vec{k}\vec{l}}\,\frac{\Delta_{\vec{k}}}{2E_{\vec{k}}}\,(\frac{e^{\beta E_{\vec{k}}}-1}{e^{\beta E_{\vec{k}}}+1}) = -\sum_{\vec{k}} V_{\vec{k}\vec{l}}\,\frac{\Delta_{\vec{k}}}{2E_{\vec{k}}}\,Tanh(\frac{1}{2}\beta E_{\vec{k}}) \tag{137}$$

In the case of the weak-coupling s-wave model, this reduces to,

$$\frac{1}{N(\epsilon_F)V} = \int_0^{\hbar\omega_c} d\epsilon\,\frac{Tanh(\frac{\beta}{2}(\epsilon^2+\Delta^2)^{1/2})}{(\epsilon^2+\Delta^2)^{1/2}} \tag{138}$$

Though this integral must be evaluated numerically, the critical temperature can be found by setting $\Delta = 0$, so that,

$$\frac{1}{N(\epsilon_F)V} = \int_0^{\beta_c\hbar\omega_c/2} dx\,\frac{Tanh(x)}{x} = ln(x)Tanh(x)|_0^{\beta_c\hbar\omega_c/2} - \int_0^{\infty} ln(x)Sech^2(x)dx \tag{139}$$

In writing this last expression, we have used the fact that the integrand is now convergent at large x. The upper limit of the integral $\beta_c\hbar\omega_c/2 >> 1$ in all known cases of superconductivity, so we take the upper limit to infinity. In evaluating the first term note that the limit $x \to 0$ of $ln(x)Tanh(x)$ is convergent even though $ln(x)$ diverges as $x \to 0$. The integral that remains is a tabulated definite integral and its value is $ln(4e^\gamma/\pi)$. In the first term we also set $Tanh(\beta\hbar\omega_c/2) \to 1$, again due to the fact that $\beta\hbar\omega_c/2$ is large, then

$$\frac{1}{N(\epsilon_F)V} = ln(\beta_c\hbar\omega_c/2)Tanh(\infty) + a_1 \tag{140}$$

where $a_1 = ln(4e^{\gamma}/\pi) \sim ln(2 * 1.13..)$ (here $\gamma = 0.577..$ is Euler's constant). Eq. (137) then implies that,

$$k_B T_c = 1.13\hbar\omega_c e^{-1/N(\epsilon_F)V}; \quad \text{and} \quad \frac{k_B T_c}{\Delta(0)} = 1.13/2.0 = 0.565 \tag{141}$$

This ratio has been checked for a variety of low temperature superconductors and it is quite a good approximation.

To find the behavior of the gap near T_c, carry out a first order Taylor expansion of Eq. (137) using Δ^2 as the small quantity. This leads to,

$$\frac{1}{N(\epsilon_F)V} = \int_0^{\hbar\omega_c} d\epsilon \, \frac{Tanh(\frac{\beta\epsilon}{2})}{\epsilon} + \Delta^2 \int_0^{\hbar\omega_c} d\epsilon \, [\frac{\beta}{4}\frac{Sech^2(\frac{\beta\epsilon}{2})}{\epsilon^2} - \frac{1}{2}\frac{Tanh(\frac{\beta\epsilon}{2})}{\epsilon^3}] \tag{142}$$

This expression may be written in the form, write this in the form,

$$\frac{1}{N(\epsilon_F)V} = ln(\frac{1}{2}\beta\hbar\omega_c) + a_1 + \Delta^2\frac{\beta^2}{8}a_2 \tag{143}$$

where,

$$a_1 = Ln(4e^{\gamma}/\pi) \; ; \quad \text{and} \;\; a_2 = \int_0^{\infty} dx[\frac{Sech^2(x)}{x^2} - \frac{Tanh(x)}{x^3}] = -0.853 \tag{144}$$

After some algebra, we find that,

$$\frac{\Delta(T)}{k_B T_c} \approx 3.06(1 - \frac{T}{T_c})^{1/2}; \qquad T \to T_c \tag{145}$$

