A study of annealed and quenched averaging of the thermodynamic potential in a disordered system: an augmented space approach

A study of annealed and quenched averaging of the thermodynamic potential in a disordered system: an augmented space approach

Tanusri Saha† and Abhijit Mookerjee‡§

† S N Bose National Centre, DB17, Sector 1, Salt Lake City, Calcutta 700064, India
‡ International Centre for Theoretical Physics, Trieste 34100, Italy

Abstract. We use the augmented space method, introduced by one of us, to study the configurational average of the thermodynamic potential of electrons in a disordered system. Invoking the relationship between the scattering diagram summation and the algebraic approaches to cluster generalizations of the coherent potential approximation, we indicate how such an approximation may be carried out on the thermodynamic potential. We also study the difference between annealed and quenched averaging from the scattering diagrammatic approach, to obtain insight into the difference between the two processes.

1. Introduction

The study of phase transformations and stability of solid solution phases requires knowledge of and accurate approximations to the configurational free energy. In particular, for disordered phases, physical properties may not be specific to a particular disordered configuration. By a disordered configuration we mean a microscopic realization of the random Hamiltonian specified by some set of random Hamiltonian parameters and their probability distributions. Hence one has to speak in terms of configurationally averaged quantities [1]. A convenient method for calculating a configurationally averaged quantity was introduced by Mookerjee [2] through the augmented space formalism (ASF). Earlier this formalism was applied successfully to obtain density of states and response functions for disordered systems. The main aim of this communication is to extend the fermion field theoretic approach to the ASF [2, 3] to calculate the thermodynamic potential for disordered solid solution phases in a way independent of any single-site, mean field theories. This is important, since in most of the current work the internal energy is averaged using a single-site, mean field approach, neglecting the effect of clusters. On the other hand, the entropy contribution is estimated using the cluster variation method, where the cluster effects predominate. In our approach, the entire free energy contribution will be averaged together in a cluster generalization of the coherent potential approximation (CPA). In addition, we intend to study the difference between quenched and annealed averaging using scattering diagrams.

Configuration averaging of the thermodynamic potential can be done in two different ways: the so called *annealed averaging* and *quenched averaging*. If the system is allowed to cool slowly from its melt, so that the time scales associated with disorder and thermal

§ Permanent address: S N Bose National Centre, DB17, Sector 1, Salt Lake City, Calcutta 700064, India.

fluctuations are comparable and the subsystems comprising it can relax to their minimum-energy state, then the disorder and thermal averaging can be done on the same footing. This is *annealed averaging*. If on the other hand, the system is cooled so rapidly that the subsystems freeze in metastable local minima and the time scale associated with thermal fluctuations is much smaller than that for the disorder fluctuations, then thermal fluctuation averaging preceeds disorder configuration averaging. This is *quenched averaging*. The mathematical distinction between the two averaging processes lies in the fact that, in annealed averaging, disorder averaging is done on the grand potential *before* the logarithm is taken to yield the thermodynamic potential (free energy). In contrast, in quenched averaging, the disorder averaging is carried out on the thermodynamic potential itself, i.e. *after* taking the logarithm of the grand potential.

Quenched averaging of thermodynamic potential was carried out by Ducastelle and Gautier [4] for studying ordering effects in alloys. It was also used by Paquet and Leroux-Hugon [5], in a generalized version of the ASF, for studying magnetic transitions in the Hubbard model. However their methodology is applicable in the framework of the single-site CPA. On the other hand the ASF can include the effect of clusters and treat the internal energy and entropy contributions on the same footing.

In section 2 we briefly review the ASF and its fermion field version. Section 3 involves disorder averaged thermodynamic potential calculation and corresponding scattering diagrams. Section 4 is devoted to the summation of the scattering diagrams, representing perturbation series expansion of disorder averaged thermodynamic potential and calculation of chemical potential from it. Section 5 deals with the study of the difference between annealed averaging and quenched averaging and summation of self-energy diagrams for the annealed case within a single-loop approximation.

2. The augmented space formalism and fermion field theory

In ASF configuration averaging is done by extending the usual Hilbert space H to include a configuration space Φ. As the name suggests disorder effects are described in Φ.

Basic steps of this formalism are as follows. The probability density $p_i(\epsilon_i)$ of some random variable ϵ_i satisfies the property

$$p_i(\epsilon_i) \geqslant 0 \text{ and } \int p_i(\epsilon_i) = 1. \tag{1}$$

These properties are specific to the imaginary parts of herglotz functions. So one can find a self-adjoint operator $\mathbf{M}^{(i)}$ in a configuration space ϕ^i such that $p_i(\epsilon_i)$ can be expressed as

$$p_i(\epsilon_i) = -\frac{1}{\pi} \text{Im} \langle v_0^i | [(\epsilon_i + i0^+)I - \mathbf{M}^{(i)}]^{-1} | v_0^i \rangle. \tag{2}$$

