

CHAPTER IX

MOLECULAR DYNAMICS SIMULATIONS OF NETWORK GLASSES

David A. Drabold

Department of Physics and Astronomy, Ohio University, Athens, Ohio 45701-2979 USA

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1 Introduction and Background

1.1 History and use of MD

The idea of *molecular dynamics* (MD) is a very old and fundamental notion of condensed matter physics. The essential idea is very simple: if we know the interaction potential between atoms and some initial conditions, then for a classical system we can use $\mathbf{F} = m\mathbf{a}$ to obtain the full time development of the atomic coordinates by numerically integrating the equations of motion. Even simple considerations of these ideas without using much detail leads to kinetic theory. Naturally, classical statistical mechanics, a cornerstone of science, originates substantially in the statistical consequences of the equations of motions and their integrals. In fact, a goal for workers on the foundations of statistical mechanics is to derive the laws of statistical mechanics from nothing more than the equations of motion: an example is Liouville's theorem.

For a classical system, the intuitive appeal of an MD simulation is the feeling that a complex experiment can be implemented on a computer. In principle, such a calculation proceeds without information loss: the coordinates and velocities of each atom are specified at any instant of time, and with this information comparison to any experiment imaginable should be possible. We will repeatedly stress in this paper just how far an MD simulation is from this ideal because of shortcomings of interatomic potentials, and length/time scales many orders of magnitude removed from experiment; nevertheless, my essential conclusion that MD is a very powerful tool in the theorist's arsenal for studies of disordered systems. This paper will describe when such calculations are appropriate, and otherwise.

Perhaps the first many-particle classical MD simulation was carried out by an astronomer, Erik Holmberg in 1941¹, who was concerned with energy transfer between colliding galaxies. His idea was to exploit the identical radial ($1/r^2$) dependence of the light intensity and the gravitational force, to enable simulations based upon an "optical analog" of the gravitational interaction. Holmberg constructed a remarkably ingenious apparatus in which two groups of 37 lamps each (each lamp representing a star, each group representing a galaxy) interacted optically, and the light intensity at each lamp ("star") was measured with photocells. Since the intensity was proportional to the interstellar forces, the time evolution of a galactic collision could then be simulated, and Holmberg was able to see spiral arms and learn something about capture probability. While there have been many MD simulations since, I wonder if any have been as clever as this one²!

Only with the advent of computers since the second World War has it become possible to directly integrate the equations of motion for systems with large numbers of particles. Probably the best known early work is that of Alder and Wainwright³ for hard spheres, and the simulations with the comparatively realistic Lennard-Jones potential due to Rahman⁴ a few years later. The field has steadily grown in activity and importance since these pioneering studies and is now almost a third paradigm of physics, intermediate between experiment and "conventional" theory, heavily relying on and contributing to both.

The synergism between MD simulations and experiment merits a little more reflection. For amorphous and glassy systems MD is absolutely essential since it is a means to a *structural model* (more bluntly – “where the atoms are”) which can never be completely inferred from experiments. The experiments nevertheless let us know whether the model is sensible: for example, an experimental static structure factor can be viewed as a “sum rule” any theoretical model must be in agreement with if it is to be seriously considered. The logic is therefore that *if* MD provides a model acceptably consistent with *all* the experiments we believe, *then* the model becomes worthy of additional study to investigate new phenomena of the glassy state, and make predictions beyond what is experimentally known or otherwise theoretically understood. It is in this mode of use that MD has come to revolutionize the study of disordered systems.

1.2 The role of the Potential

In the field of network glasses, the MD method has actually evolved in three related, but rather philosophically different ways, each with its own range of validity. The complexity of the interatomic potential defines the boundary between the approaches.

1) Use of MD with very simple potentials, which are not “realistic” for any physical system, but which include the “generic character” of a reasonable interaction (a repulsive core and some kind of weak attractive tail, possibly long range – eg power law decay). Prodigious numbers of atoms and relatively long simulations are possible for such potentials, and one can seek to grasp some characteristics of non equilibrium processes like glass formation.

2) Empirical interatomic potentials constructed to model a given material. Here, one uses more or less ingenious functional forms built to mimic the configurational (potential) energy of a given type of glass. “Empirical” means that the scheme requires input from an external source: experiment or better theory. The venerable, but still useful Stillinger-Weber⁵ potential for Si is the classic of this approach, and consists of the sum of a pair and three-body term; the later unapologetically built to favor tetrahedral bonding. More recent empirical models can mimic many particle correlations in more subtle and reliable ways^{7,8}. The fanciest empirical models are based on empirical electronic structure (tight-binding) Hamiltonians.

