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PART I

Electronic Properties

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ELECTRONIC STATES IN AMORPHOUS SOLIDS, LIQUIDS, AND ALLOYS

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DEDICATED TO DAVID ADLER OUR FRIEND AND COLLEAGUE

ABSTRACT

We describe elements of a thermodynamical ensemble theory of electronic states in a variety of disordered systems. Equilibrium energies and kinetics of phase space exploration combine to determine the ensembles describing disordered systems. Electronic properties are then related to structural energies. This relationship serves to determine the distribution of electronic states present in real materials. Thus we obtain directly electronic properties without a need for detailed microscopic information about the diverse systems. Applications range from the Urbach edge to defect properties providing a unified understanding.

I. INTRODUCTION

Theoretical approaches to understanding the electronic states in the presence of disorder[1] have generally been based on model Hamiltonians in which disorder arises as a distribution of values of some Hamiltonian parameter. The application of results of these models for properties of liquids, amorphous solids, and alloys are motivated by either the assumption that the type of disorder is not crucial to determining properties being considered or the assumption that random alloy models correctly describe the disorder. Moreover, the phenomenological presence of defects has been included "by hand" relying on requirements of a predetermined but unknown microstructure[2] to determine their properties.

In this paper we provide an alternative understanding of disordered systems[3] in which the relevance of the *type* of ensemble describing the material is directly considered and, in particular, thermodynamical constraints (the relevance of system energy) can be used to obtain electronic properties. The fundamental connection arises, in large part, from the definition of single particle state energies as differences of system energies with different occupation. In addition to describing many known experimental phenomena, new predictions and experimental tests can be proposed.

We begin (section II) with general statistical properties of ensembles, and describe (section III) the ground state and elementary excitations and their relevance to electronic properties. We then discuss in general the Urbach edge (section IV), and defects (section V). Finally we consider specifically a-Si:H (section VI) and non-equilibrium excitations and devices (section VII).

II. ENSEMBLES FOR DISORDERED SYSTEMS.

Theoretical studies of the properties of disordered systems typically are motivated by consideration of the ideal alloy problem in which all realizations of a system have equal statistical weight.[1] Model Hamiltonians specifying the electronic potential implicitly incorporate assumptions regarding underlying structure. For example, application of the central limit theorem to the depth of potential fluctuations is not generally justified since the presence of many similar sized though independent contributions to disorder is not apparent.

In our discussion of material properties we focus on the ensemble[4] which correctly describes the material as defined by the statistical weight P(S) assigned to phase space points {S}. Statistical weights are determined by the energy of a phase space point E(S) and barriers to exploration of phase space. In the most general case the complexity of possible system energy surfaces prevents particular knowledge about statistical weights. Adequate phase space exploration results in Boltzmann statistical weights: $P(S) = e^{-E(S)/kT}$.

In general, the statistical weight of phase space points are determined by equilibration during formation of material, its subsequent processing, and during measurement. For example, phonons

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always equilibrate, electronic state occupations typically can equilibrate, point defects sometimes equilibrate, and dislocations or grain boundaries often do not equilibrate.

While some disordered systems are in active equilibrium, many are not. It is, however, generally possible to characterize materials, not in equilibrium, by ensembles with Boltzmann statistical weights of a temperature which we term the ensemble-characteristic temperature T*. This occurs because the material retains the signature of phase space exploration occurring during preparation. Several T* may apply to describing a particular material for different properties as indicated at the bottom of the previous paragraph. T* is determined by the system energy surface along with the method and specifics of material preparation. Two general cases are discussed in the following paragraphs.