This is correct near T_c. Note that,

$$\frac{2\Delta(0)}{k_B T_c} = \frac{4}{1.13} \approx 3.52, \tag{146}$$

so the interpolation formula,

$$\frac{2\Delta(T)}{k_B T_c} \approx 3.52(1 - \frac{T}{T_c})^{1/2} \tag{147}$$

has the correct gap behavior near T_c and near $T = 0$, though the coefficient of the leading term near T_c is too small. Another ratio that is compared to experiment is the additional contribution of the superconducting transition to the specific heat,

$$\frac{\Delta C}{C_n} = \frac{(C_s - C_n)}{C_n}|_{T_c} = \frac{N(\epsilon_F)}{C_n}(\frac{-d\Delta^2}{dT})|_{T_c} = \frac{(1.74)^2(1.764)^2}{2\pi^2/3} = 1.43 \tag{148}$$

This is a significant additional specific heat, however it corresponds to $\alpha = 0$ as the specific heat does not diverge.

V. PERTURBATION THEORY AND SERIES EXPANSIONS

Decoupling strategies like mean field theory, or related approaches like decoupling of integral equation hierarchies or equations of motion, may be applied to any system and are widely used. An alternative approach that can produce similar results and in some ways is more appealing is to use a systematic pertubation theory approach. This approach can always be applied at high enough temperature as we know the limiting behavior about which to carry out the perturbation. If we know the ground state we can also carry out a systematic low temperature expansion.

Two general and basic elements of thermodynamic perturbation theory are as follows: (i) *The linked cluster theorem*: Expansions in statistical physics are most naturally carried out in terms of the partition function, however the quantities of interest are the free energies, entropy and averages such as the order parameters and response functions. Many of the terms in the expansion of the partition function are not extensive, so that when we take a logarithm or carry out averages we end up with many terms that are not extensive. These terms must cancel out in the end so one approach is to ignore them on physical grounds. However it is satisfying, this ad hoc procedure is justified by rigorous work demonstrating that for most systems of interest the non-extensive terms cancel in an expansion to arbitrary order. The proof is quite technical and we shall carry it through for the classical interacting gas. (ii) *Diagrammatic expansions and resummation*: It is usually best to classify terms in perturbation theory using graphs or diagrams. This is true for the Ising model, classical gases, in field theory and in most other problems. Diagrams are just a book keeping tool. For each problem there are rules for constructing them, counting them and evaluating them. The diagrams and rules are also different for different quantities even for the same problem, though they are often quite similar. Once we have a diagrammatic expansion it is possible to classify different classes of diagrams and to resum within a class. Once the diagrams within a class are resummed, the resulting theoretical expressions may reproduce the results of a particular decoupling scheme, so we can talk about "mean field"diagrams etc.

We shall illustrate these issues using two problems, the Ferromagnetic Ising model and the classical lattice gas.

A. Perturbation theory for the spin half Ferromagnetic Ising model

We consider the square lattice Ising model with nearest neighbor interactions, so that,

$$H = -J \sum_{<ij>} S_i S_j; \qquad \text{where} \qquad S_i = \pm 1, \quad J > 0 \tag{149}$$

The partition function is then,

$$Z = \sum_{S_i=\pm 1} \prod_{<ij>} e^{KS_iS_j} = (Cosh(K))^{zN/2} \sum_{S_i=\pm 1} \prod_{<ij>} (1 + tS_iS_j) \tag{150}$$

When we take the sum of the spin values $S_i = \pm 1$, the only terms that survive in the expansion of the product are terms where the spin operators S_i are raised to an even power. We can represent this graphically, by placing a bond for each spin pair S_iS_j. Terms with n spin pairs are then represented by n edges in the square lattice. All possible placement of edges appear in the product, but only those cases where the spins appear as even powers are finite. The first "graph" or "diagram" that is finite is a square () that appears with weight t^4, with one factor of t for each edge. The number of ways of placing this diagram on a square lattice is N where N is the number of sites in the lattice. The next finite term is a rectangle with 6 sites with six edges, so it is of order t^6, and it has degeneracy $2N$. The next term is of eighth order with eight edges. This case is more interesting as there are four connected diagrams that must be considered, in addition to the disconnected diagrams. The degeneracy for the connected diagrams is $9N$, while the disconnected diagrams have degeneracy $N(N - 9/2)$. For the 2-D Ising model this procedure can be carried to infinite order leading to the exact solution (see LL). To order t^8, the partition function is,

$$-\beta F = ln(Z) = \frac{zN}{2} ln(Cosh(K)) + Nln(2) + ln[1 + Nt^4 + 2Nt^6 + N(N + \frac{9}{2})t^8 + 0(t^{10})] \tag{151}$$