As was pointed out by Mookerjee [2] this is the inverse of the well known problem of obtaining a local density of states starting from a self-adjoint Hamiltonian H. If $p_i(\epsilon_i)$ can be expressed in a continued fraction expansion, then a representation of $\mathbf{M}^{(i)}$ is a tridiagonal matrix with the continued fraction coefficients in diagonal and off-diagonal positions. The averages quantity $\int f(\epsilon_i)p(\epsilon_i)d\epsilon$ can then be shown to be given by the *ground state* average $\langle v_0^i | \tilde{f}(\mathbf{M}^{(i)}) | v_0^i \rangle$, where $|v_0^i\rangle$ is the specific member of the basis states in which (2) holds. It is called the *ground state* not in the sense of having the lowest energy but rather it represents

the reference state against which configuration fluctuations are described. For more than one random variable one defines a product space $\Phi = \prod^{\otimes} \phi^i$. This is spanned by states in which the set of variables ϵ_i assumes one of its configurations. The averaged quantity $\langle f \rangle$ is given by $\langle \nu_0 | \tilde{f}(\mathbf{M}^{(i)}) | \nu_0 \rangle$ where $| \nu_0 \rangle = \prod^{\otimes} | \nu_0^i \rangle$ is the ground state of the disorder field space Φ and $\mathbf{M}^{(i)} = I \otimes \dots \mathbf{M}^{(i)} \dots I \dots$ is an operator in the product space Φ.

For a disordered lattice problem with random site energies ϵ_i, the function f is initially a function of random elements of the Hamiltonian

$$H = \sum \epsilon_i P_i + \sum_i \sum_j V_{ij} T_{ij}. \tag{3}$$

P_i and T_{ij} are projection and transfer operators corresponding to a countable basis $\{|i\rangle\}$ spanning the Hilbert space H. The overlap matrix element V_{ij} may be assumed to be non-random. According to the augmented space theorem the configurationally averaged quantity $\langle f \rangle$ will then be given by the ground state average of the operator $\tilde{f}$ which is now the same function of an effective Hamiltonian $\tilde{H}$ defined in the augmented space $\Psi = H \otimes \Phi$

$$\tilde{H} = \sum_i \mathbf{M}^{(i)} \otimes P_i + \sum_i \sum_j V_{ij} I \otimes T_{ij}. \tag{4}$$

The effective Hamiltonian $\tilde{H}$ contains complete information about the quantum behaviour of the system described in H and its statistical behaviour described in Φ.

The effect of disorder is to cause scattering. This scattering event can be pictured as interaction between the electron and pseudo-particles describing configuration fluctuations at each site against the reference state. If the disorder on each site is binary the statistics of these pseudo-particles should be fermionic because no two pseudo-particles can occupy the same site. The effective Hamiltonian $\tilde{H}$ can now be written in second quantized form [6] in both spatial and disorder parts giving

$$\tilde{H} = \sum_i \epsilon_A a_i^\dagger a_i + \sum_i \sum_k \sum_{k'} \mathbf{M}_{kk'}^{(i)} a_i^\dagger a_i b_{ik}^\dagger b_{ik'} + \sum_i \sum_j V_{ij} a_i^\dagger a_j. \tag{5}$$

$b_{ik}^\dagger$ and b_{ik} create and annihilate pseudo-fermions at the ith site. k, k' are additional quantum numbers specifying the orthogonal basis states in ϕ_i. They specify distinct values or configurations assumed by ϵ_i. The rank of the matrix $\mathbf{M}^{(i)}$ is given by the number of orthogonal basis states in ϕ_i, i.e. by the number of k numbers.

3. Calculation of the quenched averaged thermodynamic potential and scattering diagrams

Since the effective Hamiltonian $\tilde{H}$ in augmented space has now been recast in second quantized form characterizing the disorder scattering as an interaction between the electron and pseudo-fermion present at the scattering site, the usual tools of diagrammatic field theoretic techniques can be applied.

The quenched thermodynamic potential of a disordered alloy at temperature T can be written as

$$\langle \Omega \rangle_{av} = -\frac{1}{\beta} \langle \nu_0 | \ln \text{Tr} \exp[\beta(H - \nu N)] | \nu_0 \rangle. \tag{6}$$

$\beta = 1/k_B T$, μ is the chemical potential of the system, and N is the operator giving the number of electrons. $|\nu_0\rangle = \prod^{\otimes} |\nu_0^i\rangle$ is the vacuum state of the field space. This is the state in disorder space that has no fluctuation, i.e. all the sites are assumed to be filled with pseudo-fermions of one specific field quantum number. As usual in the interaction picture formalism we define quantity $U(\beta)$ through

$$\exp[-\beta(H_0 - \nu N + H')] = \exp[-\beta(H_0 - \nu N)]U(\beta).$$

H_0 is the unperturbed and H' the interaction Hamiltonian. $U(\beta)$ satisfies the equation

$$\frac{\partial U(\beta)}{\partial \beta} = -H'(\beta)U(\beta)$$

with $H'(\beta) = \exp(\beta H_0)H' \exp(-\beta H_0)$ and $U(0) = 1$. The solution of $U(\beta)$ in terms of the Dyson ordering operator is

$$U(\beta) = 1 + \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \int \ldots \int d\tau_1 \ldots d\tau_n \, P[H'(\tau_1) \ldots H'(\tau_n)]. \tag{7}$$

Let us now consider the specific problem of AB, an alloy with impurity concentration c of A atoms. The effective Hamiltonian H can be split up into two parts: (i) the unperturbed Hamiltonian of the host A atom

$$H_0 = \sum_i \epsilon_A a_i^\dagger a_j + \sum_i \sum_j V_{ij} a_i^\dagger a_j$$

and (ii) the interaction Hamiltonian

$$H' = \sum_i \sum_k \sum_{k'} \mathbf{M}_{kk'}^{(i)} a_i^\dagger a_i b_{ik}^\dagger b_{ik'}.$$

The matrix $\mathbf{M}^{(i)}$ takes into account fluctuation of the ith site energy ϵ_i against ϵ_A. Thus this fluctuation $x = \epsilon_i - \epsilon_A$ can be either zero with probability $(1-c)$ or $W = (\epsilon_B - \epsilon_A)$ with probability c. So, $p(x) = (1-c)\delta(x) + c\delta(x - W)$.