Many material systems can be characterized as having typical energy barriers separating regions of phase space. These typical energy barriers, energies of local reorganization, reaction, or migration, then define a temperature above which adequate phase space exploration (equilibration) would be possible during experimental times. In such disordered systems, with typical energy barriers, the energy barrier height E_B also defines a temperature scale: the temperature at which experimental times *just* result in equilibration. We call this (range of) temperature the freezing-in or pixing temperature T^x. T^x is a range of temperature because the particular relevant temperature depends on relevant experimental time scales. If a material is cooled from above to below a pixing temperature, the relative weights of phase space regions which are no longer able to communicate below T^x, are given by Boltzmann weights at the pixing temperature or $T^*\sim T^x$. Classic examples are provided by glass transitions, and defect concentration freezing in crystals. The range of temperature constituting T^x is typically small because activated equilibration processes lead to logarithmic dependence on time. Specifically, if the rate of phase space exploration steps is given by $R=A\ e^{-E_B/kT}$ and N* steps are required for equilibration then $kT^x=-E_B/\ln(N^*/\tau A)$ where τ is the relevant experimental time. While $T^*\sim T^x$ more precise values of T* can be obtained by generic models including the effects of partial equilibration.

For materials deposited below T^x, bulk phase space exploration and energies do not apply, however, surface exploration must be possible to some degree (even sticking is phase space exploration). The energies of surface configurations, typically, though not without exception, are related to bulk energies. Thus the deposition temperature T_d should serve to determine T* after proper ensemble convolution to account for the difference between surface and bulk. Partial restrictions on equilibration can be shown to affect the ensemble in different ways depending on the energy surface, for some properties T* is typically elevated relative to T_d for others T* is unaffected in first order.

The dependence of the ensemble on T* leads to a wealth of predictions of changes in material properties with processing. As will be shown, T* directly enters into the behavior of material properties. Thus, for example, experiments which measure T^x and vary T* by changing annealing times or cooling rates can directly test predictions of our theory.

In summary, different classes of disordered materials: liquids, glasses, deposited amorphous materials, phonons and defects in crystals, and alloys have different or similar behavior specified by T*. $T^*=T$ for liquids and phonons and sometimes for crystal defects, alloys, glasses, and deposited amorphous materials when equilibrating in the solid state. $T^*\approx T_g$ for some properties of glasses. $T^*\approx T^x$ for materials cooled through T^x. $T^*=T^*(T_d)$ is a more material specific function for materials deposited below T^x.

III. GROUND STATES AND ELEMENTARY EXCITATIONS.

While the statistical description of a material's properties resides in the ensemble, substantial simplification is achieved if it can be adequetly described in terms of a ground state and excitations. For our purposes we are concerned with the static not the dynamic properties of excitations. While we generally think of a ground state as a state which can be achieved to a greater and greater approximation by cooling to lower temperatures, this is not essential. We can also allow a greater flexibility in defining the ground state: For example - it may not be unique (ie may constitute a class of states), it may be defined in terms of local parameters, it may not be realizable eg. in a flat space, and for alloys effective atoms may be used to specify it. The ground state thus does not necessarily have a unique definition, it is a convenient starting point for description of material properties to which the contribution of excitations must be added to yield material properties. "Idealized" models and simple approximations to real systems may often be properly adapted as ground states.[5]

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We distinguish between elementary excitations whose relaxation to the ground state is continuous through successively lower energy states and those whose relaxation to the ground state must pass over a free energy barrier - (such a barrier may exist for energetic or entropic reasons). This distinction enables us to define as defects the latter, and we then call the former "devions" (see Fig. 1). Thus we would define superfluid rotons as defects. The flexibility in choice of ground state may also lead in some cases to changes in the categories of devions and defects. Nevertheless, our definition is convenient because devions contribute continuously varying properties to those of the ground state, while defects, corresponding to independent minima in the system free energy surface, provide distinct contributions.

The definition of the ground state generally involves structural coordinates which are most essential to determining the system energy. For example, bond lengths and angles in covalent systems, neighboring atom types for alloys, local atomic density for simple metals. Typically, continuous changes away from the ground state are devions, discontinuous changes are defects. However, structure in the energy surface may make the result of even a continuously changing variable into a defect. In contrast, the local alloy configuration which appears discontinuous, may be treated continuously for many purposes because of the many possible arrangements with small changes in energy.

