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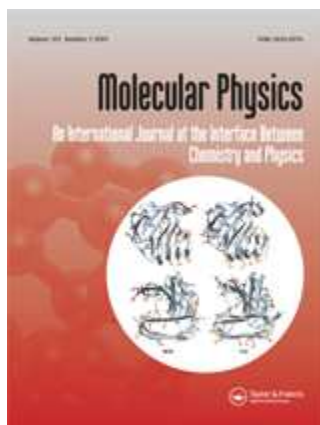
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First principles Landau Theory of symmetry
breaking

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February 15, 2011

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Abstract

Starting with a model of electrons interacting with point-like positively charged nuclei I derive an approximate but parameter free and quantitative theory of the coefficients in a Landau theory of second order phase transition. I then point out that the same arguments can be deployed to derive classical density-functional theories for emergent classical variables such as the order parameter used to describe symmetry breaking in condensed matter.

1 From electrons to models and to phenomenology

To a very good approximation condensed matter consists of point like positively charged nuclei and the electron 'glue' which holds them together. From this point of view, what a particle physicist would call the 'Theory of Everything' is Quantum Electrodynamics. In short all we need to concern ourselves with are point charges, described by the Dirac or Schrödingers equations, interacting via the Coulomb potential, or more precisely the electromagnetic field described by the Maxwells equations, with a single coupling constant $\alpha = e^2/\hbar c$. That this remarkably simple conceptual framework should give rise to an account of all forms of matter we encounter in our daily lives from gases to solids to soft matter etc.. all the way to the phenomena of life is one of the most surprising examples of the fact that simple rules can, and usually have, spectacularly complex consequences. The challenge to make sense of this inspires much good theoretical and experimental physics .

The by now generally accepted way to proceed is to establish, by mathematical analysis and expererimental observations, hierarchies of theories each with its appropriate spacial and time scales of applicability. Thus one goes from 'first principles' calculations involving electrons, ions and photons to microscopic models of interacting atoms and molecules and on to phenomenological equations such as those Navier-Stokes equation of hydrodynamics to mention but the first few steps. Usually, it is the transition from one level to an other that represents the most conceptual difficulties. Here I will illustrate this by a theory of getting from 'first principles' to the frankly phenomenological Landau Theory of symmetry breaking in condensed matter physics[1] . Appropriately in this volume I will also aim to elucidate how classical density theories[2] [3] can arise from the quantum density functional theory (DFT) for electrons and ions[4]. The focus will be on the change in the level of description and therefore the phrase 'first principles' should not be taken to imply that the theory is in any way exact but only that it is a one parameter, α , electron-ion theory in some commonly used approximation like the Local Density Approximation (LDA)[4]

Recall that the construction of a Landau Theory consists of three separate maneuvers: a.) The choice of the order parameter η which is zero in the high temperature high symmetry phase and non zero, indicating that some of the symmetry has been lost, below the transition temperature T_c . In general η has a number of components and is defined at a continuum of spacial pints \vec{r} or lattice sites labeled by i . It stands to reason that near T_c η is small and the appropriate part of the free energy $\delta\Phi$ can be expanded in powers of η . b.) Writing $\delta\Phi$ as a sum of polynomials in η that are invariants under symmetry G of the high temperature phase using group theory. In such expansion each of such invariant polynomial has a coefficient γ_n which is a function of T and other thermodynamic variables and is to be determined by experiments.c.) Finally in the pre Wilson, original formulation, $\delta\Phi$ is minimized with respect to arbitrary variations in η . The value of η which minimizes $\delta\Phi$ is its thermodynamic value

and it is zero or non-zero depending on whether $T > T_c$ or $T < T_c$. Evidently, because of the nature of γ_n this theory is frankly phenomenological. What I shall mean by a 'first principle' Landau theory is the one where such coefficients are calculated from 'first principles' in the sense I referred to this notion above.

Landau Theories are a powerful way of describing a great variety of phase transitions. Perhaps the most noted examples are those in ferromagnets, ferroelectrics, superfluids, superconductors and multi-component alloys. To discuss all of them within a single framework would lead to a level of abstraction out of place in this volume. Therefore, I have chosen the classic example, treated in Landau's original paper[7], of 'ordering and clustering in binary crystalline alloys' to illustrate the central points I wish to make.

2 Landau Theory of compositional order in crystalline binary alloy

A liquid mixture of A and B atoms have two independent thermodynamic densities: $\rho^A(\vec{r})$ and $\rho^B(\vec{r})$ or, equivalently, the total density $\rho(\vec{r}) = \rho^A(\vec{r}) + \rho^B(\vec{r})$ and the concentration $c(\vec{r})$ defined by $\rho^A(\vec{r}) - \rho^B(\vec{r}) = \rho(\vec{r})(2c(\vec{r}) - 1)$. Usually, as the temperature lowered, order appears in the variable $\rho(\vec{r})$ while the concentration variable remains disordered. Once the system crystallized a thermodynamic state is characterized by a configuration $\{c_i\}$ where c_i is the probability that a site located at \vec{R}_i is occupied by an A atom. Just below the temperature of crystallization, namely the melting temperature T_M , the equilibrium state is characterized by $c_i = \bar{c}$ for all i and is often referred to as a solid solution. On further lowering the temperature at some critical temperature T_0 the alloy will either order or phase separate[5]. These are the phenomena I shall be concerned with here.

