Spatial Ergodicity and Configuration averaging in disordered systems

Suman Chowdhury\textsuperscript{b}, Banasree Sadhukhan\textsuperscript{a}, Dhani Nafday\textsuperscript{c}, Santu Baidya\textsuperscript{c}, Debnarayan Jana\textsuperscript{b}, Tanusri Saha-Dasgupta\textsuperscript{c}, Abhijit Mookerjee\textsuperscript{c,a,d,1,*}

\textsuperscript{a}Department of Physics, Presidency University, 86/1 College Street, Kolkata 700073, India
\textsuperscript{b}Department of Physics, University of Calcutta, 92 Acharya Prafulla Chandra Road, Kolkata 700009, India
\textsuperscript{c}Department of Condensed Matter and Materials Science, S.N. Bose National Centre for Basic Sciences, JD-III, Salt Lake, Kolkata 700098, India.
\textsuperscript{d}Lady Brabourne College, 1/2 Suhrawardy Street, Kolkata, India.

Abstract

We examine the concept of spatial ergodicity in disordered systems. Our aim is to understand why experimenters in some situations observe the configuration average of global properties in a single sample. We describe two techniques: one of which directly calculates the spatial average of a single sample, and another which explicitly obtains the configuration average over many samples with different samples. For graphenes with random voids we argue that the assumption of spatial ergodicity is indeed valid.

Keywords: Spatial ergodicity, Configuration averaging, Spatial averaging
PACS: 61.46+w, 36.40.Cg, 75.50.Pp

*Corresponding author
Email address: abhijit.mookerjee61@gmail.com (Abhijit Mookerjee)

\textsuperscript{1}Distinguished Visiting Professor at Presidency University, Visiting Professor at Lady Brabourne College, Kolkata

Preprint submitted to Physica B April 29, 2014
1. Introduction

In many works on the theoretical aspects of a problem, the technical and mathematical sophistications are attractive, but exclusive concentration on them may sometimes tend to defocus the essential physics and intuition that lies at their very core. Expositions on these basic questions can discourage many readers from reading and assessing the work. Nevertheless a serious understanding of these aspects is crucial before further theoretical and computational advance. In this paper we shall examine the idea of spatial ergodicity in quenched disordered systems and explain both the physics and technical mathematics associated with the problem\textsuperscript{(6)}.

2. Configuration averaging in disordered systems

The study of averaging over all possible different ‘configurations’ of a quenched disordered system, has been a focus problem in the theory of measurements. Configuration averaging is ubiquitous both in quantum mechanics and statistical physics. For annealed disorder, where the disorder driven fluctuations themselves vanish in the large size systems, the idea of spatial ergodicity is essential. At finite temperatures different possible states of a canonical ensemble, for example, are occupied with Boltzmann probabilities, and observable physical properties are averaged over the ensemble. Similarly, when we wish to measure a given physical observable in a quantum system, the result of the measurement is spread over different possible states with probabilities given by squared amplitudes of the wave function projection onto those states. Our discussion will be essentially at 0K and we shall focus on frozen or quenched disorder as in a glass or disordered alloy. During the
last four decades considerable effort has gone into devising methods for carrying out averages of physical observables over different configurations realized by disordered systems.

Why do we wish to carry out such averages and is such a procedure meaningful?\(^{(6)}\)

The problem is clearly understood if we examine a specific example. An experimentalist is carrying out energy resolved photo-emission studies on a disordered binary alloy \(A_xB_y\). Varying the frequency of this incident photon and keeping the energy window of the excited outgoing electrons reasonably narrow, one can map out the density of states of the valence electrons for the alloy. Ideally, if experimentalist carries out the experiment on ten different samples of the same alloy he should obtain slightly different results. Two different samples of the disordered alloy have different distributions of the A and B constituents and hence should give slightly different random results. Yet, in practice, the variation the experimenter sees in the different samples is well within his experimental error bars. What he observes is an average result, averaged over different realizable configurations of atomic arrangements in the alloy. The interesting fact is that he sees the averaged result in a single sample. The same is true for other measured bulk properties like the specific heat, conductivity and different response functions.