3) “*Ab initio*” calculations of the interatomic interactions. Here, one starts from a more basic view that the complexity of the interatomic potential originates in the details of the electronic structure of the material. In this approach, one tries to accurately approximate the electronic eigenstates of the model without appeal to external information. As the reader will recall, the quantum many-body problem presents a formidable challenge, even with serious approximations. Acceptably accurate schemes do exist however, and have the key feature that they *do not depend upon fits to external information (eg. experiments)*: this is essential for studies of new materials very different than those for which adequate empirical potentials have been formulated, as for example amorphous GaN⁹. A serious *shortcoming* of the *ab initio* approach is that it is much slower than its competitors (1)

and (2), and therefore must be used sensibly often in conjunction with (2) above to make optimal progress. Also, there are many “theoretical knobs” (approximations) in any *ab initio* simulation, and it takes experience to know what approximations are acceptable and which are not (this depends critically on the questions being addressed). Certainly, improperly conceived *ab initio* simulations can do worse than a proper empirical potential calculation.

1.3 Scope of the Method

Thanks to a happy coincidence of continuing algorithmic breakthroughs and ever faster/cheaper computers, the frontier for MD is ever receding, and more and more systems are proving to be susceptible to MD modeling. There have been important and very different breakthroughs in both *ab initio*¹⁰ and empirical methods¹¹ enabling computational cost to scale linearly with the number of atoms in the system. At the same time, accuracy continues to improve on both fronts. So while there are severe limits on what MD can accomplish, rapid progress is being made on most of the outstanding problems.

The MD methods are often used directly to simulate a glass (by simulated quenching from an equilibrated liquid). It is sometimes asserted that a MD approach to obtaining a topologically disordered model is intrinsically superior to other methods which are entirely based on the principle of “the end justifies the means”, since the MD method provides an explicit trajectory. In fact, this argument by itself is not at all convincing, since the time scales (and sometimes the potential itself) in the MD simulation is qualitatively different from Nature. For a system like a-Si, a simulated quench from an equilibrated liquid always freezes in an unphysical concentration of electronically active defects, because the extreme quench rates of MD freeze in an unrealistic concentration of strained and over-coordinated conformations: remnants of the metallic-coordinated liquid Si phase (exceedingly different from the essentially tetrahedral character of the amorphous matrix). Thus, a key feature determining the realism of an MD quench model of a glass is the similarity (or lack thereof) between the liquid phase and the glass. It is undoubtedly the case that this is important in Nature too: good glass formers (from the melt) like SiO₂ and GeSe₂ are known to have liquid topology much like the glass¹²; whereas it is hard or impossible to make a-Si with a sensible defect density by a quench from liquid Si. Thus, while Angell’s emphasis on the importance of the crystalline phases to glass formation¹³ is well founded, one cannot neglect the topology of the liquid (relative to the glass and crystal) either.

1.3.1 Use of *a priori* information

Conventional “cook and quench” MD may be used to model complex systems, provided that one uses *a priori* information. For example, to properly model a glass which is known to exhibit strong chemical ordering (for example, GeSe₂¹²), it is foolish to start with an initial configuration which is remote from this order. In other words, we cannot expect an MD procedure with its picosecond time scales to fully sort out the detailed chemical ordering given only the right number of each atomic species in the right volume at the first

time step. Not only would substantial diffusion be required, but also “diffusion to the right place” – eg. to where an atom which would yield proper chemical order resides. Thus, for our work with GeSe_2 ^{14,15,12}, we started with a periodic lattice with the chemical order built in (Ge surrounded by Se, Se by Ge); this structure then was “melted” so that the original lattice structure was forgotten *but* the chemical ordering initially in place by fiat was largely maintained (presumably because there is an energetic reward for heteropolar bonding). The net result was a model in pleasing agreement with most of the experimentally available information, and some new observations based upon the models.