It is conventional to develop the theory of such concentration fluctuations by introducing the occupational variables ξ_i which take on the value 1 if the site i is occupied by an A atom and 0 if the atom at that site is of the B type. Then

$$\langle \xi_i \rangle = c_i \quad (1)$$

where the average denoted by the brackets is with respect to an ensemble of compositional configurations with an appropriate measure. An elegant way to study ordering processes is to look for the temperature T_0 below which the equilibrium concentration is given by a superposition of concentration waves[5]

$$c_i = \bar{c} + \frac{1}{2} \sum_{\nu} \left(c_{\nu} e^{i\vec{k}_{\nu} \cdot \vec{R}_i} + c_{\nu}^* e^{-i\vec{k}_{\nu} \cdot \vec{R}_i} \right)$$

with characteristic wave vectors \vec{k}_{ν} and amplitudes c_{ν} . For instance the L1₂ ordered state of Cu₃Au on an FCC lattice is described by

$$c_i = \bar{c} + \frac{1}{4} \eta \left(e^{i\vec{k}_1 \cdot \vec{R}_i} + e^{i\vec{k}_2 \cdot \vec{R}_i} + e^{i\vec{k}_3 \cdot \vec{R}_i} \right) \quad (2)$$

where the wave vectors are $\vec{k}_1 = \frac{2\pi}{a}(1, 0, 0)$, $\vec{k}_2 = \frac{2\pi}{a}(0, 1, 0)$, $\vec{k}_3 = \frac{2\pi}{a}(0, 0, 1)$ and η is the convenient order parameter whose non zero value below T_0 indicates that the translational symmetry of the homogeneous solid solution has been broken and only the $L1_2$ symmetry remains'

According to Landau what drives such ordering process is the generalized free energy difference $\delta\Phi(\{c_i\})$ between that of the state characterized by the configuration $\{c_i\}$ and that of the solid solution. Assuming that near T_0 the deviations $\delta c_i = c_i - \bar{c}$ are small he then expands $\delta\Phi(\{c_i\})$ as follows

$$\delta\Phi(\{c_i\}) = \frac{1}{2!} \sum_{i,j} \gamma_{i,j}^{(2)} \delta c_i \delta c_j + \frac{1}{3!} \sum_{i,j,k} \gamma_{i,j,k}^{(3)} \delta c_i \delta c_j \delta c_k + \dots \quad (3)$$

where the $\gamma_{ij\dots}^{(n)}$ s are the symmetry allowed coefficients referred to in the introduction. The equilibrium configuration is then determined by minimizing $\delta\Phi(\{c_i\})$ with respect to all configurations by solving

$$\sum_i \frac{\partial \delta\Phi}{\partial \delta c_i} \Big|_{\{\bar{c}_i\}} = 0 \quad (4)$$

where $\{\bar{c}_i\}$ is the equilibrium configuration. For instance, for parametrization of $\delta\Phi$ appropriate to $Cu_{.75}Au_{.25}$ the solution is the concentration wave given in eq.2 and 4 turns into an algebraic equation which determines the size of η .

Up to now, apart from symmetry restrictions, the above coefficients are material dependent characteristics of the solid solution. They are to be determined by experiments. Clearly much would be gained if they could be calculated either from semi-phenomenological models or from 'first principles'. What concerns us here are ways of accomplishing this task.

3 Effective model Hamiltonians versus 'first principles' calculations.

A conceptually simple procedure is to start by forgetting the electrons altogether and assuming that the lattice sites are occupied by atoms interacting by effective pair potentials $v_{i,j}^{A,A}$, $v_{i,j}^{A,B}$, $v_{i,j}^{B,A}$, $v_{i,j}^{B,B}$. Then, determine these pair potentials by demanding that the energy of a selection of configurations $\{\xi_i\}$:

$$H^{eff}(\{\xi_i\}) = \sum_{i,j} \xi_i \xi_j v_{i,j}^{A,A} + \xi_i (1 - \xi_j) v_{i,j}^{A,B} + (1 - \xi_i) \xi_j v_{i,j}^{B,A} + (1 - \xi_i)(1 - \xi_j) v_{i,j}^{B,B} \quad (5)$$

agrees with the result of 'first principles' ground state calculations of $E_0(\{\xi_i\})$ for the same configurations. Evidently, one must choose configurations $\{\xi_i\}$ such that they represent periodic arrangements of A and B atoms so that the Bloch

Theorem can render such calculations tractable. Moreover, the number of potential parameters, $\mathbf{v}_{i,j}^{A,A}$ etc..., can not be larger than a few nearest neighbours. Once such fit to 'first principles' calculations have been achieved, the second step of the procedure is to use $H^{eff}(\{\xi_i\})$ as a model Hamiltonian in a standard classical statistical mechanics calculation on a lattice[6]. Namely, for instance, calculate the partition function

$$Z(T, V, N, \nu) = \sum_{\{\xi_i\}} \exp -\beta \left[H^{eff}(\{\xi_i\}) + \nu \sum (1 - 2\xi_i) \right] \quad (6)$$

and the grand potential

$$\Omega(T, V, N, \nu) = -\frac{1}{\beta} \ln Z(T, V, N, \nu) \quad (7)$$

where T is the temperature, $\beta = 1/k_B T$, V is the volume, N the number of sites and ν is the chemical potential difference $\nu = \mu^A - \mu^B$. The object of the exercise here is to develop an alternative to the above scheme for eliminating the electrons in favor of a classical Hamiltonian.

Whilst the above route from a one parameter theory of electrons and ions to the classical statistical mechanics of interacting atoms, with many materials dependent parameters, performs the theoretical task set in the introduction it has a number of shortcomings. The problem is not that it is in no way exact, the alternative I shall propose will not be exact either, but that, from the point of view of the Landau theory, it starts at the wrong place in the phase diagram. In short, the information that goes into the determination of the effective Hamiltonian $H^{eff}(\{\xi_i\})$ refers to the electrons in one of the many selected, low symmetry, ground states where as the Landau parameters in eq.3 are properties of the high temperature high symmetry phase. Thus other things being equal one should start with electronic structure calculations in the high symmetry phase Namely, the first principles approach should be deployed in the disordered, solid solution phase. How one might implement this idea is the theme of what follows

4 The concentration 'functional' approach on a lattice

For the purpose at hand, it turns out to be very convenient to rephrase the classical configurational statistical mechanical problem in Sec2 as a classical concentration 'functional' theory CCFT. This approach is the lattice-gas analogue of the genuinely density *functional* theories such as those for classical liquids[2] or electrons[4] where the relevant densities, unlike the countably infinite concentration variable c_i , are continuous functions of the spacial position \vec{r} . As its predecessor CCFT is based on a surprising theorem. In the present context it may be summarized as follows:

Take a lattice Hamiltonian of the form

$$H(\{\xi_i\}) = H_0(\{\xi_i\}) + \sum_i \mathbf{v}_i(1 - 2\xi_i) \quad (8)$$

where $H_0(\{\xi_i\})$ is an arbitrary generalization of the effective lattice Hamiltonian $H^{eff}(\{\xi_i\})$ in eq.5 and the second term is an external perturbation specified by the set of local chemical potentials parameters $\{\mathbf{v}_i\}$. Using eqs 6 and 7 the Hamiltonian in eq.8 leads to a grand potential $\Omega(T, V, N, \nu; \{\mathbf{v}_i\})$ 'functional' (function of countable infinitely many variables) of the external 'potential' $\{\mathbf{v}_i\}$ and is the generator of correlation functions as in $\frac{\partial \Omega}{\partial \mathbf{v}_i} = 2 \langle \xi_i \rangle - 1$, $\frac{\partial^2 \Omega}{\partial \mathbf{v}_i \partial \mathbf{v}_j} = q_{i,j} \equiv \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle$ etc.. Clearly, for every set of external potentials $\{\mathbf{v}_i\}$ one can find a set of concentrations $\{c_i\}$ by applying the above rules of statistical mechanics. The first part of the theorem is that this relation can be inverted. That is to say the for any chosen set $\{c_i\}$ one can find a unique set $\{\mathbf{v}_i\}$ such that it will produce $\{c_i\}$. The proof is straight forward following the arguments of Mermin[8] and Evans[2]. The next move is to show that there is a generalized internal Helmholtz free energy $\Omega(T, V, N, \nu, \{c_i\})$ such that its minimum with respect to arbitrary variations of $\{c_i\}$ is the thermodynamic equilibrium value of the internal Helmholtz free energy. Moreover, the concentration configuration $\{\bar{c}_i\}$ for which the minimum $\Omega(T, V, N, \nu, \{\bar{c}_i\})$ occurs is the equilibrium concentration distribution. Finally one finds that $\Omega(T, V, N, \nu, \{c_i\})$ can be written in the following very convenient form

$$\Omega(T, V, N, \nu, \{c_i\}) = \sum_i \mathbf{v}_i(1 - 2c_i) + F(\{c_i\}) + \nu \sum_i (1 - 2c_i) \quad (9)$$

where, remarkably, the 'functional' $F(\{c_i\})$ is independent of $\{\mathbf{v}_i\}$. Note however that it depends on the potential parameters which define $H_0(\{\xi_i\})$.

In the non-interacting limit, namely when $H_0(\{\xi_i\})$ is independent of the occupation configuration $\{\xi_i\}$, and $F_0(\{c_i\}) = \beta^{-1} \sum_i [c_i \ln c_i + [(1 - c_i) \ln(1 - c_i)]]$. Thus, with great generality, we may write

$$F(\{c_i\}) = \beta^{-1} \sum_i [c_i \ln c_i + [(1 - c_i) \ln(1 - c_i)]] - \Phi_{int}(\{c_i\}) \quad (10)$$

where $\Phi_{int}(\{c_i\})$ is an interaction functional independent of the external perturbations $\{\mathbf{v}_i\}$.

Ofcourse, whilst the above theorem is an exact statement in itself it is not helpful because the exact functional $F(\{c_i\})$ is not known. However, if useful approximate interaction functionals can be constructed eq.4 becomes a powerful tool [2],[4]. In the next section I will discuss an approximate functional which can be calculated using a first principles method without an intermediate step of fitting such calculations to classical model Hamiltonians. However, before moving on I pause to conclude this section with a brief summary of how this CCFT is to be used.

As mentioned above $\Omega(T, V, N, \nu; \{\mathbf{v}_i\})$ is the generator of the occupation variable correlation functions. As it turns out, in a similar manner, $\Phi_{int}(\nu, \{c_i\})$ is the generator of the direct correlation functions:

$$S_i^{(1)} = -\beta \frac{\partial \Phi_{int}}{\partial c_i} |_{\{\bar{c}_i\}}, \quad S_{i,j}^{(2)} = -\beta \frac{\partial \Phi_{int}}{\partial c_i \partial c_j} |_{\{\bar{c}_i\}} \quad \text{etc..} \quad (11)$$

In terms of these the equation of state, which follows from the extremal condition $\frac{\partial \Omega}{\partial c_i} = 0$, is

$$\frac{1}{\beta} \ln \frac{c_i}{1 - c_i} + \frac{1}{\beta} S_i^{(1)} - 2\mathbf{v}_i = 0 \quad (12)$$

and the two point correlation function is given by

$$q_{i,j} = c_i(1 - c_i)\delta_{i,j} - c_i(1 - c_i) \sum_l S_{i,l}^{(2)} q_{l,j}$$

These are the most useful relations in studies of binary alloy phase diagrams on the bases of pair-wise interacting atoms. Indeed one readily recalls that in the mean-field approximation $S_{i,l}^{(2)}$ is the pairwise interchange energy $v_{i,j}^{A,A} + v_{i,j}^{B,B} - 2v_{i,j}^{A,B}$ and $q_{i,j}$ measures the chemical short range order (SRO) in an alloy. Moreover its the lattice Fourier transform $q(\vec{k})$ is proportional to the X-ray diffuse scattering intensity.

Here the relevant point is that $\Omega(T, V, N, \nu, \{c_i\})$ provides a means of calculating the Landau parameters defined in eq.3. Namely

$$\begin{aligned} \gamma_{i,j}^{(2)} &= \frac{k_B T}{\bar{c}(1 - \bar{c})} \delta_{i,j} - S_{i,l}^{(2)} \\ \gamma_{i,j,k}^{(3)} &= \frac{k_B T (2\bar{c} - 1)}{6\bar{c}^2(1 - \bar{c})^2} \delta_{i,j} \delta_{i,k} - S_{i,j,k}^{(3)} \\ &\text{etc..} \end{aligned} \quad (13)$$

where \bar{c} is the equilibrium concentration in the high symmetry disordered state where $\bar{c}_i = \bar{c}$ for all i . As mentioned above Landau regarded these coefficients as phenomenological properties of the high symmetry phase. By contrast, according to the view taken here they should be calculated on the bases of microscopic models either based on interacting atoms or on interacting electrons and ions.