Note that all these measured properties are global to the system. Should there be a difference if we measure local properties with local probes? Take another example of a magnetically disordered alloy AuFe (with < 10% of Fe). If we measure the magnetization of a sample it remains zero up to liquid He temperatures. Yet, if we carry out a Mössbauer study on the same alloy,
there is clear indication of a frozen local exchange field at low temperatures, indicating the existence of non-zero local magnetization. Configuration averaging will be meaningless if we wish to look at local properties. Even here, a degree of averaging over the far environment is relevant. Although the radioactive Fe atom giving rise to the Mössbauer spectrum sits in different environments in different samples, yet experiments yield an average exchange field distribution.

Why do we observe configuration averaged results in a particular macroscopic sample? The answer lies in the idea of spatial ergodicity. Let us look at the example of a random binary alloy as illustrated in Fig.1. The left panel shows a number of different samples each with N atoms and its own A-B distribution. There are in all $2^N$ configurations. Let us label each configuration by $C_n$, formally the configuration average of a physical quantity $A$ is

$$\ll A \gg_{\text{conf}} = \frac{1}{2^N} \sum_n A(C_n) \gamma(C_n)$$  \hspace{1cm} (1)
where $\gamma(C_n)$ is the number of times a given configuration $C_n$ occurs in the collection (space) of configurations shown in the left panel of Fig.1. Now, if $N \to \infty$ then $\gamma(C_n)/2^N$ is the probability associated with the configuration and

$$\langle A \rangle_{\text{conf}} = \sum_n A(C_n) \mathcal{P}(C_n)$$  \hspace{1cm} (2)$$

Let us now take a large single sample with $2^N$ atoms and partition it into subsystems each with $N$ atoms. The spatial average taken over this one single sample is:

$$A_{\text{spat}} = \langle 1/2^N \sum_{n=1}^{2^N} A(\vec{r}_n) \rangle$$  \hspace{1cm} (3)$$

where $\vec{r}$ denotes the positions of the atoms. We shall now partition the sample as shown in the right panel of Fig.1 and group these sites into microsystems of size $N$ atoms, so there are $2^N/N$ such partitions which we shall call $C'_m$, then

$$\langle A \rangle_{\text{spat}} = \langle N/2^N \sum_{m=1}^{2^N/N} 1/N \sum_{\vec{r}_m \in C'_m} A(\vec{r}_m) \rangle$$  \hspace{1cm} (4)$$

In the collection $C'_m$ all distributions are not distinct. Assume that there are $\gamma(C'_m)$ identically distributed microsystems, then the above equation can be written as:

$$\langle A \rangle_{\text{spat}} = \langle N/2^N \sum_{m=1}^{2^N/N} A(C'_m) \gamma(C'_m) \rangle$$  \hspace{1cm} (5)$$

If we now we let $N \to \infty$ then we get:

$$\langle A \rangle_{\text{spat}} = \sum_{m=1} \mathcal{A}(C'_m) \mathcal{P}(C'_m)$$  \hspace{1cm} (6)$$
Is it then true that it follows from Eqns. (1) and (5) that the configuration average taken over many different samples is the same as the spatial average over a single sample? The answer is in general in the negative. We should note that:

(i) The statement is untrue for any finite system.

(ii) The statement remains true if, as $N \to \infty$ in such a way that each partition of the single sample also becomes infinitely large, but for every configuration (shown on the left of Fig. 1) there is a one-to-one correspondence with a partition shown on the right panel of Fig. 1 and vice versa. This is a very strong statement and is known as the "Spatial Ergodic Principle" for quenched disordered systems.

(iii) If these averages diverge as $N \to \infty$, but the variance diverges faster, then there is no point in talking about averages, since the fluctuations about the average dominate. Example of such a system is the intensity of starlight after it passes through a disordered dielectric medium. The fluctuations in intensity dominate causing star to twinkle even outside our atmosphere. Same holds for conductance fluctuations in disordered media.