The $\mathbf{M}^{(i)}$ matrix appropriate to this probability distribution is

$$\mathbf{M}^{(i)} = \begin{pmatrix} c & \sqrt{c(1-c)} \\ \sqrt{c(1-c)} & 1-c \end{pmatrix}.$$

The disorder quantum number k takes two values, k_0 and k_1. For simplicity let us define $B_{ik_0}^\dagger = \sqrt{c} b_{ik_0}^\dagger$ and $B_{ik_0} = \sqrt{c} b_{ik_0}$, $B_{ik_1}^\dagger = \sqrt{1-c} b_{ik_1}^\dagger$ and $B_{ik_1} = \sqrt{1-c} b_{ik_1}$.

Now

$$H'(\tau) = \exp(\tau H_0) H' \exp(-\tau H_0) = W \sum_i \sum_k \sum_{k'} a_i^\dagger(\tau) a_i(\tau) B_{ik}^\dagger(\tau) B_{ik'}(\tau).$$

Further, defining $W_{ij}(\tau, \tau') = W\delta_{ij}\delta(\tau - \tau')$, the above equation may be written as

$$H'(\tau) = \int d\tau' \sum_i \sum_j \sum_k \sum_{k'} W_{ij}(\tau, \tau') a_i^\dagger(\tau) a_i(\tau) B_{jk}^\dagger(\tau') B_{jk'}(\tau').$$

Written in terms of $U(\beta)$, the expression for the quenched thermodynamic potential becomes

$$\langle \Omega \rangle_{\mathrm{av}} = \Omega_0 - \frac{1}{\beta} \langle \nu_0| \ln \mathrm{Tr} \exp\left[\beta(\Omega_0 - H_0 + \mu N)\right] U(\beta)|\nu_0\rangle \tag{8}$$

where Ω_0 is the thermodynamic potential for the unperturbed system characterized by the Hamiltonian H_0. In order to visualize how the scattering diagrams are generated in the augmented space, let us examine in detail the first-order term in the perturbation series expansion of (7):

$$\Omega_1 = -\frac{1}{\beta} \int \mathrm{d}\tau \langle \nu_0| \left[\mathrm{Tr}\ \exp(\beta(\Omega_0 - H_0 + \mu N)) H'(\tau)\right]_{\mathrm{con}} |\nu_0\rangle.$$

The subscript con refers to the fact that only connected diagrams in the Hilbert space H are to be considered, since it is straightforward to show that the effect of taking the logarithm is to eliminate the contribution of all *unconnected* diagrams.

Let us now define

$$\mathrm{Tr}\left[\exp(\beta(\Omega_0 - H_0 + \mu N)a_i^\dagger(\tau_1)a_j(\tau_2))\right] = \begin{cases} -G_{ij}^0(\tau_1, \tau_2) & \text{for } \tau_1 \geqslant \tau_2 \\ G_{ij}^0(\tau_1, \tau_2) & \text{otherwise} \end{cases}$$

G^0 is the finite temperature Green function corresponding to the ordered system. The corresponding Green function in the disorder field space is defined by

$$\langle \nu_0| B_{ik_n}^\dagger(\tau_1) B_{ik_m}(\tau_2)|\nu_0\rangle = g_{ik_n, jk_m}(\tau_1, \tau_2) = \gamma_n \delta_{nm}\delta_{ij}\theta(\tau_1 - \tau_2)$$

where $\gamma_0 = -c$ and $\gamma_1 = (1-c)$.

The above definitions follow from choice of the *vacuum state* as $|\nu_0\rangle$ in the disorder field space Φ which is a state in which all sites are described by quantum number k_0. Thus $b_{k_0}^\dagger|\nu_0\rangle = 0$ and $b_{k_1}|\nu_0\rangle = 0$.