5 A 'First Principles' theory of the interaction functional $\Phi_{int}(\{c_i\})$

5.1 The Mean-field Theory of concentration fluctuations

The quantum mechanical Density Functional Theory of Hohenberg and Kohn[9] and Kohn and Sham[10] provides a method for calculating the electronic grand

potential $\Omega_e(V, \{\xi_i\}, \mu, T)$ at a volume V , temperature T , electronic chemical potential μ for a fixed occupational configuration $\{\xi_i\}$. On a time scale long compared with the diffusion time of the atoms on the lattice $\Omega_e(V, \{\xi_i\}, \mu, T)$ can be used as the effective configuration Hamiltonian $H_0(\{\xi_i\})$ in the previous section. Then an interaction 'functional' $\Phi_{int}(\{c_i\})$ can, in principle, be constructed as follows

$$\Phi_{int}(\{c_i\}) = \sum_{\{\xi_i\}} P(\{\xi_i\}; \{c_i\}) \Omega_e(V, \{\xi_i\}, \mu, T)$$

where $P(\{\xi_i\}; \{c_i\})$ the probability that a given configuration $\{\xi_i\}$ occurs under the constraint that the configuration of the averages $\{\langle \xi_i \rangle\}$ has been prescribed by $\{c_i\}$. Of course this recipe poses an impossible task. However, interestingly, it becomes tractable in a sequence of mean field approximations.

Firstly, one assumes, as is appropriate in a mean-field theory, that the occupation of a site i fluctuates independently from the others. Namely, the probability that the site is occupied by an A atom is c_i and that for a B atom is $1 - c_i$. Then, the distribution function $P(\{\xi_i\}; \{c_i\})$ factorizes:

$$P(\{\xi_i\}; \{c_i\}) = \prod_i P_i(\xi_i; c_i) \quad (14)$$

$$P_i(\xi_i; c_i) = c_i \xi_i + (1 - c_i)(1 - \xi_i)$$

Clearly, as advertised, $P(\{\xi_i\}; \{c_i\})$ is parametrized by the concentration configuration $\{c_i\}$

Secondly, let us imagine that the electronic grandpotential $\Omega_e(V, \{\xi_i\}, \mu, T)$ is calculated in the Local Density Approximation (LDA) to the quantum mechanical DFT for the electrons. This is a very successful approximation for describing the energetics of interacting electrons in the external field due to the charged nuclei of a solid and is widely regarded of the meanfield theory for this problem. Thus

$$\Phi_{int}(\{c_i\}) = - \int_0^{\mu} d\epsilon \langle N^{LDA}(\epsilon; \{\xi_i\}) \rangle + \delta\bar{\Omega} \quad (15)$$

where $N^{LDA}(\epsilon; \{\xi_i\})$ is the LDA integrated density of state and $\delta\bar{\Omega}$ is the fully averaged double counting correction fully discussed in [15] but, in the interest of accessible presentation, will be neglected here.

Thirdly, the appropriate method for taking the average over an ensemble of independent random occupation numbers in eq.15 is chosen to be the Coherent Potential Approximation (CPA) which the mean field theory of such disorder for electrons moving in a random potential field [11]. Thus

$$\Phi_{int}(\{c_i\}) = - \int_0^{\mu} d\epsilon \langle N^{LDA}(\epsilon) \rangle^{CPA} + \delta\bar{\Omega} \quad (16)$$

where the CPA averaged integrated density of state $\langle N^{LDA}(\epsilon) \rangle^{CPA}$ depends on the whole concentration configuration $\{c_i\}$ and hence may be usefully referred to as $\bar{N}^{CPA}(\epsilon; \{c_i\})$. The way the average of $\{\xi_i\}$ is to be implemented will be described in the next section.

5.2 The combined Local Density and Coherent Potential Approximation

The LDA for a fixed occupation number configuration $\{\xi_i\}$ requires the solution of a selfconsistent one electron Schrodingers equation, namely the Kohn-Sham equation, for the corresponding arrangement of the atoms. In principle, using such solution one can calculate the integrated density of states $N(\epsilon; \{\xi_i\})$ and average it with respect to the distribution function given in eq.14. Given the number of such configurations and the fact that the crystal potential for most of them is not periodic, and therefore one can not make use of the Boch Theorem, this is still an impossible task. Remarkably the CPA render this problem tractable at the cost of inverting the order in which the averaging over all configurations and the iterating to charge selfconsistency required by the Kohn-Sham equation are implemented. This inversion is facilitated by the local nature of LDA and made the maximal use of by the single site nature of the local CPA. How this central maneuver of present the approach to the problem works can be readily see as follows:

Recall that for a fixed configuration the Kohn-Sham equation[10] can be written as

$$\left(-\frac{\hbar^2 \nabla^2}{2m} + \sum_i v_i(\vec{r}_i; [\rho]) \right) \psi_n(\vec{r}) = \epsilon_n \psi_n(\vec{r})$$

where $v_i(\vec{r}_i; [\rho])$ describes the external, Hartree and exchange correlation potentials in the i-th unit cell as a function of the position vector \vec{r}_i measured from the centre of the i-th unit cell which is, for simplicity, assumed to contain only one atom. Whilst in general the local potential $v_i(\vec{r}_i; [\rho])$ depends on the full configuration $\{\xi_i\}$ in the combined LDA and CPA theory it depends only on the local density

$$\rho_i(\vec{r}, \xi_i) = \xi_i \rho_i^A(\vec{r}) + (1 - \xi_i) \rho_i^B(\vec{r}) \quad (17)$$

where $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$ are the local charge densities averaged over all configurations with the local occupation number fixed at $\xi_i = 1$ or 0 respectively. If we assume that each unit cell is neutral on the average and therefore the Madelung contribution to the selfconsistent potential can be neglected the local potential $v_i(\vec{r}_i; [\rho])$ at the site i takes the same form as the local charge density in eq.17

$$v_i(\vec{r}, \xi_i) = \xi_i v_i^A(\vec{r}) + (1 - \xi_i) v_i^B(\vec{r}) \quad (18)$$

where the partially averaged potentials $v_i^A(\vec{r})$ and $v_i^B(\vec{r})$ depend only on the partially averaged charge densities $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$. This approximation, which is remedied in the more recent versions of the theory based on the non-local version of the KKR-CPA [12],[13],[14], then solves the inversion problem mentioned above since the KKR-CPA provides as an output partially averaged charge densities $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$ from which a new random crystal potential can be constructed as follows:

$$\sum_i v_i(\vec{r}_i; [\rho]) \simeq \sum_i \xi_i v_i^A(\vec{r}) + (1 - \xi_i) v_i^B(\vec{r}) \quad (19)$$

and hence at the end of a KKR-CPA calculation the procedure can be repeated until convergence on $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$ is reached. At this point it should be stressed that the partially averaged quantities $v_i^A(\vec{r})$, $v_i^B(\vec{r})$, $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$ depend not on the occupation configuration $\{\xi_i\}$ but on the concentration configuration $\{c_i\}$. As a consequence, at least in principle, the result is a fully self-consistent combined LDA CPA calculation of the 'total energy' $\Phi_{int}(\{c_i\})$. Of course, this is still only a formal theory since the corresponding calculations can not be implemented for an arbitrary inhomogeneous set $\{c_i\}$. However, the standard single site KKR-CPA solves the problem for the case where all the concentrations are the same. Namely $c_i = \bar{c}$ for all i . Moreover, the calculation of the low order derivatives of $\Phi(\{c_i\})$, evaluated in the homogeneous $c_i = \bar{c}$, state are also tractable. Thus, the above 'first principles' material specific procedure represents a practical scheme for calculating the 'first principles' Landau parameters defined in eq. 13. For the sake of completeness, how the above program can be actually implemented using a multiple scattering approach to calculating the electronic structure of condensed matter will be presented in the next section.

5.3 The self-consistent Korringa-Kohn Rostoker-Coherent-Potential-Approximation:SCF-KKR-CPA

Unlike most band theory methods those based on Multiple Scattering Theory, like the KKR or LMTO, can deal directly, if approximately, with disorder. For the problem at hand these approaches begin by constructing non overlapping potential wells $v_i^A(\vec{r})$ about each atom using the local charge density $\rho_i(\vec{r})$ and the recipe of the LDA. Since the interstitial potential is assumed to be a constant it turns out to be sufficient to solve the local Schrödinger equation for the 'on the energy shell' part of the t-matrix to construct the energy spectrum for the whole lattice. For spherically symmetric potentials the t-matrix is diagonal in the angular momentum labels $L \equiv l, m$ and can be represented in terms of the scattering phase shifts $\eta_L(\epsilon)$ at the energy ϵ as

$$t_{i;L}(\epsilon) = -\frac{\sin \eta_{i,L}(\epsilon)}{\sqrt{\epsilon}} e^{i\eta_{i,L}(\epsilon)} \quad (20)$$

Then the condition that the incident wave to each site should be the sum of the outgoing waves from all other sites leads to the requirement on ϵ that

$$\left\| t_{L,i}^{-1}(\epsilon) \delta_{L,L'} \delta_{i,j} - G_{L,i;L',j}(\epsilon) \right\| = 0 \quad (21)$$

where $G_{L,i;L',j}(\epsilon)$ is the so called structure constant which is the angular momentum expansion of the free space Greensfunction about the sites i and j and the determinant is that of the KKR matrix [17],[16] in lattice site i and angular momentum L space. Remarkably, the energies ϵ , for which eq.21 holds are energy eigenvalues, ϵ_ν , of the Schrödinger equation for the whole lattice even if the potential wells at each site are different. If, in addition to the spectrum,

the calculation of the charge density $\rho_i(\vec{r})$ at each site i is called for the exact formal result to be used is

$$\rho_i(\vec{r}) = \sum_{L,L'}^{\mu} \int d\epsilon Z_{i,L}^*(\vec{r}, \epsilon) \tau_{L,L'}^{i,i}(\epsilon) Z_{i,L'}(\vec{r}, \epsilon) \quad (22)$$

where the scattering path matrix $\tau_{L,L'}^{i,j}(\epsilon)$ [18] is the inverse of the KKR-matrix

$$\tau_{L,L'}^{i,j}(\epsilon) = \left(t_{L,i}^{-1}(\epsilon) \delta_{L,L'} \delta_{i,j} - G_{L,i;L',j}(\epsilon) \right)^{-1}$$

and $Z_{i,L}(\vec{r}, \epsilon)$ is the single site scattering solution for the local potential $v_i(\vec{r})$. Thus, for a fixed configuration $\{\xi_i\}$ and a corresponding set of local potentials $\{v_i\}$ by solving for local orbitals $Z_{i,L'}(\vec{r}, \epsilon)$ and the scattering path matrix $\tau_{L,L'}^{i,j}(\epsilon)$ we can calculate the local charge densities $\{\rho_i\}$ and from these, using the LDA functional, we can recalculate the local potentials for the next iteration. At least formally such iterations can be continued to convergence and the result is a remarkably succinct formulation for of the LDA for an arbitrary arrangement of A and B atoms on a lattice. With this in hand one can embark on CPA program of averaging outlined in the previous section.

Clearly the local charge density $\rho_i(\vec{r}; \{\xi_i\})$ averaged over all configurations $\{\xi_i\}$ with the constraint that at \vec{R}_i the potential is $v_i^{\alpha}(\vec{r})$ for $\alpha = A, B$ is determined by the local scattering solution $Z_{i,L'}(\vec{r}, \epsilon)$ and the similarly averaged site diagonal part of the scattering path matrix $\left\langle \tau_{L,L'}^{i,i}(\epsilon) \right\rangle_{i,\alpha}$:

$$\rho_i^{\alpha}(\vec{r}) = \sum_{L,L'}^{\mu} \int d\epsilon Z_{i,L}^{\alpha*}(\vec{r}, \epsilon) \left\langle \tau_{L,L'}^{i,i}(\epsilon) \right\rangle_{i,\alpha} Z_{i,L'}^{\alpha}(\vec{r}, \epsilon) \quad (23)$$