Although numerous very detailed and rigorous works exist on temporal ergodicity, a similar detailed exposition on spatial ergodicity is scarce. The concept of spatial ergodicity is a conjecture; its mathematical proof involves many stringent pre-conditions. Many systems do not satisfy them and therefore not spatially ergodic. In order to develop an algorithm for
configuration averaging, we have to be careful to ensure that the assumption of spatial ergodicity remains valid.

The aim of this paper is to introduce two different numerical techniques: one of which explicitly calculates the spatial average and the other the configuration average and then compare the two results. We shall apply them to the problem of graphene with random voids. Since we shall need to compare results, we have to be careful to derive every parameter from ab initio calculations.

3. A simple model for disordered graphene

Let us introduce a simple, non-trivial model of a disordered graphene sheet. This is described by a tight-binding Hamiltonian with a single band $(p_z)$ per site. Anderson studied this model in his now celebrated 1958 paper \(^{(2)}\) and it goes under his name.

\[
H = \sum_R \varepsilon_R P_R + \sum_R \sum_{R'} t_{RR'} T_{RR'}
\] (7)

Here $P_R = |R\rangle \langle R|$ and $T_{RR'} = |R\rangle \langle R'|$ are projection and transfer operators on the space spanned by the tight-binding basis $\{|R\rangle\}$. The simplest model of a void is just the removal of an atom from a site $R$, putting $t_{R'R} = 0$ and $\varepsilon_R \rightarrow -\infty$.

For any approximation to be physically valid, the resolvent of the Hamiltonian $G(R, z) = \langle R|(zI - H)^{-1}|R\rangle$ has to satisfy the following conditions:

(i) $G(R, z)$ has singularities only on the real $z$ axis.
(ii) It is analytic everywhere outside the real z axis. The imaginary part of $G(R, z)$ is always negative or zero in the upper half $z$-plane and always positive or zero in the lower half.

(iii) In case the spectrum of $H$ is bounded, $G(R, z) \to 0$ as $z \to \pm \infty$ along the real $z$ axis.

The resolvent function is said to be herglotz if it satisfies these properties. This ensures that the density of states is always positive or zero, integrable and the spectrum is always real. Resolvents of hermitian Hamiltonians are always herglotz. However, effective Hamiltonians are not necessarily hermitian and we must ensure that they yield herglotz resolvents to be physically relevant approximations.

To start with we derive from first-principles density functional ideas, a tight-binding Hamiltonian appropriate to graphene.

We start with a self-consistent ground state calculation for the single layer graphene using the tight-binding, linear muffin-tin orbitals (TBLMTO) method within atomic sphere approximation. Three empty spheres were needed to achieve space filling. The muffin tin radii used for Carbon (C)
and the empty spheres (ES) were 1.56 a.u. and 2.76 a.u. respectively. The minimal basis set for the self-consistent calculation consisted of Carbon s,p and empty sphere s states. The results are shown in the left panel of Fig. 2. The $\pi$-bonding bands straddling the Dirac point are shown emphasized. In the next step, $N^{th}$ Order Muffin Tin Orbital (NMTO) method was used to construct the low-energy Hamiltonian consisting of only C-p$_z$ states. The NMTO method carries out massive downfolding starting from the all-orbital local density approximation (LDA) calculation. This energy selective procedure enables a down-folded Hamiltonian defined in the basis of a minimal set of active orbitals. The remaining degrees of freedom are integrated out\(^{(1,21)}\). The integrated out orbitals renormalized the active C-p$_z$ orbital.