Expanding the logarithm and dropping terms that are not extensive (using the linked cluster theorem), gives,

$$-\beta F = \frac{zN}{2} ln(Cosh(K)) + Nln(2) + N[t^4 + 2t^6 + \frac{9}{2}t^8 + ...] \tag{152}$$

Note that the higher order terms in the expansion of the logarithm are not needed (linked cluster theorem) as they lead to non-extensive terms. This clearly simplifies the analysis a great deal. Note also that the expansion of the logarithm is clearly divergent, so that only the linked cluster theorem makes the expansion valid. Similar expansions may be carried out for different properties, for any lattice or graph structure, and for Ising model with spins different than $S_i = \pm 1$. For each case the appropriate diagrams have to be designed.

Now consider the low temperature series expansion about the ferromagnetic state. In this case, we consider a perturbation about the ground state. The ground state has all spins in one direction, so we choose all up spins. The first excited state has one down spin, so it differs in energy from the ground state by $8J$. The number of ways of choosing to flip one spin in the system is N. The next contribution is from flipping two spins. These two spins can be neighbors (connected) or non-neighbors (disconnected). The connected case has energy $12J$ with respect to the ground state, and they have degeneracy $2N$. The disconnected two spin flip diagrams have energy $16J$ with respect to the ground state and have degeneracy $N(N - 5/2)$. There are two connected third order diagrams that also have energy $16J$ with respect to the ground state, and they have degeneracy $4N$ and $2N$. There is also a connected four flip cluster with energy $16J$ with respect to the ground state. It has degeneracy N. The disconnected diagrams with three flipped spins are of higher order. The low temperature series expansion is then

$$Z = \sum_{S_i=\pm 1} \prod_{<ij>} e^{KS_iS_j} = e^{KzN/2}[1 + Ns^4 + 2Ns^6 + N(N + \frac{9}{2})s^8 + O(s^{10})] \tag{153}$$

so the Helmholtz free energy is given by,

$$-\beta F = N[\frac{1}{2}Kz + s^4 + 2s^6 + \frac{9}{2}s^8 + ...] \tag{154}$$

where again we invoked the linked cluster theorem to omit any non-extensive diagrams. Comparing Eq. () and (), we see that term by term they look the same. This equivalent turns out to be true to all orders, and is called duality. It corresponds to mapping the high temperature phase to the low temperature phase of the Ising system. This kind of mapping has been used extensively in other contexts. The Ising model on a square lattice is "self-dual" which leads to the idea that there is a special point at which the high and low temperature phases look the same, except for irrelevant prefactors in Z. These prefactors are irrelevant as the behavior near the critical point is determined by high order terms in the series expansions. Based on this observation, for this self dual model, we can find the critical point from the relation,

$$e^{-2K_c} = tanh(K_c); \quad so; \quad x = \frac{1-x}{1+x} \tag{155}$$

where $x = Exp(-2K_c)$. Solving we find $x = \frac{1}{2}(\sqrt{2}-1)$, so that,

$$K_c = \frac{J}{k_B T_c} = -\frac{1}{2}ln[(\sqrt{2}-1)] \approx 0.441, \tag{156}$$

which is the exact critical point of the square lattice Ising ferromagnet.

Series expansions have been carried out to high order from many spin systems. Critical behavior can be deduced by various extrapolation procedures, such as Pade approximates. Prior to the RG and advanced MC high order series expansions were the most accurate approach for finding critical exponents.

B. High temperature expansions for particle systems - the virial expansion

The virial expansion leads to a systematic series of corrections to the ideal gas law, in the form,

$$\frac{Pv}{k_B T} = \sum_{l=1}^{\infty} a_l(T)(\frac{\lambda^3}{v})^{l-1} \tag{157}$$

where $v = V/N$ and the thermal wavelength $\lambda = h/\sqrt{2\pi m k_B T}$, and $a_l(T)$ is the l^{th} virial coefficient. $a_1(T) = 1$, so the first non-trivial terms is the second virial coefficient. The expansion variable λ^3/v is small at high temperature and low density.