In order to proceed we provide a connection between the ensemble statistics, as manifest through the elementary excitations, and electronic properties of the material eg. the electronic density of states (DOS). A simple example of structural excitations and their relation to electronic states is provided by defects in crystals. Defects generally equilibrate diffusively and above some temperature they exist in a concentration given by $Ne^{-F/kT}$ which is also the number of electronic states to be associated with the defect type.

In this paper we focus on the electronic density of states in the low density regions or "gaps" in the spectrum. Because of their low density, the use of elementary excitations to describe electronic states is easily justified by their statistical independance.[4] In this low density region, the particular (eg. Fermion or Boson) statistics of the elementary excitations do not enter and their concentration is given by Boltzmann probability[6] which is also the density of electronic states:

$$D(\varepsilon) = N_0 e^{-F(\varepsilon)/kT^*} \qquad (1)$$

In the following two sections we discuss in turn the contributions to D(ε) of devions and defects using equation (1) in both cases. Devions responsible for continuously varying properties from the ground state are associated with band tails and the Urbach edge. Defects introduce peaks into D(ε) and control the position of the Fermi energy (along with carriers which we treat together with defects).

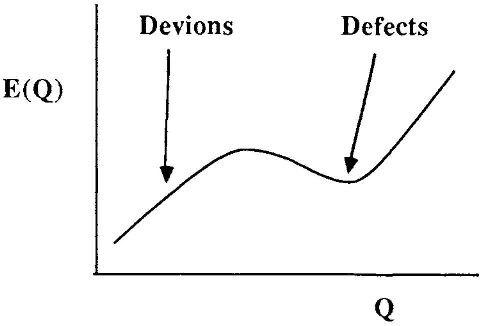

Fig. 1: Schematic drawing of elementary excitation spectrum as a function of an arbirtrary coordinate Q showing the distinction between structural deviations which can relax continuously to the ground state ("Devions") and those which must overcome a barrier to relax to the ground state ("Defects").

IV. THE URBACH EDGE: DEVIONS AND THE BAND TAIL DENSITY OF STATES.

Substantial theoretical effort has been dedicated to explaining the seemingly simple experimental observation of an exponential absorbtion (Urbach[7]) edge in many disordered systems.[8] Some theories address particularly the optical absorbtion in crystals (electron-phonon interaction) where experiment shows a temperature dependant decay length ε_0= s kT (often T must be corrected for zero point motion) with s~1. Others, motivated by the exponential edges in other disordered materials have sought such behavior as characteristic of any disorder, and especially random. Of central importance for such theories is the Halperin-Lax[9] band tail behavior for random disorder which is not simple-exponential. Different ways of modifying this result have been suggested. Explanations in which optical matrix elements are the source of exponential tails have been considered. However, experimental association[10,11] of transport and the optical edge have reinforced explanations in which the DOS is responsible for the absorbtion edge in disordered systems, including as a special case phonons in crystals through the adiabatic approximation.

Our consideration of equilibrated structural degrees of freedom[12,13] leads simply to an exponential DOS when the energy of structural deviations (devions) is proportional to the displacement of the electronic state energy into the gap: $F(\varepsilon) = \alpha\varepsilon$ yields $D(\varepsilon)= D_0 e^{-\varepsilon/\varepsilon_0}$ where $\varepsilon_0 = T^*/\alpha$. The relationship $F(\varepsilon) = \alpha\varepsilon$ may be expected in disordered systems with α of order 1 as suggested by variing the definition ε=F[n]-F[n-1] (F[n] being the total energy with n electrons) with introduction of a structural change which displaces ε. The direct relationship of ε_0 to T* is simply the Urbach edge behavior with T*=T for crystals[7]. Moreover, it sugests experimental tests in eg. glasses.

We discuss briefly three special cases and predictions which arise out of this theory: 1) Low levels of excitation, 2) Ideal alloys, 3) Disorder addition.