The effective C-p$_z$-C-p$_z$ hopping interaction: $t(R, R')$, connecting C-p$_z$ NMTO-s $\chi(R)$ centered at the site $R$ to the neighboring C-p$_z$ NMTO $\chi(R')$ centered at the $R'$, were obtained by Fourier transformation of the low energy C-p$_z$ Hamiltonian $H_{p_z}(\vec{k})\(^{(7,21)}\)$. The off-diagonal elements $t(R)$ are shown in the Fig. 3 and Table 1. Please note that the overlap rapidly decays with distance. In this work we have truncated at the next-near neighbour distances.

The subsequent aim of this communication is to describe a technique which provides configuration averaging both via the configuration ensembles of Fig.1(a) and by direct spatial averaging over the single macrosystem of

| (eV) | $\varepsilon$ | $t_1$ | $t_2$ | $t_3$ |
|------|--------------|-------|-------|-------|
| -0.291 | -2.544 | 0.1668 | -0.1586 |

Table 1: Tight-binding parameters generated by NMTO.
Fig. 1(b). We shall then compare the results and comment on the system being spatially ergodic or not.

4. Spatial averaging and the Recursion Method

Having obtained a minimal, tight-binding Hamiltonian, we next turn to real space techniques for spatial averaging. We shall first propose a methodology to deal with spatial averaging in disordered systems. Heine, in an article\(^\text{(10)}\) argued that many of the properties of solids are crucially dependent on the local chemistry of the atoms constituting the solid. For such properties he enunciated a *Black Body Theorem*, which essentially states that the very far environment of an atom in a solid has very little influence on its local chemistry. This local environment approach to the electronic structure of solids requires an alternative to band theory for solving the Schrödinger equation. Band theory is invalid in disordered systems. Supercell methods can only deal with disorder up to the size of the supercell. Longer ranged disorder which
leads to disorder broadening of states cannot be adequately described by supercell methods. The only exception is the method of Zunger\textsuperscript{(25)}. Physics is better understood by means of a solution that explicitly accounts for the role of local environment. The recursion method introduced by Haydock et al\textsuperscript{(11)} is a lucid approach in this direction. It expresses the Hamiltonian in a form that couples an atom to its first nearest neighbour, then through them to its distant neighbours and so on.

Mathematically, a new orthonormal basis set $|n\rangle$ in which the Hamiltonian is tridiagonal is constructed by a three term recurrence formula. The starting state $|0\rangle$ of recursion is:

$$|0\rangle = \frac{1}{\sqrt{N}} \sum_i \eta_i |R_i\rangle$$  \hspace{1cm} (8)

where, $\eta_i$ take the values $\pm 1$ randomly, so that:

$$\langle 0|G(z)|0\rangle = \frac{1}{N} \left\{ \sum_i \eta_i^2 \langle R_i|G(z)|R_i\rangle + \sum_i \sum_j \eta_i \eta_j \langle R_i|G(z)|R_j\rangle \right\}$$  \hspace{1cm} (9)

Since $\eta_i^2 = 1$ and the second term $O(\sqrt{N})$, the spatial average of the total density of states is:

$$-\frac{1}{\pi} \Im m \text{ Tr} G(E + i0) = \ll n(E) \gg_{sp}$$  \hspace{1cm} (10)

The whole set of orthonormal states are generated by the following three term recurrence relation:

$$\beta_{n+1}|n + 1\rangle = H|n\rangle - \alpha_n|n\rangle - \beta_n|n - 1\rangle$$  \hspace{1cm} (11)

Since we cannot apply Bloch theorem for systems where periodic symmetry is lost, we take recourse to an alternative approach of obtaining physical
properties from the averaged resolvent. Haydock et al.\textsuperscript{(11)} showed that using Equations (11) we can expand the resolvent as a continued fraction:

\[
\ll G_{RR}(z) \gg_{sp} = \frac{1}{z - \alpha_0 - \frac{\beta_1^2}{z - \alpha_1 - \frac{\beta_2^2}{z - \alpha_2 - \frac{\beta_3^2}{z - \alpha_3 - \beta_4^2}}}}
\]

In practice, the continued fraction is evaluated to a finite number of steps.