Derivation of the virial expansion is best carried out using the Grand Canonical Ensemble, where we will see that the pressure may be expanded as a power series in the fugacity, so that,

$$\frac{P}{k_B T} = \frac{1}{\lambda^3}\sum_{l=1}^{\infty} b_l z^l; \qquad N = z\frac{\partial(ln(\Xi))}{\partial z} = \frac{V}{\lambda^3}\sum_{l=1} l b_l z^l \tag{158}$$

where we used the relations $PV = k_B T ln(\Xi)$, $N = z\partial(ln(\Xi))/\partial z$, and $b_1 = 1$ to recover the ideal gas law at high enough temperatures. If we find the coefficients b_l in the fugacity expansion then the virial coefficients, $a_l(T)$ may be found by noting that,

$$\frac{Pv}{k_B T} = \frac{\sum_{l=1}^{\infty} b_l z^l}{\sum_{l=1}^{\infty} l b_l z^l} = \sum_{l=1}^{\infty} a_l(T)(\frac{\lambda^3}{v})^{l-1} \tag{159}$$

and using the fugacity equation for N/V in Eq. (158), we write

$$\sum_{l=1}^{\infty} b_l z^l = [\sum_{l=1}^{\infty} a_l(T)(\sum_{k=1} k b_k z^k)^{l-1}][\sum_{l=1}^{\infty} l b_l z^l]. \tag{160}$$

Expanding and keeping terms to order z^3 gives,

$$b_1 z + b_2 z^2 + b_3 z^3 = [a_1 + a_2(b_1 z + 2b_2 z^2 + 3b_3 z^3) + a_3(b_1 z + 2b_2 z^2 + 3b_3 z^3)^2 + ...](b_1 z + 2b_2 z^2 + 3b_3 z^3) \tag{161}$$

Equating the coefficients of z^n in this expression leads to relations between a_l and b_l, for example,

$$a_1(T) = 1; \quad a_2(T) = -b_2(T); \quad a_3(T) = 4b_2^2 - 2b_3 \quad etc \tag{162}$$

where $b_1 = 1$.

Now we want to find the coefficiencts b_l. For the ideal Bose and Fermi gases we already know that,

$$b_l = \frac{(-1)^{l+1}}{l^{5/2}}; \quad (Fermi) \qquad b_l = \frac{1}{l^{5/2}}; \quad (Bose) \tag{163}$$

Moreover, a general expression for b_l is found from the relation between the grand canonical partition function and the canonical partition function,

$$\Xi = \sum_{N=0} z^N Z_N; \qquad \textbf{so that} \quad \frac{PV}{k_BT} = ln(1 + zZ_1 + z^2 Z_2 + z^3 Z_3 + ...) = \frac{V}{\lambda^3}\sum b_l z^l \tag{164}$$

Expanding the logarithm and comparing coefficients, we can find a relation between b_l and the canonical partition functions Z_l. For example,

$$b_1 = \frac{\lambda^3}{V} Z_1; \quad b_2 = \frac{\lambda^3}{V}(Z_2 - \frac{1}{2}Z_1^2); \quad b_3 = \frac{\lambda^3}{V}(Z_1^3 - Z_1 Z_2 + \frac{1}{3}Z_3) \tag{165}$$

Though this is useful, the canonical partition function (Z_l) grows rapidly with l, so we have to subtract large quantities to find small residuals. In this case, it is better to try to find a smaller quantity to use for the perturbation theory. We shall do this for a classical particle system with pair interactions $u(\vec{r}_{ij})$, with partition function,

$$Z_N = \frac{1}{\lambda^{3N} N!} I_N; \qquad \text{where} \qquad I_N = \int \prod_i d^3 r_i e^{-\beta \sum_{i<j} u(\vec{r}_{ij})} \tag{166}$$

We define the quantity $f_{ij} = Exp[-\beta u(\vec{r}_{ij})] - 1$ that is small at high temperatures. We therefore write,

$$I_N = \int \prod_i d^3 r_i \prod_{i<j}(1 + f_{ij}) = \int \prod_i d^3 r_i [1 + \sum_{i<j} f_{ij} + \sum_{i<j,k<l} f_{ij} f_{kl} + ...] \tag{167}$$