1) Our discussion of the band tail DOS must be modified for low levels of excitation or equivalently for structures very close to the ideal ground state (this may not be attainable in some crystals because of zero point motion). For these conditions the special condition of quadratic expansion of system energy in atomic displacements (not generally possible for electronic energies), leads to $F(\varepsilon) \sim s\,\varepsilon^2$ or a Gausian tail. In this way we make contact with Toyozawa's two-mode model.[8] For high symetry ground states special considerations apply. This is in accord with experimental disapearance of the Urbach edge at low temeprature in some crystals, its absence in others, and combined Gausian and exponential tails for excitons.

2) The relationship of our theory to conventional theories, which should apply to random ensembles where preferential energy selection does not apply, can be seen by writing:

$$D(\varepsilon) = g(\varepsilon)\, e^{-F(\varepsilon)/kT^*} \qquad (2)$$

Where $g(\varepsilon)$ is known as the complexion number corresponding to the statistical weight of a random ("infinite temperature") ensemble. In general, a free energy appears in the Boltzman factor but is redefined. $g(\varepsilon)$ is the subject of conventional theories. For an ideal alloy where energy differences are small compared to T* the Boltzmann factor is unity and $g(\varepsilon)$ describes the DOS. Thus we suggest that Halperin-Lax behavior[9] may be observed in specially constructed ideal alloys at low temperatures (to remove phonon contributions). Note that in this case band tail decay must be more rapid than kT*/α. In contrast, in amorphous semiconductors or glasses random disorder would eliminate the gap implying that $g(\varepsilon)\sim 1$.

3) The addition of different kinds of disorder does not in itself increase the band tail width in our theory, in contrast to conventional theories. This is because the essential quantity is the lowest typical energy cost for the largest change in electronic state energy. Addition of similar disorder arising from eg. phonons and structural atomic displacements leads to addition of decay parameters in agreement with experimental results.[14]

V. DEFECTS: TOTAL CONCENTRATIONS AND CONTRIBUTIONS TO THE DENSITY OF STATES.

The conventional approach suggests that defects within disordered systems can be understood by simply broadening into Gausian shaped bands the discrete spectrum of electronic states which are introduced by defects in crystals. This picture becomes much richer when the electron-electron interaction leads to a separation of singly and doubly occupied levels. Possible strong coupling of structural and electronic energies enables both positive and negative values of the electron-electron effective correlation energy.[15]

The possibility of impurity doping covalently bonded amorphous semiconductors was originally rejected[1] based on an idealized model of perfect bonding (which we use as the ground state). Experimental observation[16] of doping has led to explanations based on defect reactions,[17] structural constraints[18] or impurity/defect reactions during deposition[19] similar to thermodynamic processes.

In our theory, the DOS introduced into a disordered system by a defect has some additional interesting features because of the direct relationship between the energy of charged defects and the position of transition energies with respect to the Fermi energy. This relationship changes the proper interpretation of macroscopic material properties in terms of microscopic defect properties. In particular, it has the effect of displacing peaks in the DOS associated to different charge states from those expected in the conventional model. Consider a system in equilibrium containing a defect which can exist in more than one charge state. In this case the interchangeability of different charge states is part of dynamic equilibrium and we can separate the DOS introduced by defects with each charge state q:

$$D(\varepsilon) = \Sigma_{D,q}\, D(D,q,\varepsilon) = \Sigma_{D,q,p} \int d(\varepsilon(p/p-1))\, N\, e^{-F(D,q,\{\varepsilon\})/kT^*}\, \delta(\varepsilon(p/p-1)-\varepsilon). \qquad (3)$$

$F(D,q,\{\varepsilon(p/p-1)\})$ is the formation energy of a defect D with charge q having charge state transitions from charge p to p–1 at energies $\{\varepsilon(p/p-1)\}$. We then use the relationship (definition of $\varepsilon(q/q-1)$):

$$F(D,q\text{-}1,\{\varepsilon\}) = F(D,q,\{\varepsilon\}) + \varepsilon(q/q-1) - \mu \qquad (4)$$

to relate the contributions of different charge states.