Applying Wick's theorem to both the configuration and the spatial part of Ω_1 and employing the definition of G^0 and g we obtain an expression for the first-order correction as

$$\Omega_1 = -\frac{1}{\beta} \sum_i \sum_j \int \mathrm{d}\tau_1\, \mathrm{d}\tau_2\, G_{ij}^0(\tau_1, \tau_1^+) W_{ij}(\tau_1, \tau_2) g_{jk_0, jk_0}(\tau_2^+, \tau_2).$$

The corresponding scattering diagram is shown in figure 1. The solid lines represent the ordered Green function G^0 and the dotted lines represent the disorder field Green function g while the dashed lines represent the interaction $W_{ij}(\tau_1, \tau_2)$. Using the expressions for the Green functions we obtain

$$\Omega_1 = -\frac{cW}{\beta} \sum_i \int \mathrm{d}\tau_1\, G_{ii}^0(\tau_1, \tau_1^+).$$

Expressing in terms of Matsubara frequencies $\omega_n = \mathrm{i}(2n+1)\pi\beta + \mu$ with $n = 0, \pm 1, \pm 2, \ldots, \pm\infty$. Going over to momentum space we have

$$\Omega_1 = -\frac{cW}{\beta} \lim_{\tau \to 0} \int \frac{\mathrm{d}^3 p}{8\pi^3} \sum_{\omega_n} G^0(p, \omega_n) \exp(-\mathrm{i}\omega_n\tau).$$

Figure 1. The first-order scattering diagram for the thermodynamic potential. Full lines indicate electron propagators, the dashed line the disorder propagator and the dotted line the interaction W_{ij}.

(a)   (b)

Figure 2. The two second-order scattering diagrams for the thermodynamic potential.

Similarly the contributions in second order originating from scattering diagrams shown in figure 2 will be

$$-c^2 \frac{W^2}{\beta} \int \int \frac{\mathrm{d}^3 p_1}{8\pi^3} \frac{\mathrm{d}^3 p_2}{8\pi^3} \sum_{\omega_n} G^0(p_1, \omega_n) G^0(p_2, \omega_n)$$

and

$$c(1-c) \frac{W^2}{\beta} \int \int \frac{\mathrm{d}^3 p_1}{8\pi^3} \frac{\mathrm{d}^3 p_2}{8\pi^3} \sum_{\omega_n} G^0(p_1, \omega_n) G^0(p_2, \omega_n).$$

4. Summation of the perturbation series for the thermodynamic potential

In order to sum up the perturbation series of the averaged thermodynamic potential it is not sufficient to consider only skeleton diagrams and to add the self-energy parts to the ordered

state Green function G^0 because this leads to over-counting difficulties. To get a summed-up expression for $\langle \Omega \rangle$ we notice that if we open up any of the n closed solid line loops of any the nth order diagram for the thermodynamic potential, we obtain a possible nth order diagram for the configurationally averaged finite-temperature Green function. This is seen if we compare figure 3 with figure 1.

Figure 3. The scattering diagram obtained by opening up one of the closed electron loops in the diagram for thermodynamic potential in figure 1. This belongs to the scattering diagram set for the averaged electron propagator.

The configurationally averaged finite-temperature Green function can be introduced as

$$\langle G_{xy}(\tau_1, \tau_2) \rangle = \langle v_0 | \frac{\langle a_x(\tau_1) a_y^\dagger(\tau_2) U(\beta) \rangle}{\langle U(\beta) \rangle} | v_0 \rangle.$$

where $\langle \ldots \rangle$ indicates thermal and $\langle v_0 | \ldots | v_0 \rangle$ indicates configurational averaging. Expanding $U(\beta)$ as a perturbation series and considering only connected diagrams in the Hilbert space H so as to cancel $\langle U(\beta) \rangle$ in the denominator the first-order contribution to the perturbation series will be

$$\sum_i \sum_j \int \int d\tau_1 d\tau_2 \sum_k \sum_{k'} W_{ij}(\tau_1, \tau_2) a_x(\tau_x) a_y^\dagger(\tau_y) a_i^\dagger(\tau_1) a_i(\tau_1) B_{jk}^\dagger(\tau_2) B_{jk'}(\tau_2)$$

$$= \sum_i \sum_j \int \int d\tau_1 d\tau_2 W_{ij}(\tau_1, \tau_2) G_{xi}^0(\tau_x, \tau_1) G_{iy}^0(\tau_1, \tau_2) g_{jk_0, jk_0}(\tau_2^+, \tau_2)$$

$$= -cW \sum_i \int d\tau_1 G_{xi}^0(\tau_x, \tau_1) G_{iy}^0(\tau_1, \tau_y).$$

Changing over to momentum and frequency space the above contribution becomes $-cW$ $[G^0(p, w_n)]^2$. This is shown in figure 3.

Similarly second-order contributions corresponding to figure 4(a) and (b) are

$$c(1 - c) W^2 \left[G^0(p, \omega_n) \right]^2 \int \frac{d^3 p_1}{8\pi^3} G^0(p_1, \omega_n)$$

and

$$- c^2 W^2 \left[G^0(p, \omega_n) \right]^2 \int \frac{d^3 p_1}{8\pi^3} G^0(p_1, \omega_n).$$

(a)   (b)

Figure 4. The scattering diagrams obtained by opening up one of the closed electron loops in the second-order scattering diagrams for the thermodynamic potential in figure 2.