4.1. The far environment: terminators

Right at the start we chose the real space algorithm over mean-field and supercell approaches because we did not wish to introduce artificial periodicity and miss out on the effects of long-ranged disorder. The problem with any numerical calculation is that we can deal with only a finite number of operations. In the recursion algorithm, we can go up to a finite number of steps and if we stop the recursion, this would lead to exactly what we wish to
avoid. The analysis of the asymptotic part of the continued fraction is therefore of prime interest to us. This is the “termination” procedure discussed by Haydock and Nex\textsuperscript{(12)}, Luchini and Nex\textsuperscript{(14)}, Beer and Pettifor\textsuperscript{(4)} and in considerable detail by Viswanath and Muller\textsuperscript{(24)}. This terminator $T(z)$ which accurately describes the far environment, must maintain the herglotz analytical properties. We have to incorporate not only the singularities at the band edges, but also those lying on the compact spectrum of $H$. Viswanath and Muller\textsuperscript{(24)} has proposed a terminator:

$$T(z) = \frac{2\pi(E_m)^{(p+2q+1)/2}}{B\left(\frac{p+1}{2}, 1+q\right)}|z - E_0|^p \left\{ (z - E_1)(E_2 - z) \right\}^q$$ \hspace{1cm} (13)

The spectral bounds are at $E_1, E_2$ with square-root singularities, $E_m^2 = E_1 E_2$ and there is a cusp singularity at $E_0$ if $p = 1, q = 1$ or infra-red divergence if $p = -1/2, q = 0$. $E_0$ sits on the compact spectrum of $H$. Magnus\textsuperscript{(15)} has cited a closed form of the convergent continued fraction coefficients of the terminator:

$$\beta_{2n}^2 = E_m^2 \frac{4n(n+q)}{(4n+2q+p-1)(4n+2q+p+1)}$$
$$\beta_{2n+1}^2 = E_m^2 \frac{(2n+2p+1)(2n+2q+p+1)}{(4n+2q+p+1)(4n+2q+p+3)}$$ \hspace{1cm} (14)

The parameters of the terminator are estimated from the asymptotic part of the continued fraction coefficients calculated from our recursion. We shall use the Viswanath-Müller termination appropriate for infra-red divergences was used and seamlessly enmeshed with the calculated coefficients as shown

13
In this way both the near and the far environments are accurately taken into account.

5. Ensemble averaging and the Augmented Space technique

The augmented space or configuration space method had been proposed as early as 1973 by Mookerjee\textsuperscript{(19)}. Some of the most successful beyond single-site, mean-field averaging techniques in random systems are based on this
method: e.g. the CA$^{(17)}$ and the itinerant CPA$^{(9)}$. In this approach we work not with individual configurations of the sample but with collection of all possible configurations. Let us examine the basic concepts in this methodology. Take the example of a random variable $n_i$ which takes $m$ values $n_1^i, n_2^i \ldots n_m^i$. Let us associate with the variable $n_i$ an operator $\tilde{N}_i$ such that the random values taken by the variable are the eigenvalues of the operator and the spectral density of the operator is the probability density of the variable. We now deal with the space $\Phi$ of such operators, i.e. the collection of all ‘configurations’ of $n_i$. The Augmented space Theorem$^{(20)}$ tells us that the configuration average of any function $f(n_i)$ of these variables is the matrix element of the same operator function of $N_i$:

$$\langle \emptyset | \tilde{f}(\tilde{N}_i) | \emptyset \rangle$$

where $|\emptyset\rangle = \sum_{\lambda} \sqrt{\lambda} |\lambda\rangle$.

From the formulation of the methodology it is clear that we work on the space or collection of all configurations and consequently the result is the configuration average. The generalization to many random variables $\{n_i\}, i = 1, \ldots N$ is now clear. We work in the space $\Psi = \prod \otimes N_i$ of rank $m^N$ which is spanned by all configurations of $\{n_i\}$.