Graphically, I_N consists of all graphs with N circles and n lines joining the circles, with at most one line between each pair of circles. The integrals corresponding to these graphs can be broken up into separate pieces. The first reduction considers connected clusters. A connected cluster is as it sounds, the circles are connected by edges. We define,

$$b_l = \frac{1}{l!\lambda^{3l-3}V}(sum\ over\ all\ l - connected - cluster\ integrals) \tag{168}$$

so that $b_1 = \frac{1}{V}\int d^3 r = 1$; and,

$$b_2 = \frac{1}{2!\lambda^3 V}\int d^3 r_1 d^3 r_2 f_{12} = \frac{1}{2\lambda^3}\int dr_{12} f_{12} \tag{169}$$

The third order term is more complex. However in general we note that the set of N particle graphs are composed of all clusters with the restriction,

$$\sum_{l=1}^{N} l m_l = N \tag{170}$$

where l is the size of a connected cluster and m_l is the number of times that cluster size appears. The contribution of each graph has a degeneracy factor due to the number of ways of arranging the clusters, each of which has degeneracy m_l. We then have to assign lines within these clusters. We may then write,

$$I_N = \sum_{m_l} T_1 T_2 = \sum_{m_l} \frac{N!}{\prod_l m_l!} \prod_l \frac{(l!\lambda^{3(l-1)} V b_l)^{m_l}}{(l!)^{m_l}} = \sum_{m_l} \frac{N!}{\prod_l m_l!} \prod_l (\lambda^{3(l-1)} V b_l)^{m_l} \tag{171}$$

where the sums over m_l must satisfy the constraint (170). The canonical partition function is then

$$Z_N = \sum_{m_l} \prod_{l=1}^{N} \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3}\right)^{m_l} \tag{172}$$

This sum is hard to do as the configurations $\{m_l\}$ are constrained by Eq. (170). The grand partition function that is given by,

$$\Xi = \sum_{N=0}^{\infty} z^N Z_N = \sum_{m_l} z^{\sum_l l m_l} \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\frac{V b_l}{\lambda^3}\right)^{m_l} = \sum_{m_l} \prod_{l=1}^{\infty} \frac{1}{m_l!} \left(\frac{V b_l z^l}{\lambda^3}\right)^{m_l} \tag{173}$$

where now the sums $_l$ can be carried out without the constraint. which simplifies to,

$$\Xi = \prod_{l=1} Exp[\frac{V}{\lambda^3} z^l b_l]; \quad \text{so} \quad \frac{PV}{k_B T} = ln(\Xi) = \frac{V}{\lambda^3} \sum_{l=1}^{\infty} b_l z^l \tag{174}$$

Which proves that the cluster integrals appear in the virial expansion, and that the terms in the expansion are extensive.

Assigned problems and sample quiz problems

Sample Quiz Problems

Quiz Problem 1. Draw the phase diagram of the Ising Ferromagnet in an applied magnetic field. Indicate the critical point. Plot the magnetization as a function of the applied field for three temperatures $T < T_c$, $T = T_c$, $T > T_c$.

Quiz Problem 2. Plot the behavior of the magnetization of the Ising ferromagnet as a function of the temperature, for three applied field cases: $h < 0$, $h = 0$, $h > 0$. Indicate the critical point.

Quiz Problem 3. Write down the definition of the critical exponents α, β_e, γ, δ, η and ν. What values do these exponents take within mean field theory.

Quiz Problem 4. Write down the mean field equation for the Ising ferromagnet in an applied field, on a lattice with co-ordination number z and exchange constant J. From this equation find the critical exponent δ for the Ising ferromagnet within mean field theory.

Quiz Problem 5. Write down the van der Waals equation of state. Draw the P, v phase diagram of the van der Waals gas and indicate the critical point.

Quiz Problem 6. Make plots of the van der Waals equation of state isotherms, for $T > T_c$, $T < T_c$ and for $T = T_c$. For the case $T < T_c$ explain why the non-convex part of the curve cannot occur at equilibrium and the Maxwell construction to obtain a physical P, v isotherm.

Quiz Problem 7. Write down the Landau free energy for the Ising and fluid-gas phase transitions. Explain the correspondences between the quantities in the magnetic and classical gas problems.