1.3.2 Appraising a Model

Obviously a critical element of MD simulations of complex materials involves criteria for whether a model is acceptable or otherwise. The mission, of course, is to “match” as many experiments as possible at the same time. It is cause for great concern if a model matches some experiments and not others which we have equal confidence in. Thus, global quantities like the radial distribution function (or static structure factor), the (total) electronic density of states or the (total) vibrational power spectrum offer global information averaged over of order 10^{22} atoms. Such spectra must be faithfully reproduced by a model. The electronic and vibrational states will typically exhibit “gaps”, such that there are few or no states in the “gap” energy range. To the extent that such states do exist, they originate in some type of defective structure in the network, sufficiently different (chemically and/or topologically) to be pushed out of the bands into the gap. Agreement or discrepancy between gap features will usually imply *spatially local* information involving a modest number of atoms. Such isolated states (electron or vibrational) are usually localized (in the technical sense of Anderson localization¹⁶). Properly reproducing this local information is important for example, if one is interested in transport, and the defects are electron states near the Fermi level. Then the concentration, and position of the states will determine the entire transport process. To be specific, the literature is replete with models of a-Si with ridiculous concentrations of defects (10% or even more), with satisfactory radial distribution functions. Such a model is quite unacceptable, since the concentration of defect states in the gap is about 1 in 10^{3-4} .

2 MD Method

There is a considerable technical lore available for “classical” (based upon assumed interaction potentials) MD simulations. There are several books and review articles written on the “nuts and bolts”. Here, I will survey the kinds of calculations that are available and point the interested reader to the appropriate literature for derivations and details. There is an unfortunate tendency, especially displayed by workers using *ab initio* methods, to neglect the vast amount of excellent work performed with empirical potentials, and many important generic findings about how best to implement simulations, how to deal with artifacts of simulations etc. My favorite source of information on these questions is the delightful book by Allen and Tildesley¹⁷. See also the recent work of Frenkel and Smit¹⁸.

2.1 Equations of Motion

As the name suggests, MD implies *time evolution*: the time evolution of Newton's equation $\mathbf{F} = m\mathbf{a}$; a coupled system of nonlinear ordinary differential equations (in general depending on $3N$ coordinates and requiring $3N$ velocities as initial conditions.) The forces $\mathbf{F}_i = -\nabla_i\Phi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ where Φ is a potential energy function (not necessarily expressed in any closed form, as from an *ab initio* calculation of the total energy Φ). There are many methods available for integrating the equations of motion, ranging from the simple first order Taylor method, which is nothing more than using $\delta\mathbf{R}_i = \mathbf{V}_i\delta t$, and $\delta\mathbf{V}_i = \mathbf{a}_i\delta t = \mathbf{F}_i\delta t/m$, and δt is a small time interval, the "time step", typically of order 1fs (1fs= 10^{-15} sec). Low order methods like this are sometimes used, especially for cases where potential energies and forces are obtained from lookup tables or are otherwise not very smooth. *If* the force is a very smoothly changing function of interatomic coordinates, then it pays to use a *higher order method*, which extrapolates \mathbf{R} and \mathbf{V} to higher order in δt ; this enables a longer time step, while still faithfully tracking the equations of motion. Allen and Tildesley¹⁷ discuss a predictor-corrector method, which should be ideal for most applications. Some authors¹⁹ particularly encourage the use of the Bulirsch-Storer method for the smooth case.

A simple but dependable means of gauging the reliability of a particular quadrature scheme is to check numerically the value of conserved quantities (like the total energy) in a microcanonical thermal simulation. If a time step is selected to be too long to properly track the equations of motion, the energy will not be constant.

2.2 Energy Minimization and Equilibration

To find a set of coordinates which minimize the total energy (eg, such that the forces vanish), one can employ one of many strategies. For cases where *any* nearby energy minimum conformation is sufficient, a steepest descent quench may be sufficient. In this approach, atomic positions are iteratively changed to push the coordinates to the closest accessible energy minimum in configuration space, by changing coordinates \mathbf{R}_i to iteratively follow the local downhill gradient, $\mathbf{F}_i = -\nabla_i\Phi$, until a set of coordinates \mathbf{R}_i is obtained such that all $\mathbf{F}_i = 0$. A better method¹⁹ for getting to a minimum more rapidly is the "conjugate gradient" scheme, which determines an optimal sequence of directions in which to displace the atoms to get to the minimum efficiently. The conjugate gradient method has the advantage that it requires the storage only of a few vectors of length $3N$, for N the number of atoms. A result of considerable *theoretical* interest is that the conjugate gradient scheme is guaranteed to find the exact minimum of a *quadratic form* potential in N dimensions in N steps. There is no such guarantee for a general potential, of course. An alternate group of "Newton" methods can in principle be applied for energy minimizations, but the storage requirements are more stringent (the Hessian matrix, which involves $O(N^2)$ elements must be saved), and in general the method is no more efficient than conjugate gradient anyway.