One of the main conceptual hurdles in understanding the augmented space theorem has been the visualization of and mathematical manipulations in the space of configurations $\Psi$. A very simple, yet essentially non-trivial example is that of the Ising model. Since most readers seem comfortable enough with this model, we shall illustrate some of the basic ideas behind our description with it.

The model consists of a set of spins $\{\sigma_R\}$ arranged on a discrete lattice labeled by $R$. Each spin $\sigma_R$ can have two possible states or configurations
which we can denote as \( |\uparrow_R\rangle \) and \( |\downarrow_R\rangle \). The collection of all independent linear combinations of these two states : \((1/\sqrt{2})\{ |\uparrow_R\rangle \pm |\downarrow_R\rangle \}\) is called the configuration space of \( \sigma_R \). It is of rank two and is spanned by the states \( |\uparrow_R\rangle \) and \( |\downarrow_R\rangle \). Let us call this space \( \phi_R \).

The set of, say, \( N \) spins then have \( 2^N \) possible configurations each of which can be written as a sequence of \( m \) up-states and \( N-m \) down-states. The ordering of this sequence is crucial, since different orderings correspond to different configurations. The number \( N-m \) is defined as the cardinality of the configuration and the sequence \( \{C\} \) of sites \( \{R_{i_1}, R_{i_2}, \ldots R_{i_k} \ldots R_{i_{N-m}}\} \) where the down-states sit is called the cardinality sequence of the configuration. The cardinality sequence uniquely describes the configuration and is a very convenient way of labeling the different configurations \( |\{C_k\}\rangle \) (where \( k=1,2,\ldots 2^N \)) of the set of \( N \) spins. The configuration space \( \Phi \) is of rank \( 2^N \) and can be written as a direct product of the configuration spaces of the individual spins.

\[
\Phi = \prod_R \otimes \phi_R
\] (15)

When the Hamiltonian parameters have binary disorder their configuration space is isomorphic to the one for a collection of Ising half spins. Let us now assume that the random variables independently distributed and their probability densities are given by \( p(x_R) \). We shall assume probability densities have finite moments to all orders. Physically relevant densities almost all fall in this category. Since the probability densities are positive definite functions, we can always write them as spectral densities of positive definite operators as follows(22) :

16
\[ p(x_R) = (-1/\pi) \Im \langle \emptyset | (x_R + i0)I - N_R^{-1} | \emptyset \rangle \]
\[ = (-1/\pi) \Im m g(x_R + i0) \] (16)

If \( x_R \) has a binary distribution, taking the values 0 and 1 with probabilities \( x \) and \( y = 1-x \), then a representation of \( N \) is

\[
\begin{pmatrix}
  x & \sqrt{xy} \\
  \sqrt{xy} & y
\end{pmatrix}
\] (17)

\[ |\emptyset \rangle = (\sqrt{x}|0_R \rangle + \sqrt{y}|1_R \rangle) \]
\[ |\{R\} \rangle = (\sqrt{y}|0_R \rangle - \sqrt{x}|1_R \rangle) \]

Let us now consider the average of a well-behaved function \( f(x_R) \) of \( x_R \). By definition

\[
\ll f(x_R) \gg = \int f(x_R)p(x_R)dx_R = \oint f(z) g(z) \, dz
\] (18)

The integral is taken over a closed contour enclosing the singularities of \( g(z) \) but not any of \( f(z) \). We assume here that \( f(z) \) is well behaved, in the sense that it has no singularities in the neighbourhood of a singularity of \( g(z) \).