Quiz Problem 8. Explain the meaning of second quantization. Discuss the way that it can be used in position space and in the basis of single particle wavefunctions. Write down the commutation relations for Bose and Fermi second quantized creation and annihilation operators.

Quiz Problem 9. Write down the Hamiltonian for BCS theory, and the decoupling scheme used to reduce it to a solvable form. Explain the physical reasoning for the decoupling scheme that is chosen.

Quiz Problem 10. Consider the inverse Bogoliubov-Valatin transformation,

$$\gamma_{\vec{k}\sigma} = u^*_{\vec{k}} a_{\vec{k}\sigma} - \sigma v_{\vec{k}} a^\dagger_{-\vec{k}-\sigma}. \tag{175}$$

Show that if the operators $a, a^\dagger$ obey standard fermion anti-commutator relations, then the operators $\gamma, \gamma^\dagger$ also obey these relations, provided,

$$|u_k|^2 + |v_k|^2 = 1 \tag{176}$$

Quiz Problem 11. Given that the energy of quasiparticle excitations from the BCS ground state have the spectrum,

$$E = [(\epsilon - \epsilon_F)^2 + \Delta^2]^{1/2}, \tag{177}$$

where Δ is the superconducting gap and E_F is the Fermi energy, show that the quasiparticle density of states if given by,

$$D(E) = \frac{N(\epsilon_F)E}{(E^2 - \Delta^2)^{1/2}} \tag{178}$$

Quiz Problem 12. Describe the physical meaning of the superconducting gap, and the way in which BCS theory describes it.

Quiz Problem 13. (omit) BCS theory works very well even quite near the superconducting transition, despite the fact that it is a mean field theory. Use the Ginzburg criterion to rationalize this result. (we will do this after midterm III)

Quiz Problem 14. Given the general solutions to the BCS mean field theory

$$\Delta_{\vec{k}} = -\sum_{\vec{l}} V_{\vec{k}\vec{l}} \frac{\Delta_{\vec{l}}}{2E_{\vec{l}}}, \qquad E_{\vec{k}} = ((\epsilon_{\vec{k}} - \mu)^2 + |\Delta_{\vec{k}}|^2)^{1/2} \tag{179}$$

Describe the assumptions that are made in deducing that,

$$1 = \frac{N(\epsilon_F)V}{2} \int_{\epsilon_F - \hbar\omega_c}^{\epsilon_F + \hbar\omega_c} \frac{d\epsilon}{((\epsilon - \epsilon_F)^2 + |\Delta|^2)^{1/2}} =$$

$$N(\epsilon_F)V \int_0^{\hbar\omega_c/\Delta} \frac{dx}{(1+x^2)^{1/2}} = N(\epsilon_F)V \ Sinh^{-1}(\frac{\hbar\omega_c}{\Delta}) \tag{180}$$

and hence,

$$\Delta = 2\hbar\omega_c Exp[\frac{-1}{N(\epsilon_F)V}] \tag{181}$$

Quiz Problem 15. Explain the importance of the "linked-cluster" theorems in perturbation theory of many particle systems.

Quiz Problem 16. Draw the high temperature series expansion diagrams to order t^8 (where $t = tanh(\beta J)$) for the square lattice, nearest neighbor, spin half Ising ferromagnet partition function. What is the degeneracy of each of these diagrams? Write down the expansion for the Helmholtz free energy and give a physical reason why only the terms of order N are kept.

Quiz Problem 17. Draw the low temperature series expansion diagrams to order s^8 (where $s = Exp[-2\beta J)$ for the square lattice, nearest neighbor, spin half Ising ferromagnet partition function. What is the degeneracy of each of these diagrams? Write down the expansion for the Helmholtz free energy and give a physical reason why only the terms of order N are kept.

Quiz Problem 18. Write down the mathematical form of the virial expansion for many particle systems and explain why it is important. What physical properties can be extracted from the second virial coefficient?

Assigned problems

Assigned Problem 1. Consider the Ising ferromagnet in zero field, in the case where the spin can take three values $S_i = 0, \pm 1$. a) Find equations for the mean field free energy and magnetization. b) Find the critical temperature and the behavior near the critical point. Are the critical exponents $(\beta_e, \gamma, \alpha, \delta)$ the same as for the case $S = \pm 1$? Is the critical point at higher or lower temperature than the spin ± 1 case? c) Is the free energy for the the spin $0, \pm 1$ case higher or lower than the free energy of the ± 1 case? Why?