If $\Sigma'_{(n)}(p, \omega_n)$ denotes the total self-energy part of the nth order diagrams, proper or improper, then the nth-order contribution to the quenched thermodynamic potential will be

$$\Omega_n = \frac{1}{n\beta} \int \frac{d^3p}{8\pi^3} \sum_{\omega_n} G^0(p_1, \omega_n) \Sigma'_{(n)}(p, \omega_n)$$

$$\langle \Omega \rangle = \sum_{n=0}^{\infty} \Omega_n.$$

The factor $1/n$ arises due to the over-counting difficulty mentioned earlier. The difficulty of carrying out the summation with the factor $1/n$ can be overcome by using a mathematical trick. We may consider the coupling parameter W to be varying, and integrate over different values of this parameter keeping the chemical potential μ fixed.

$$\langle \Omega \rangle = \Omega_0 + \frac{1}{\beta} \int \frac{d^3p}{8\pi^3} \sum_{\omega_n} \int \frac{dW'}{W'} G^0(p, \omega_n) \Sigma'_{W'}(p, \omega_n)$$

where $\Sigma'(p, \omega_n)$ is the sum of all possible self-energy parts, proper or improper.

Expressing in terms of the proper self-energy:

$$\Sigma' = \Sigma + \Sigma G^0 \Sigma + \dots$$

we have an expression

$$\langle \Omega \rangle = \Omega_0 + \frac{1}{\beta} \int \frac{d^3p}{8\pi^3} \sum_{\omega_n} \int \frac{dW'}{W'} \frac{\Sigma_{W'}(p, \omega_n)}{[G^0(p, \omega_n)]^{-1} - \Sigma_{W'}(p, \omega_n)}. \qquad (9)$$

The chemical potential μ can be determined from this by solving

$$N = -\frac{\partial \langle \Omega \rangle}{\partial \mu}.$$

N is the mean number of electrons present. From equation (10) one has

$$N = -\frac{\partial \Omega_0}{\partial \mu} - \frac{1}{\beta} \sum_m \sum_{\omega_n} \int \frac{d^3 p}{8\pi^3} \Sigma'_m(p, \omega_n) \partial/\partial \mu [G^0(p, \omega_n)].$$

The ordered free energy is given by

$$\Omega_0 = -\frac{1}{\beta} \int \frac{d^3 p}{8\pi^3} \ln[1 + \exp(-\beta(E_p - \mu))]. \tag{10}$$

Using this expression of the ordered free energy and the fact that differentiating any nth order diagram is equivalent to differentiating any of its n solid lines, it follows that

$$N = \int \frac{d^3 p}{8\pi^3} \sum_{\omega_n} \frac{1}{\omega_n - E_p - \Sigma(p, \omega_n)}. \tag{11}$$

(a)   (b)   (c)   (d)   (e)

Figure 5. Irreducible scattering diagrams for the self-energy for the averaged electron propagator.

Equation (9) relates the quenched thermodynamic potential to the self-energy part of the configurationally averaged finite-temperature Green function. The self-energy Σ can be determined by summing up the irreducible scattering diagrams as shown in figure 5. Summing up various infinite sets of scattering diagrams leads to various approximations. If we take into account correlated scattering from all sites within a cluster C exactly but ignore all scattering diagrams involving correlated scattering between sites inside and outside the cluster, the resulting approximation is a C-cluster coherent potential approximation (CCPA). The diagram for one such correlated scattering involving two sites is shown in figure 6. One of the simplest of these approximations is the single-site CPA. In this approximation only uncorrelated scatterings are taken in account. In diagrammatic language this amounts to considering only diagrams with non-overlapping pseudo-fermion loops associated with more than one site. Mookerjee [6] has shown that the summed-up series for the scattering diagrams in augmented space in this case is identical to that of the algebraic approach of the

CPA. Using the correspondence between scattering diagrams and the graphical techniques of Haydock [7] and the direct relation between the algebraic and the graphical techniques, he has argued that a identical relationship holds for the summation of scattering diagrams for the correlated scattering from clusters and the algebraic, partitioning method for the CCPA. Recently a fast and accurate method for obtaining the averaged Green function and the self-energy has been developed by applying the ideas of the recursion method [8] directly on the augmented space [9]. The equivalence of scattering diagram summation to this algebraic method will allow us to use the above ideas to obtain the averaged thermodynamic potential in a generalized cluster approximation.

Figure 6. A scattering diagram for correlated scattering from two sites. Such diagrams are neglected in the single-site coherent potential approximation.

5. Annealed averaging of the thermodynamic potential

The essential difference between quenched and annealed averaging of the thermodynamic potential is whether configuration averaging is done before or after taking the logarithm of the grand potential. In diagrammatic language, before a matrix element is taken in the configuration space, each vertex has two free arrows (see figure 7(a)). The operation of taking the matrix element between $|v_0\rangle$ in configuration space, i.e. configuration averaging, amounts to joining these arrows in pairs to form disorder propagators. The same procedure is true for the trace operation in the real Hilbert space. Moreover, taking the logarithm amounts to discarding unconnected diagrams. In quenched averaging, since we take the trace first, followed by the logarithm, a diagram like figure 7(b) will be considered as an unconnected diagram and hence discarded. On the other hand, for the annealed averaging, since we take the matrix element in configuration space after taking the trace, the same unconnected diagram now becomes connected in the full augmented space and hence when the subsequent logarithm is taken its contribution is not zero. Such diagrams in the full augmented space constitute the difference between the two different averaging procedures.