We illustrate by a simple example of a defect which can assume two charge states (+,0) and thus has a transition energy $\varepsilon(+/0)$. Equation (4) becomes: $F(D,+) = F(D,0) - \varepsilon(+/0) + \mu$. The DOS introduced by neutral defects is given by $D(0,\varepsilon)$ then our theory gives the contribution of positive defects in equilibrium as

$$D(+,\varepsilon) = D(0,\varepsilon)\, e^{(\varepsilon-\mu)/kT^*} . \qquad (5)$$

When $D(0,\varepsilon)$ can be approximated as a Gaussian peak $D(0,\varepsilon)=e^{-(\varepsilon-\varepsilon_1)^2/bkT^*}$ then $D(+,\varepsilon)$ is a Gaussian shifted by $b/2$ and multiplied by $e^{((\varepsilon_1-\mu)+b/4)/kT^*}$. For $\mu = \varepsilon_1$ and for a choice of b,T* we obtain the DOS of Fig 2. If we now allow the defect to be negative with an effective correlation energy of zero then the contribution of negative defects in equilibrium yields an additional (for this choice of μ) symetric peak shown in Fig 3. Shifting μ has dramatic effects as shown in Fig 4. If we now consider the effects of a non-zero correlation energy U (constant as a function of other defect properties) the effect on the density of states associated with the neutral defect is exactly the usual effect causing a separation between single particle transitions $\varepsilon(+/0)$, $\varepsilon(0/-)$. The effect on states introduced by charged defects is two-fold. First, the separation between single particle transitions reproduces the usual changes. Second, the whole DOS is rescaled by the factor $e^{-U/2kT^*}$. Positive correlation energies tend to supress the states introduced by charged defects and return the conventional picture for $U>kT^*,b$.

We also note that similar to the case of excitons[7] or band tails the tails of defect DOS should also be simple exponential. Thus an experimental measurement of exponential DOS may be either that of a band tail or of defect states.

The total concentration of defects, which may obtained by integrating the above $D(\varepsilon)$, is given by a Boltzmann factor of their formation energies. Recently, evidence has accumulated that defects in glasses and amorphous solids equilibrate in solid state.[20-24] Viewed from the perspective of defects in crystals this is a minor observation that defect equilibration processes can occur in the solid state of amorphous materials or glasses. Viewed from the perspective of a model in which the structure of disordered systems is prespecified this is a dramatic result.

The Fermi energy adjusts for neutrality from all elementary excitations. This leads directly to a theory of doping which arises as a statistical shift balancing the numbers of positive and negative low energy charged excitations. Impurity doping occurs because impurities can introduce low energy charged defects. This theory encompasses also the doping of crystals, the difference in observed behavior between crystals and the most commonly doped amorphous material, *a*–Si:H, can be understood in two steps. First, by considering statistics of the elementary excitations and, second, by considering the nature of the lowest lying native charged elementary excitation - carrier or defect.

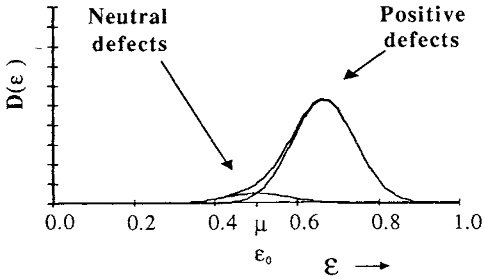

Fig. 2: Electronic Density of States introduced by a defect into a disordered system having two possible charge states (+,0). In equilibrium the two defect charge states contribute independently to the DOS. Represented for particular choices of width b and T*.

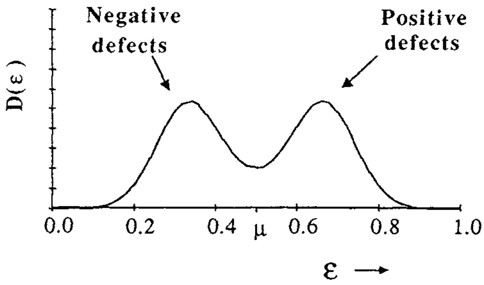

Fig. 3: As Fig. 2 for a defect with three charge states (+,0,-). We show only the total DOS.