We now expand the function \( g(z) \) in the basis of its eigenstates \( \{|\mu\rangle\} \) of \( M_i \). These may be either discrete or continuous. This expansion can be written as a Stielje’s integral in terms of the spectral density function \( \rho(\mu) \) of \( M_i \).
\[ \ll f(x_R) \gg = \int d\rho(\mu) \langle \emptyset | \mu \rangle \left[ \int f(z)(z - \mu)^{-1} \right] \langle \mu | \emptyset \rangle \]

\[ = \langle \emptyset | \left[ \int d\rho(\mu) | \mu \rangle f(\mu) \langle \mu | \right] | \emptyset \rangle \quad (19) \]

The second line requires the function to be well behaved at infinity. The expression in brackets on the right side of the bottom equation is, by definition, the operator \( f(M_R) \). It is the same functional of \( M_R \) as \( f(x_R) \) was of \( x_R \). For example, if \( f(x_R) \) is \( x_R^2 \) then \( f(M_R) \) is \( M_R^2 \).

This yields the central equation of the augmented space theorem:

\[ \ll f(x_R) \gg = \langle \emptyset | f(M_R) | \emptyset \rangle \quad (20) \]

The result is significant, since we have reduced the calculation of averages to one of obtaining a particular matrix element of an operator in the configuration space of the variable. Physically, of course, the augmented Hamiltonian is the collection of all Hamiltonians.

If we wish to carry out the configuration averaging of, say, the Green function element

\[ G_{RR}(z) = \langle R | (zI - H(\{x_{R'}\}))^{-1} | R \rangle \quad (21) \]

The theorem leads to:

\[ \ll G_{RR}(z) \gg = \langle R \otimes \emptyset | \left( z\tilde{I} - \tilde{H}(\{\tilde{M}_{R'}\}) \right)^{-1} | R \otimes \emptyset \rangle \quad (22) \]

From the form of \( | \emptyset \rangle \) it is easy to see that during the calculation of the average we visit every possible configuration (m,0-s and N-m,1-s) in the
ensemble of Fig 1(a) and with the proper statistical weight $x^m y^{N-m}$. The augmented space approach then calculates the average in the standard way of visiting each configuration of the ensemble with its appropriate statistical weight. The augmented Hamiltonian is constructed out of the original random Hamiltonian by replacing the random variables by the corresponding configuration space operators built out of their probability distributions. This augmented Hamiltonian is an operator in the augmented space $\Psi = \mathcal{H} \otimes \Phi$ where $\mathcal{H}$ is the space spanned by the tight binding basis and $\Phi$ the full configuration space. The result is exact.

Approximations can now be introduced in the actual calculation of this matrix element in a controlled manner. The augmented Hamiltonian has no randomness in it and therefore various techniques available for the calculation of the Green functions for non-random systems may be resorted to. In particular we shall show that the recursion method suggested by Haydock et al.$^{(11)}$ is ideally suited for obtaining matrix elements in augmented space. Since configuration averaging is an intrinsically difficult problem, we must pay the price for the above simplification. This comes in the shape of the enormous rank of the augmented space. For some time it was thought that recursion on the full augmented space was not a feasible proposition. However, if randomness is homogeneous in the sense that $p(x_R)$ is independent of the label $R$, then the augmented space has a large number of local point group and lattice translational symmetries. These can be utilized to reduce vastly the rank of the effective space on which the recursion can be carried out. Recursion on augmented space can be done with ease, even on desktop computers.
Figure 6: TDOS for Graphene using spatial averaging (right panels) and configuration averaging (left panels) all with Viswanath-Muller terminators. The void concentrations are shown.
6. Results and Discussion

We have applied the two above techniques: the real space recursion and augmented space to obtain the density of states for graphene with random voids. The former yields the spatial averages while the latter yields configuration averages. The set of figures 6 compares the spatial and configuration averages of three void compositions. At first glance they seem to agree and we conclude that the ergodic hypothesis does hold for this system. However there are subtle differences which should be commented on:

(i) If we examine the band edges, we note that whenever there is periodicity at any scale at all, the band edges are sharp and quadratic. Long range disorder leads to band tailing. This disorder induced band tailing has been known for decades and it would be interesting to examine if the tail states are localized or not.

(ii) Again periodicity at whatever scale leads to structure in the DOS. This is smoothed out by the disorder scattering induced complex ‘self-energy’. Occasionally practitioners of super-cell techniques introduce an artificial imaginary part to the energy. This smooths these structures too, but the procedure is entirely ad hoc. Augmented space leads to an energy dependent self-energy systematically.