Inspecting diagrams of various orders of the interaction parameter, it is straightforward to identify diagrams which, though unconnected in real space, are connected in the full augmented space via the disorder propagator. Some of these diagrams are shown in figure 8. Physically it is understandable why the annealed averaging should have extra scattering diagrams and why these should lead to a renormalization of the disorder propagator. In quenched averaging, the disorder fluctuations are frozen. Thermal fluctuations have no effect on disorder propagators. Once a system is in a disorder configuration, it always remains so. The picture of disorder propagators as *propagators* is a mathematical artifact, as was

Figure 7. (a) A scattering vertex in augmented space. (b) A new scattering diagram for the annealed average. Note that for the annealed average electron propagators renormalize the disorder propagator.

clearly understood in the scattering picture of the CPA earlier by Leath and co-workers [10]. The delta function time dependence of the disorder propagator is a reflection of this fact. In annealed averaging, however, thermal fluctuations and fluctuations in disorder configurations take place on the same footing. It is therefore not surprising that we have to consider extra scattering diagrams that express these fluctuations and we do expect thermal fluctuations to renormalize the disorder propagators and vice versa.

Summation of the perturbation series of the annealed thermodynamic potential requires the introduction of a new type of configurationally averaged finite temperature Green function. Let us call this the *annealed averaged Green function* G^A in order to distinguish it from the configurationally averaged Green function introduced in section 4. Scattering diagrams for the annealed averaged Green functions obtained by breaking open solid lines of the diagrams for the annealed thermodynamic potential are shown in figure 8. Considering the specific case of figure 8(c), its contribution to the averaged Green function can easily be obtained by using the previously mentioned rules for dotted, dashed and solid lines:

$$\sum_{x_1} \cdots \sum_{x_8} \int \cdots \int d\tau_1 \ldots d\tau_8 \, W_{x_1,x_2}(\tau_1, \tau_2) W_{x_3,x_4}(\tau_3, \tau_4) \ldots W_{x_7,x_8}(\tau_7, \tau_8) \ldots$$

$$G_{x,x_1}(\tau_x, \tau_{x_1}) G_{x_1,x_7}(\tau_1, \tau_7) G_{x_7,y}(\tau_7, \tau_y) G_{x_3,x_5}(\tau_3, \tau_5) G_{x_5,x_3}(\tau_5, \tau_3) \ldots$$

$$g_{\uparrow\uparrow}(x_2\tau_2, x_8\tau_8) g_{\downarrow\downarrow}(x_8\tau_8, x_6\tau_6) g_{\downarrow\downarrow}(x_6, \tau_6, x_4\tau_4) g_{\downarrow\downarrow}(x_4\tau_4, x_2\tau_2).$$

For convenience we denote the quantum number k_0 by $\uparrow$ and k_1 by $\downarrow$. Expressing in terms of Matsubara frequencies, the contribution of above diagram to the self-energy will be

$$c(1-c) W^2 G_{x_1,x_1}(\omega_n) \sum_{\omega_m} (1-c)^2 W^4 G_{x_1,x_1}(\omega_m) G_{x_1,x_1}(\omega_m).$$

Thus we notice that the effect of the unconnected electronic Green function in the Hilbert space is to renormalize the right-going and left-going disorder propagators. If we denote the contribution of the right-going disorder propagator by g_r instead of $-c$ and that

Figure 8. Scattering diagrams that arise in annealed averaging of the thermodynamic potential but not its quenched average.

Figure 9. Scattering diagrams for an *annealed* propagator obtained by opening up one of the electron loops in the scattering diagrams shown in figure 8.

of the left-going disorder propagator by g_ℓ instead of $1 - c$ then the summed-up self-energy diagrams including all connected diagrams in the full augmented space, connected either via the electronic propagator or via disorder propagator and containing only single propagator loops can be written as

$$\Sigma^A(\omega_n) = -W \sum_{n=0}^{\infty} \sum_{s+t=n} \gamma_r^s \gamma_\ell^t (1 + \sigma_{\uparrow\downarrow}) \left[G_{x_1,x_1}(\omega_n) W \right]^{s+t-1} N_{s,t}$$

$$+ \sum_{\omega_n} \sum_{n=0}^{\infty} \sum_{s+t=n} W \gamma_r^s \gamma_\ell^t (1 + \sigma_{\uparrow\downarrow}) \left[G_{x_1,x_1}(\omega_n) W \right]^{s+t-1} N_{s,t} - W \gamma_r \qquad (12)$$

where γ_r and γ_ℓ give the renormalized contributions of right-going and left-going disorder propagators; $\sigma_{\uparrow\downarrow}$ represents the contribution from the disconnected portions of the electronic

propagator in the Hilbert space that simultaneously renormalizes a left-going and a right-going disorder propagator, an example of this being figure 8(a); $N_{s,t}$ represents the number of diagrams containing s right-going and t left-going propagators.

It is easy to check that $N_{s,t} = sN_{s-1,t} + tN_{s,t-1}$ with $N_{s,0} = \delta_{s,1}$ and $N_{0,t} = 0$. The second term in the above expression for $\Sigma_A(\omega_n)$ represents the correction from self-energy diagrams independent of ω_n, an example of this being figure 8(a).