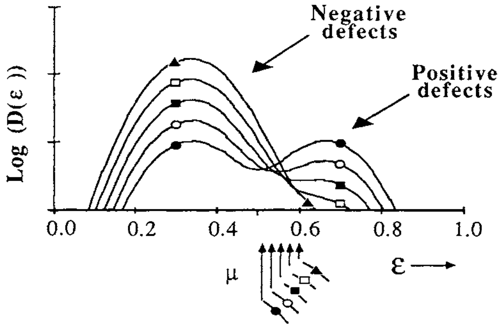

Fig. 4: As Fig. 3 showing the effect of shifting the Fermi energy. Note change of scale.

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1) Defect Statistics: Defects, like carriers, obey Fermi statistics - the number of defects can not exceed the number of sites at which such a defect can be created. Charged states associated with impurities may have two extreem behaviors if for all positions of the Fermi level relevant for structural equilibration: a) the charged state is the lowest in energy or b) the fraction of charged states is low and may be described by Boltzmann statistics. Case a) is the usual model of crystal doping with doping efficiency of unity, case b) results in an exponentially supressed doping efficiency and appears to adequetly describe single impurity doping in *a*–Si:H. More generally the Fermi-Dirac probability for the presence of charged defects must be used for doping efficiencies ranging from unity to exponentially supressed.

2) Carrier or defect lowest lying native elementary excitation: Doping results in the introduction of native elementary excitations of opposite charge to that of the dopant species. Traditionaly in crystals carriers are predominatly introduced, in *a*–Si:H charged defects are primarily introduced.

In contrast to theories which rely upon particular defect reactions to describe doping in *a*–Si:H, our theory suggests the possibility[25] of doping in amorphous materials as an equilibrium between dopant states and free carriers or even with doping efficiencies approching unity. The doping of crystalline semiconductors may also fall into categories or intermediate behaviors different from traditional crystal doping behavior. The measurement of doping properties provides valuble information for determining defect formation energies once T* is known.

VII. APPLICATION TO A-SI:H.

We address here three central questions regarding *a*–Si:H and describe the perspective which can be gained from our approach to disorder: 1) the nature of microstructure, 2) the role of hydrogen, 3) the controversies regarding defect properties and doping.

Microstructure of a–Si:H: In addition to yielding many general results about the electronic properties without knowledge of microstructure, our theory also suggests a new approach to understanding microstructure. As described above we discuss the nature of structure in terms of a ground state and elementary excitations. The natural ground state is a network with first neighbor bond lengths and angles, which effectively describe the energy of covalent systems, at their minimum energy values. As stated by Phillips[18] this is an overconstrained system in three (flat) dimensions. Our theory suggests that elementary excitations which are thermally generated enables a particular set of such networks to exist in flat space. Thus we allow our ground states to exist in locally distorted three dimensional manifolds. Specific curved space descriptions[26] are a possible special case. The nature of low-lying elementary excitations in *a*–Si:H should then determine which description: the general continuous random network, a specific curved space model, or the submicrocrystallite model[2b,18] provide useful descriptions of the ground state. Our theory does not a-priori favor either one. It does, however, require a continuum of elementary excitations to explain the observed band tails. Since grain boundaries in the submicrocrystallite model may or may not provide such a continuum, it would be interesting to see whether material in which evidence for submicrocrystalites exist display similar band tails.

Also of particular importance are the variety of experiments showing that properties of a–Si:H change in films greater than one micron. This suggests an unusually long (correlation) length scale for sensitivity to boundary conditions. This may imply a range of microstructures are available.

Role of hydrogen in a–Si:H : Hydrogen acts to reduce defect densities and band tail widths. This is generally expressed as defect passification and weak bond breaking corresponding to a model of specified microstructure. The simplest analogy to this picture in our theory is that the effect of hydrogen would be to reduce the formation energies of defects and band tail states in the ensemble. This is one possible interpretation within our theory, though the formation energy of band tail states (αε above) is likely to be relatively insensetive to impurities. In our theory, a second possibility is that hydrogen indirectly affects the concentrations of both defects and band tails by reducing the ensemble temperature through enhancing equilibration processes. This may be effected by either a reduction in the barrier height or increase in the prefactor of phase space exploration steps. Combinations of different effects are possible and other impurities are likely to yield different effects. For example, the observation[27] that fluorine does not affect band tails as suggests that it may directly affect formation energies of defects.