Assigned Problem 2. (i) Starting from Eq. (36) of the lecture notes, prove Eq. (39) of the lecture notes. (ii) From Eq. (44) or (45) of the lecture notes prove Eq. (46) in three dimensions.

Assigned Problem 3. The Dieterici equation of state for a gas is,

$$P = \frac{k_B T}{v - b} e^{-a/(k_B T v)} \tag{182}$$

where $v = V/N$. Find the critical point and the values of the exponents β, δ, γ.

Assigned Problem 4. Consider the Landau free energy,

$$F = a(T)m^2 + b(T)m^4 + c(T)m^6 \tag{183}$$

where $c(T) > 0$ as required for stability. Sketch the possible behaviors for $a(T), b(T)$ positive and negative, and show that the system undergoes a first order transition at some value T_c. Find the value of $a(T_c)$ and the discontinuity in m at the transition.

Assigned Problem 5. The BCS pairing Hamiltonian is a simplified model in which only pairs with zero center of mass momentum are included in the analysis. We also assume that the fermion pairing that leads to superconductivity occurs in the singlet channel. The BCS Hamiltonian is then,

$$H_{pair} - \mu N = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}\sigma} - \mu)\ a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} + \sum_{\vec{k}\vec{l}} V_{\vec{k}\vec{l}}\ a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k},\downarrow} a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow}, \tag{184}$$

where $N = \sum_{\vec{k}\sigma} n_{\vec{k}\sigma}$ is the number of electrons in the Fermi sea. By making an expansion in the fluctuations and defining,

$$b_{\vec{k}} = < a_{-\vec{k}\downarrow} a_{\vec{k}\uparrow} >, \quad \text{and} \quad b^*_{\vec{k}} = < a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k}\downarrow} > . \tag{185}$$

where $b^*_{\vec{k}}$ is the average number of pairs in the system at wavevector $\vec{k}$, show that the mean field BCS Hamiltonian is given by,

$$H_{MF} - \mu N = \sum_{\vec{k}\sigma} (\epsilon_{\vec{k}\sigma} - \mu)\ a^\dagger_{\vec{k}\sigma} a_{\vec{k}\sigma} + \sum_{\vec{k}\vec{l}} V_{\vec{k}\vec{l}}\ (a^\dagger_{\vec{k}\uparrow} a^\dagger_{-\vec{k},\downarrow} b_{\vec{l}} + b^*_{\vec{k}} a_{-\vec{l}\downarrow} a_{\vec{l}\uparrow} - b^*_{\vec{k}} b_{\vec{l}}) \tag{186}$$

This is the Hamiltonian that we will solve to find the thermodynamic behavior of superconductors, using an atomistic model.

Assigned Problem 6. Using the Bogoliubov-Valatin transformation (Eq. 107), show that the mean field BCS Hamiltonian (Eq. (106)) reduces to Eq. (110), provided Equations (111) and (112) are true.

Assigned Problem 7. If we define,

$$v_{\vec{k}} = \frac{g_{\vec{k}}}{(1 + |g_{\vec{k}}|^2)^{1/2}} \tag{187}$$

show that Eq. (111) reduces to (117).

Assigned Problem 8. Show that $E_{\vec{k}}$ as defined in Eq. (118) is in agreement with Eq. (112).

Assigned Problem 9. Prove the relations Eq. (119-121).

Assigned Problem 10. Prove the relation (135).

Assigned Problem 11. Starting from Eq. (137), prove the relation (145).

Assigned Problem 12. Consider a ferromagnetic nearest neighbor, spin 1/2, square lattice Ising model where the interactions along the x-axis, J_x, are different than those along the y-axis, J_y. Extend the low and high temperature expansions Eq. (150) and Eq. (152) to this case. Does duality still hold? From your expansions, find the internal energy and the specific heat.

Assigned Problem 13. Find the second virial coefficient for four cases: (i) the classical hard sphere gas; (ii) Non-interacting Fermions; (iii) Non-interacting Bosons; (iv) The van der Waals gas.