The Dyson equation corresponding to the right-going and left-going disorder propagators can be written as (with α denoting either right (r) or left (l) propagators)

$$\gamma_\alpha = g_\alpha + g_\alpha \sigma_\alpha \gamma_\alpha$$

with the self-energies σ_r and σ_ℓ given by

$$\sigma_\alpha = -\sum_{\omega_n}\sum_{n=0}^{\infty}\sum_{s+t=n} W^{s+t}\left[G_{x_1,x_1}(\omega_n)\right]^{s+t}\gamma_\alpha^{s+t-1}N_{s,t}. \tag{13}$$

The contribution of $\sigma_{\uparrow\downarrow}$ is given by

$$\sigma_{\uparrow\downarrow}\omega_n = -\sum_{\omega_n}\sum_{n=0}^{\infty}\sum_{s+t=n}\sum_{s'+t'=n}\gamma_r^s\gamma_\ell^t W^n\left[G_{x_1,x_1}(\omega_n)\right]^{s'+t'}$$
$$\times N_{s,t}N_{s',t'}\ldots + W\gamma_r G_{x_1,x_1}(\omega_n). \tag{14}$$

The last term is included to avoid double counting a factor already included in $\sigma_\uparrow\gamma_r$.

Thus the evaluation of the summed-up expression for the self-energy requires knowledge of σ_r, σ_ℓ and $\sigma_{\uparrow\downarrow}$. Inspecting equations (13a-c) it appears that, apart from the summation over Matsubara frequencies, the formally summed-up expression is similar to that of the quenched self-energy under the single-loop approximation, in which the roles of the electronic propagators and the disorder propagators have been interchanged. Hence, in order to perform the double summation over various orders of interaction and over the number of distinct ways of arranging s right-going and t left-going electronic propagators in equation (13a-c) let us define, analogous to Schultz and Shapero [3], a generating function for σ_r, σ_ℓ and $\sigma_{\uparrow\downarrow}$

$$\Gamma_1(u,v) = \sum_{s=1}^{\infty} u^s f_s(u)$$

with $f_s(u) = \sum_{t=0}^{\infty} v^t N_{s,t}$. This satisfies the recursion relation

$$f_s(v) = \sum_{t=0}^{\infty} \frac{v}{1-v} f'_{s-1}(v)$$

where $f' = df/dv$ along with the initial condition $f_0 = \ln v$.

Utilizing the recursion relation of $f_s(v)$, the partial differential equation satisfied by generating function Γ_1 can be given by

$$(1/vu - \partial/\partial u)\Gamma_1(u,v) = 1/v + \partial\Gamma_1(u,v)/\partial v.$$

Changing variables to $\xi = (u+v)/2$ and $\eta = (v-u)/2$ leads to the canonical form

$$\frac{\partial\Gamma_1}{\partial\xi} = \frac{\Gamma_1}{(\xi^2-\eta^2)} - \frac{1}{(\xi+\eta)}.$$

Writing $\sigma_\alpha = \sum \sigma_\alpha(\omega_n)$ where α can either be r or l

$$\sigma_\alpha(\omega_n) = -\frac{1}{\gamma_\alpha}\Gamma_1(WG_{x_1,x_1}(\omega_n)\gamma_\alpha, WG_{x_1,x_1}(\omega_n)\gamma_\alpha).$$

Inserting this in equation (12) leads to the first-order ordinary differential equation

$$\gamma_\alpha\frac{d\sigma_\alpha(\omega_n)}{d\xi} = \gamma_\alpha\frac{\sigma_\alpha(\omega_n)}{\xi^2} + \frac{1}{\xi} \tag{15}$$

along with the boundary condition $\sigma_\alpha \to 0$ as $\xi \to 0$.

In order to perform the summations in equation (13a) apart from the sum over Matsubara frequencies ω_n, we rewrite the formal representation of $\sigma_{\uparrow\downarrow}$ in the following way:

$$\sigma_{\uparrow\downarrow} = \sum_{\omega_n}\sigma_{\uparrow\downarrow}(\omega_n) + W\gamma_r G_{x_1,x_1}(\omega_n)$$

with

$$\sigma_{\uparrow\downarrow} = -\sum_{n=1}^\infty\left[WG_{x1,x1}(\omega_n)\gamma_\ell\right]^n\sum_{s=0}^n\gamma_r^s\gamma_\ell^{-s}N_{s,n-s}\sum_{s_1+t_1=n}N_{s_1,t_1}.$$

We notice that

$$\sum_{s_1+t_1=n}N_{s_1,t_1} = (n-1)!$$

We now define another generating function $\Gamma_2(v, u) = \sum_{n=1}^\infty(n-1)!v^n f_n(u)$ where the function $f_n(u) = \sum_{r=0}^n uN_{r,n-r}$. The recursion relation satisfied by $f_n(u)$ can be obtained easily as

$$f_n(u) = u(1-u)f'_{n-1}(u) + (n-1)uf_{n-1}(u)$$

with initial condition $f_1(u) = u$.