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Defects in a–Si:H: Defects control much of the optical and transport properties of *a*–Si:H. Nevertheless, such a basic property as the sign of the effective correlation energy has been the subject of substantial controversy. The experimental evidence from different techniques can be understood to support either a positive or a negative correlation energy.[28,29] Stated differently, pictures developed using a standard positive or negative correlation energy do not appear to describe adequetly all experimental information. Specifically, the spin signal measured (associated with gap states) requires the presence of a positive microscopic correlation energy. However, the position of the Fermi energy in undoped material, which should lie between positive and negative defect states, is found to lie above the majority of negative states (in doped material), implying a negative correlation energy. This problem may be resolved in several ways, for example, by the presence[2a] of two defects of roughly equal concentration. Alternatively, our theory provides a resolution which can be understood from Figs. 3 and 4. Here we see that energetics promotes negative states below the Fermi energy independent of the effective correlation energy. Thus with a small positive correlation energy, we can explain the experimental behavior of defects in *a*-Si:H.

VII. DEVICE APPLICATIONS - AN EXAMPLE: STABILITY AND THE STAEBLER-WRONSKI EFFECT.

The use of amorphous semiconductors in device applications has been inhibited by the degradation of such devices in the presence of exitations necessary for their operation.[30,31] This deterioration is identified with defect formation and is known as the Staebler-Wronski effect.[31] Such effects may be due to structural changes which either transform defects or create them. In some systems, however, defects form only in pairs. Guided by our theory of disordered systems we have develped[32] a model for the formation and anealing of metastable defects in these systems and proposed two approaches to elimination of material degradation. In this model defects can form essentially anywhere and defect motion is integral to formation, saturation, and annealing. Formation of defects occurs in two steps: a) creation of intimate defect pairs from electron-hole pairs, b) separation by thermally activated migration steps. Recombination, saturation or annealing of defects occurs through: a) the defect analogue of traps - low energy defect sites, with monomolecular kinetics, or b) bimolecular processes. Thus, the behavior of defects and carriers in these systems are analogous in many ways. In Fig. 5 we show relevant reactions in this model. We note that the propagation (migration) of defects *during* illumination is affected (generally speeded) by the excited carriers. This may be understood in part by a lowering in migration barrier for charged saddle points due to separation of quasi Fermi energies (an effective lowering of the pixing temperature T^x). Using this model we can explain a large variety of experimental results on *a*-Si:H including: 1) low temperature defect formation[33,34] as intimate pairs, 2) high temperature saturation with a lower activation energy than that relevant for annealing,[35] 3) monomolecular and bimolecular annealing kinetics,[35,36] 4) defect formation by hole injection[37] by emission of defects from "traps" and rapid separation due to the p-type Fermi energy shift.

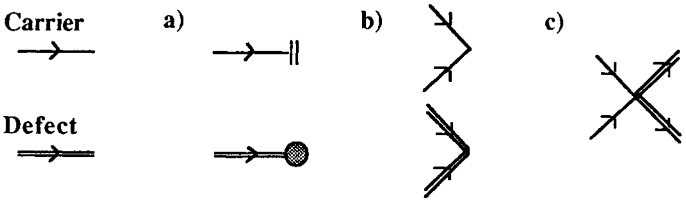

Fig. 5: Illustration of defect and carrier reactions important in modeling formation and annealing of defects in the Staebler-Wronski effect. a) trapping, b) bi-molecular recombination, c) electron and hole decay to defects. We do not indicate the charge assuming that charge conservation is imposed at vertices. Time moves from left to right (arrows) in the central reactions for the Staebler-Wronsky effect. Reverse reactions also occur. The defect propagators are diffusive and must also be "dressed" by carriers excited by illumination.