Note that, unlike $\rho_i(\vec{r}; \{\xi_i\})$ which depends on a fixed occupation configuration $\{\xi_i\}$, $\rho_i^{\alpha}(\vec{r}) \equiv \rho_i^{\alpha}(\vec{r}, \{c_i\})$ depends on the concentration configuration. Moreover, as explained in the previous section, from $\rho_i^{\alpha}(\vec{r})$ we can calculate, via the LDA, local partially averaged potentials $\bar{v}_i^A(\vec{r})$ and $\bar{v}_i^B(\vec{r})$ to be used in eq.19 to start a new random potential problem with

$$t_{L,i}^{-1} = \xi_i t_{A,L,i}^{-1} + (1 - \xi_i) t_{B,L,i}^{-1}$$

Evidently, thanks to the inversion of the order in which we average over configurations is taken and implementation of the LDA selfconsistency is accomplished this procedure can be repeated until the partially averaged charge densities $\bar{\rho}_i^A(\vec{r})$ and $\bar{\rho}_i^B(\vec{r})$ converged. In short the theory is selfconsistent on the average. Remarkably, the concentration functional $\Phi_{int}(\{c_i\})$ so obtained is stationary with respect to arbitrary variations on in the partially averaged charge densities $\rho_i^A(\vec{r})$ and $\rho_i^B(\vec{r})$ [15]. This extremely useful property is the combined consequence of the corresponding features of LDA and CPA.

Finally, we came to the implementation of the CPA idea within the KKR framework[18] to calculate $\left\langle \tau_{L,L'}^{i,i}(\epsilon) \right\rangle_{i,\alpha}$ in eq.23. The CPA is an extremely versatile, non-perturbative method for dealing with disordered systems [14]. Usually,

it is applied to cases when the disorder is uniform. However, in the problem at hand we need an inhomogeneous version of it since the lattice sites are different even on the average due to the fact that $P_i(\xi_i; c_i)$ in eq.14 varies from site to site. It is a great virtue of the real space KKR, depicted in eq.21 that it facilitates the deployment of the CPA idea even in this case. This is because the structure constants $G_{L,i;L',j}(\epsilon)$ which connect sites i and j are not dependent on the crystal potential and hence in the KKR matrix the randomness appears only on the site diagonals. In short the formal solution to the problem may be summarized as follows: replace the t-matrices on each site $t_{i;L}(\epsilon)$ by an effective (coherent potential) t-matrix $t_{c,i;L}(\epsilon)$ and consider impurities in this effective lattice by exchanging $t_{c,i;L}^{-1}(\epsilon)$ on a particular site by $\xi_i t_{A,i;L}^{-1}(\epsilon) + (1 - \xi_i) t_{B,i;L}^{-1}(\epsilon)$. As a consequence of such replacement the site diagonal component of the scattering path matrix for the effective lattice, $\tau_{L,L'}^{c;i,i}(\epsilon)$, changes to $\tau_{L,L'}^{c,A;i,i}(\epsilon)$ or $\tau_{L,L'}^{c,B;i,i}(\epsilon)$ for $\xi_i = 1$ or 0 respectively. The CPA condition, on the effective t-matrices $t_{c,i;L}^{-1}(\epsilon)$, that such replacement does not change $\tau_{L,L'}^{c;i,i}(\epsilon)$ on the average can be written as

$$c_i \tau_{L,L'}^{c,A;i,i}(\epsilon) + (1 - c_i) \tau_{L,L'}^{c,B;i,i}(\epsilon) = \tau_{L,L'}^{c;i,i}(\epsilon) \quad (24)$$

It turns out that the requirement that this relation is fulfilled on every site constitutes a set of coupled equations which determine all the effective t-matrices $t_{c,i;L}^{-1}(\epsilon)$ on every site i . Clearly, these depend on the concentration configuration. Finally, the principle results of the CPA averaging is that

$$\left\langle \tau_{L,L'}^{i,i}(\epsilon) \right\rangle_{i,\alpha} = \tau_{L,L'}^{c,\alpha;i,i}(\epsilon) = \left[\left(\underset{\approx}{1} + \tau_{\approx}^{c;ii} \left(\underset{\approx}{t}^{-1} - \underset{\approx}{t}^{-1} \right) \right)^{-1} \tau_{\approx}^{c;ii} \right]_{L,L'}$$

here symbols with curly underscores are matrices with indices L and L' and the interaction functional is given by

$$\Phi(\{c_i\}) = - \int_0^\mu d\epsilon \bar{N}^{KKR-CPA}(\epsilon; \{c_i\}) + \delta \bar{\Omega} \quad (25)$$

Moreover

$$\begin{aligned} \bar{N}^{KKR-CPA}(\epsilon; \{c_i\}) &= - \frac{1}{\pi_0} \int d\epsilon \sum_{i,\alpha} \text{Im} \ln \left\| t_{c,i,\alpha}^{-1} \underset{\approx}{1} \delta_{i,j} - \underset{\approx}{G}(i,j;\epsilon) \right\| \quad (26) \\ &\quad - \frac{1}{\pi_0} \int d\epsilon \sum_i c_i \text{Im} \ln \left\| \underset{\approx}{1} \delta_{i,j} + \left(\underset{\approx}{t}^{-1} - \underset{\approx}{t}^{-1} \right) \tau_{\approx}^{c;i,i} \right\| \\ &\quad - \frac{1}{\pi_0} \int d\epsilon \sum_i (1 - c_i) \text{Im} \ln \left\| \underset{\approx}{1} \delta_{i,j} + \left(\underset{\approx}{t}^{-1} - \underset{\approx}{t}^{-1} \right) \tau_{\approx}^{c;i,i} \right\| \end{aligned}$$

In summary the aim of providing a formal base from which tractable first-principles procedures can be derived systematically for calculating the Landau coefficients in eq.3 has been achieved and is encapsulated in Eqs.25 and 26. Some of its immediate practical consequences are explored in the next section.