(iii) This same self-energy broadens the infra-red divergences at the Dirac point. This is seen if we compare the divergent peaks in the real and augmented space results. For every composition the sharp peaks of the spatial averages are widens out by the disordered configurations.
It is important to note that the imaginary part of the self-energy, called the “life time” is accessible to neutron scattering experiments. The spatial averages can never access this “life-time” effect and it is essential to carry out configuration dependent averaging to calculate it.

In conclusion, even in cases where the ergodic hypothesis holds, there are subtle difference between different modes of averaging which should be taken care of when analyzing these systems.

Acknowledgments

SC would like to thank DST, India for financial support through the Inspire Fellowship. This work was done under the HYDRA collaboration between our institutes.

References

[1] O.K. Andersen and T. Saha-Dasgupta. Phys. Rev.B, 62:R16219, 2000.

[2] P.W. Anderson. Phys. Rev., 109:1492, 1958.

[3] M. Badino. “The Foundational Role of Ergodic Theory”. 2005.

[4] N. Beer and D.G. Pettifor. In P. Phariseau and W.M. Temmerman, editors, Electronic Structure of Complex Systems, volume 113, page 769. Plenum Press, New York, 1982.

[5] S. Chandrasekhar. Radiative Transfer. 1960.

[6] A.R. Cunha. Physicae, 10:9, 2011.
[7] H. Dreysee. *Workshop*LNP, 535:3, 1999.

[8] G. Gallavotti. and Cohen. E.G.D. *Phys. Rev. Lett.*, 74:1, 1995.

[9] S. Ghosh, P.L. Leath, and Morrel Cohen. *Phys. Rev. B*, 66:214206, 2004.

[10] R. Haydock. In H. Ehrenreich, F. Seitz, and D. Turnbull, editors, *Solid State Physics : Advances in Research and Application*, volume 35, chapter 2, pages 215–294. Academic Press, New York, 1980.

[11] R. Haydock, V. Heine, and M.J. Kelly. *J. Phys. C : Solid State Phys.*, 5:2845, 1972.

[12] R. Haydock and C.M.M. Nex. *Phys. Rev. B*, 74:20521, 2006.

[13] E.T. Jaynes. *Phys. Rev. B*, 166:620, 1957.

[14] M.U. Luchini and C.M.M. Nex. *J. Phys. C : Solid State Phys.*, 20:3125, 1987.

[15] A. Magnus. In D.G. Pettifor and D.L. Weaire, editors, *The recursion method and its applications*. Springer-Verlag, New York, 1987.

[16] U. Marini, Marconi. B., A. Puglisi, L. Rondoni., and A. Vulpiani. *arXiv-0803.071v1*, 5 March, 2008.

[17] R. Mills and P. Ratanavararaksa. *Phys. Rev. B*, 18:5918, 1978.

[18] A. Mookerjee and A.M. Jayannavar. *Pramana*, 34:441, 1990.

[19] Abhijit. Mookerjee. *J. Phys. C: Solid State Phys.*, 6:L205, 1973.
[20] Abhijit. Mookerjee. and D.D. Sarma. “Electronic Structure of Surfaces, disordered systems and clusters”. Taylor-Francis, U.K., 2003.

[21] T. Saha-Dasgupta, A. Lichtenstein, and R. Valenti. Phys. Rev. B, 71:153108, 2004.

[22] T. Saha-Dasgupta and A. Mookerjee. J. Phys. Condensed Matter Phys., 6:L245, 1994.

[23] J. van Lith. “Study of history and philosophy of modern physics.”. 2001.

[24] V.S. Viswanath and G. Müller. The user friendly recursion method. In Troisieme Cycle de la Physique, en Suisse Romande. I.C.T.P. Library, Trieste, 1993.

[25] A. Zunger. Phys. Rev. Lett, 65:353, 1990.