The generating function $\Gamma_2(v, u)$ can be shown to satisfy the the second-order partial differential equation

$$v\frac{\partial^2\Gamma_2(v, u)}{\partial v^2} - u\frac{\partial^2\Gamma_2(v, u)}{\partial v\partial u} = \frac{\Gamma_2(v, u)}{(1-u)v^2} - \frac{1}{v} - \frac{\partial\Gamma_2}{\partial v}.$$

By changing the variables u and v to $\xi = v$ and $\eta = \ln v - \ln u$, the above second-order partial differential equation can be reduced to the canonical form of a linear, inhomogeneous hyperbolic equation of second order

$$\partial^2\Gamma_2/\partial\xi\,\partial\eta = F(\xi, \eta, \partial\Gamma_2/\partial\xi, \partial\Gamma_2/\partial\eta, \Gamma_2)$$

where

$$F(\xi, \eta, \partial\Gamma_2/\partial\xi, \partial\Gamma_2/\partial\eta, \Gamma_2) = (\Gamma_2/\xi)(1-\xi/\exp(\eta)) - 1/\xi.$$

In terms of this generating function we obtain

$$\sigma_{\uparrow\downarrow} = -\Gamma_2\left(WG_{x_1,x_1}(\omega_n)\gamma_\ell, \gamma_r/\gamma_\ell\right).$$

We have to solve the equation along the curves defined by $\xi = WG_{x_1,x_1}(\omega_n)\gamma_\ell$ and $\eta = \ln(WG_{x_1,x_1}(\omega_n)\gamma_\ell^2/\gamma_r)$ in conjuction with the boundary conditions $\xi \to 0, \Gamma_2 \to 0, \partial\Gamma_2/\partial\xi \to 0$.

The solution of such hyperbolic linear partial differential equations with given sufficient boundary conditions is known exactly in terms of its Green function (see, e.g., [11]). Once we have solved the equations (15) and (16), the summation over Matsubara frequencies can be done in a trivial way by performing the contour integration

$$\sum_{\omega_n} F(\omega_n) = \oint_C \frac{F(z)\,dz}{1 + \exp[\beta(z - \mu)]}$$

where the contour is taken to encircle the zeros of the denominator.

As regards the summation in equation (9) the first and second terms are identical apart from summation over Matsubara frequencies and a change of sign in the case of the second term. If we introduce a third generating function

$$\Gamma_3(v, u) = \sum_{n=1}^\infty u^n f_n(v)$$

with

$$f_n(v) = \sum_{r=0}^\infty v^r N_{r,n-r}$$

it is easy to check that this generating function satifies the first-order partial differential equation

$$u\frac{\partial\Gamma_3}{\partial u} - v\frac{\partial\Gamma_3}{\partial v} = \Gamma_3\left[1 + \frac{1}{(1-v)u}\right]. \tag{16}$$

Along with the boundary conditions $u \to 0, \Gamma_3 \to 0$ for all values of v and $v \to 0, \Gamma_3 \to 0$ for all values of u. The solution of this equation with the given boundary conditions leads to obtaining Σ^A

$$\Sigma^A(\omega_n) = -\frac{1}{G_{x_1,x_1}(\omega_n)}(1 + \sigma_{\uparrow,\downarrow})\Gamma_3(WG_{x_1,x_1}(\omega_n)\gamma_\ell, \gamma_r/\gamma_\ell)$$

$$+ \sum_{\omega_n} \frac{1}{G_{x_1,x_1}(\omega_n)}(1 + \sigma_{\uparrow,\downarrow})\Gamma_3(WG_{x_1,x_1}(\omega_n)\gamma_\ell, \gamma_r/\gamma_\ell) - W\gamma_r. \tag{17}$$

Finally since the annealed Green function is obtained from scattering diagrams of the annealed thermodynamic potential by breaking open the electronic propagator part the annealed averaged thermodynamic potential will be given by an equation identical to equation (7) where Σ has to be replaced by Σ^A. The form of Σ^A under the single-loop approximation can be obtained in the above prescribed manner. The advantage of this formalism is since it treats the quantum as well as statistical part in a unified way, whatever approximation is made applies equally to both part . Our next plan is to extend this beyond the single-loop approximation so that the clustering effect can be treated on an equal footing for the internal energy part as well as for the configurational entropy part.

6. Summary

The fermion field theoretic approach to the augmented space formalism has been applied for obtaining the thermodynamic potential of disordered alloys. The standard diagramatic technique has been employed for both types of averaging of thermodynamic potential— quenched as well as annealed—with the following results.

(i) The quenched thermodynamic potential of disordered alloys has been obtained in this formalism in a general way extending beyond the single-site coherent-potential approximation as was done earlier by Ducastelle.

(ii) The difference between quenched and annealed averaging of the thermodynamic potential appears on considering certain additional classes of scattering diagram in the latter case. These are such that although they are disconnected in the real Hilbert space and would have no contribution if the logarithm were taken prior to averaging, they become connected in full augmented space via disorder propagators. Thus they contribute to annealed and not to quenched averages.

(iii) This difference between quenched and annealed averaging is manifested in the summed-up self-energy Σ, which in turn is related to the thermodynamic potential. Considering additional contributions to the self-energy Σ^A for the annealed case, the effect of the disconnected portion of the diagrams in Hilbert space is to renormalize the disorder propagators.

(iv) Under the single-loop approximation, two types of disorder self-energies σ_ℓ and σ_r, renormalising either the left-going or right-going disorder propagator, and another $\sigma_{\uparrow\downarrow}$, renormalizing both of them simultaneously, may be obtained from generating functions, which appear as solutions of first-order differential equations and a linear hyperbolic partial differential equation of second order followed by summations over Matsubara frequencies. Given the boundary conditions these differential equations have solutions whose formal expressions are available.

Acknowledgments

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