5.4 First principles calculations of the direct correlation functions: $\mathbf{S}_i^{(1)}, \mathbf{S}_{i,j}^{(2)} \dots$

What is meant by proceeding from eqs. 25,26 in a systematic fashion to tractable mean-field theory schemes is that one can take various, increasingly higher order, derivatives of the basic inhomogeneous KKR-CPA equation eq.24 and derive equations for the derivatives of $\tau_{L,L'}^{c;i,i}(\epsilon)$, $\tau_{L,L'}^{c,A;i,i}(\epsilon)$ and $\tau_{L,L'}^{c,B;i,i}(\epsilon)$ c_j evaluated in the homogeneous state where $c_i = c_j = \bar{c}$ for all i and j. For low order derivatives these become computationally tractable and their solutions can be used to evaluate the direct correlation functions defined in eq.11

5.4.1 Total energy:

If all the concentrations c_i are taken to be the same, say \bar{c} , the framework of the previous section reduces to what is now days called the standard SCF-KKR-CPA. In particular eq.24 can be solved numerically by codes that are part of a reasonably complete KKR package. Much useful work gets done using these but to illustrate its power in the context of the present discussion its first application will suffice. The credibility of the whole 'first principles', Density Functional Theory project rests on the fact that all modern band theory methods can solve the Kohn-Sham equation within the LDA or some other similar approximation and calculate the zero temperature total energy as a function of the lattice parameter 'a'. Moreover, they can determine the equilibrium a_{eq} by finding 'a' for which the total energy is the minimum in reasonable agreement with experiments. One of the principle virtues of the KKR and LMT -CPA methods is that they can do the same for homogeneous random alloys. This is illustrated below in Fig 1. and Fig.2 where a_{eq} is plotted as a function of concentration for the FCC solid solutions Cu_cZn_{1-c} [15]

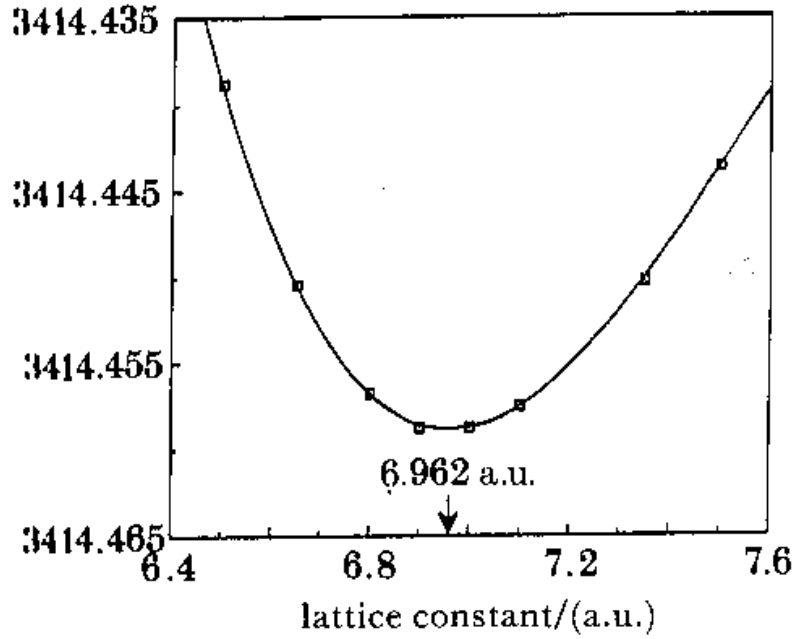


Fig.1 Variation of the total energy (Ry) with lattice parameter (a.u.) for fcc Cu₅Zn₅ alloy

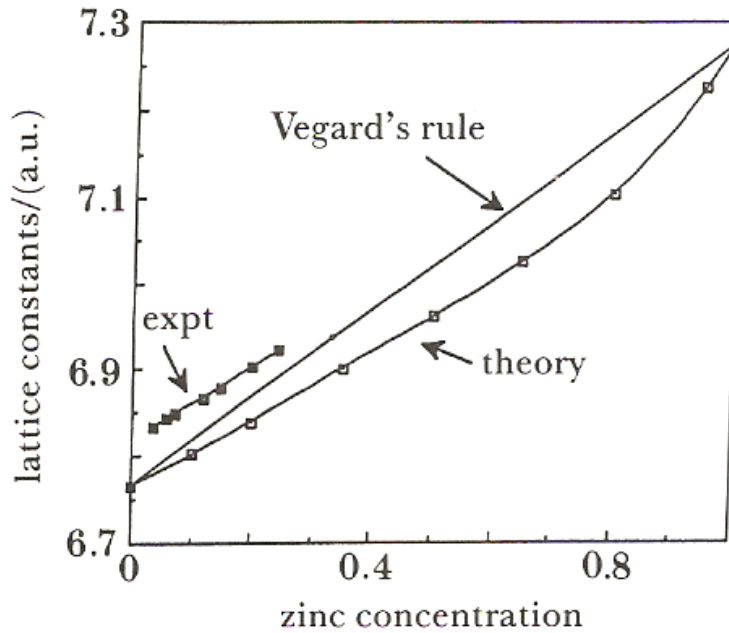


Fig.2 Variation of the lattice constant with concentration for fcc $\text{Cu}_c\text{Zn}_{1-c}$ alloys

Note that these calculations have been carried out in the high temperature high symmetry state where, according to the arguments in the introduction the Landau parameters are to be calculated.

5.4.2 Phase Diagrams

Recall that the equation of state, recorded in eq.12, involves the direct correlation function $S_i^{(1)} = \beta \frac{\partial \Phi}{\partial c_i}$ evaluated in the homogeneous state $c_i = \bar{c}$. Using the strategy outlined above one readily derives

$$\int_0^{\mu} d\epsilon (N_A^{KKR-CPA}(\epsilon) - N_B^{KKR-CPA}(\epsilon)) + k_B T \ln \frac{\bar{c}}{1-\bar{c}} = \nu$$

where the local integrated density of states are to be calculated by the standard homogeneous KKR CPA mentioned above. As an example of results from such calculation we display the coexistence curve for the phase separating, FCC $\text{Pd}_c\text{Rh}_{1-c}$ alloy system.

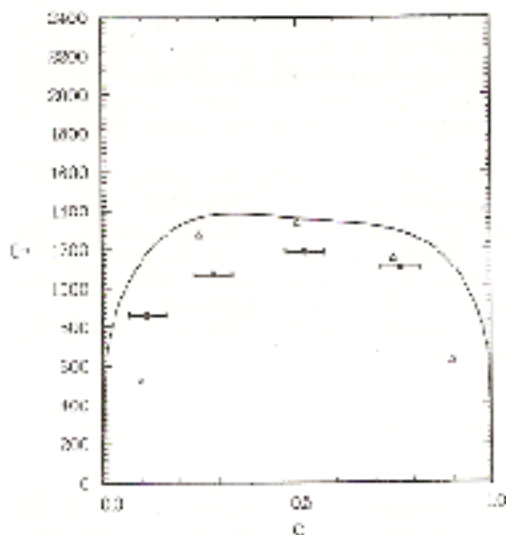


Fig.3 The phase separation phase diagram for $\text{Rh}_c\text{Pd}_{1-c}$ alloy triangles are SCF-KKR-CPS calculations and the dots are experimental data

The calculated critical temperature T_o is in good agreement with the experimental data. Once again it is to be noted that these first principle results are in no way based on zero temperature total energy calculations.

5.4.3 Correlation functions:

The calculation of the direct correlation function $S_{i,l}^{(2)}$ in the homogeneous state is also tractable. In this state $S_{i,l}^{(2)}$ depends only on the coordinate difference $\vec{R}_i - \vec{R}_j$ and hence the interest focuses on its lattice Fourier transform $S^{(2)}(\vec{k})$ which determines the correlation function $q(\vec{k})$ measured in a diffuse scattering experiments. Namely

$$q(\vec{k}) = \frac{\bar{c}(1 - \bar{c})}{k_B T - \bar{c}(1 - \bar{c})S^{(2)}(\vec{k})}$$

An example of the calculated diffuse scattering intensity for the FCC Cu_cPd_{1-c} alloy, just above its ordering temperature[19] is shown below

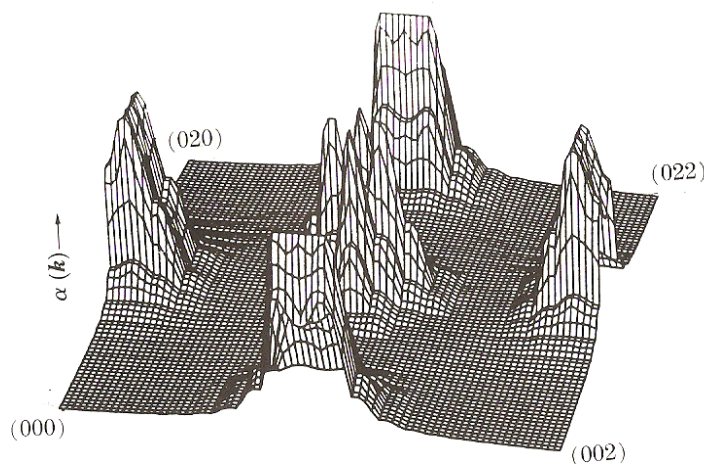


Fig.4 The concentration-concentration correlation function $q(\vec{k})$ for $Cu_{.75}Pd_{.25}$ above the ordering temperature T_0

The four peaks are the split [110] superlattice peak which, in a usual FCC lattice, indicates a tendency to order into the $L1_2$ structure. The splitting is an interesting consequence of the Fermi Surface geometry.

5.5 The higher order direct correlation functions $S_{i,j,k..}^{(n)}$ for $n > 2$

Very little is known about these beyond perturbation theory within effective pair potential models and the constraint imposed on them by group-theory. They remain a challenge to the 'first principle' approach the theory of alloy phases.

6 Concluding remarks

As was stressed in the introduction ordering and clustering in metallic alloys is just one of the many applications of the Landau theory. It is then appropriate to conclude with comments on the applicability of the above theoretical strategy to other cases of interest.

Evidently, the methodology can be viewed as a theory of disorder in the quantum density functional theory for electrons where the disorder is treated by a classical density functional theory. The approximate functional in the first part is LDA and the classical functional was provided by the CPA. The physics behind this two pronged theoretical treatment is the fact that the electrons move fast and the atomic configurations change, by interdiffusion, slowly. This separation of time scales is being exploited when the slow degrees of freedom is treated classically. Looked at it from this point of view the order parameters in the Landau theories can be identified with slow degrees of freedoms and their fluctuations, which destabilize the high symmetry phase, are good candidates for being treated by classical density functional theories. Indeed, there are a number of cases, such as magnetism[20], valance fluctuations[21] and superconductivity[22], where this kind of reasoning have paid handsome dividends although calculations of full sets of Landau parameters have not been attempted.

An other point of general interest concern the good fit between density functional theory for the electrons and the slow degrees of freedom which play the role of order parameter in the Landau theories. To be effective an electronic density functional theory feature a number of densities in addition to the charge density $n(\vec{r})$ in the original theory[10]. For instance in the case of magnetism the selfconsistent one electron, Kohn-Sham, potential is functional of both the charge density $n(\vec{r})$ and the magnetization density $\vec{m}(\vec{r})$. In the paramagnetic, high symmetry, state the thermal average of this quantity is zero but below the Curie temperature T_c it is not and hence the rotational symmetry is broken in the sense of a Landau Theory. However, even above T_c $\vec{m}(\vec{r})$ is not zero on a time scale which is, while short compared to the thermal time scale $\frac{\hbar}{k_B T}$, is long compared to the time an electron spends on a lattice site, namely the time scale of charge fluctuations. In short, in the paramagnetic state of an itinerant ferromagnet like Iron local moment form but they are randomly oriented and hence do not break the rotational symmetry. This Disordered Local Moment (DLM) picture is well capture by the two functional construction advocated in this essay: the fast charge fluctuations are described by LDA and the slow, classical, orientational fluctuations of the local moments are treated by the CPA average over the corresponding random exchange fields experienced by the electrons. In the case of alloys where the SCF-KKR-CPA calculations of the direct correlation functions gave a good account of the experimental ordering temperature T_0 the corresponding DLM predictions are also in good agreement with experiment[23]

Finally, it is noteworthy that means for going beyond the standard mean field theory functionals have also been developed. They are based on replacing

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8 the single site CPA at the heart of the above methodology by the non-local
9 SCF-KKR-CPA[12],[13],[14].which considers compact clusters in place of single
10 site impurities in defining the effective medium. As a consequence it affords a
11 much improved description of the local environmental effects.

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18
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