While the question of energy minimization is distinct from that of thermal MD, the two are closely related. In fact, the usual "MD" approach to forming a model of a glass

(equilibrating a liquid and rapidly quenching it to $T=0$) is usually accomplished by a velocity rescaling scheme. The simplest approach is due to Berendsen and coworkers^{20,17}. Suppose that one wishes to drive a system to some predetermined temperature T . Then one can simply rescale all the velocities according to the rule:

$$\chi = \sqrt{1 + \delta t(T/T_i - 1)/t_r} \quad (1)$$

where, T_i is the current instantaneous temperature, δt is the time step, and t_r is a relaxation time, which determines how rapidly the system is to be driven to the target temperature T . While the method is very simple, it works quite well for equilibrating a system to some desired temperature, or for quenching a liquid into a disordered solid. In general one cannot make t_r too long; for quenches from a liquid to a glass, I have found that $t_r \approx 500fs$ is both computationally tolerable and can produce good results for g-GeSe₂. It is obviously desirable to probe the effect of the cooling rate on the final structure obtained.

2.3 Deeper or Global Minima

It is in general a famous outstanding problem of computational physics to reliably determine a *global*, or at least deeper *local* minimum of the potential energy function. For our interests here, we can contrast the physical glass formation process which occurs sufficiently slowly in Nature to enable much annealing, and therefore a rather “deep” (but local!) minimum in the potential energy to a “shallow” minimum that comes from an extremely rapid simulated quench.

2.3.1 Simulated Annealing

A method somewhat similar in spirit to the velocity rescaling scheme above is the simulated annealing method of Kirkpatrick *et al*²¹. Rather than using (velocity rescaled) MD to determine the atomic trajectories, a set of rules (the exact choice of which is investigator and problem dependent) is invoked according to which atoms can explore a larger volume of configuration space before finally getting trapped in some (probably local) minimum. A typical process is to accept new coordinates according to a Metropolis²² (Monte Carlo) rule: 1) if a change lowers the total energy keep that change, 2) if the change increases the total energy, keep that change with probability $\propto \exp(-\Delta E/k_B T_A)$, where ΔE is the (positive) energy difference between the original coordinates and the “trial” coordinates, k_B is Boltzmann’s constant and T_A is the “annealing temperature”. T_A is analogous to a true annealing temperature in the sense that the higher one chooses T_A , the more freedom the system has to explore the configuration space.

2.3.2 Genetic Algorithms

In a related vein, so called *genetic algorithms* have recently been applied to complex optimization problems in physics including simple problems involving disorder²³. Ho²⁴ has

recently applied the method to essentially random (in an appropriate volume) collections of 60 carbon atoms and found that the method can consistently find the icosahedral fullerene (“bucky ball”) structure as the deepest minimum when used with a tight-binding Hamiltonian and some rules about how the “evolution” proceeds. While this result is very impressive, its relevance to glasses is not yet clear both because even for 60 atoms in free space huge amounts of computer time are needed, and also the determination of “rules” is substantially an art form.

2.3.3 Activation-Relaxation technique

Away from the melting temperature, many materials explore a sequence of metastable states separated by energy barriers much larger than $k_B T$, the typical excitation energy scale at the atomic level. For long periods of time, the configuration vibrates around a given metastable state, then, due to rare energy fluctuations, it will find enough energy to jump over a barrier and move to a new metastable state. The dynamics of these materials is therefore dominated by the rates controlling the jumps from one metastable state to another.

It is possible to do better by directly focusing on the rare events. To a first approximation, these are fully determined by the activation energy, i.e. the energy needed to bring a configuration from a local configurational minimum to a nearby saddle point. A low temperature characterization of the dynamical properties of a disorder system can therefore be made by reducing the configuration energy landscape to a network of local minima connected by paths going through first order saddle points. Recently, Barkema and Mousseau have proposed such a procedure, the activation-relaxation technique (ART), which provides a local prescription for moving from one minimum to another one with a trajectory passing by a shared saddle-point (event)²⁵.

The advantage of ART is that it defines moves directly in the configurational energy landscape, which really controls the dynamics, instead of trying to map events into complicated real-space moves. ART is independent of the details of the interaction potential and the specificity of a given material and requires only a local and continuous description of the energy landscape.

An event in ART is defined as a move from a local energy minimum $\mathbf{M}^{(0)} \equiv (\mathbf{x}_1^{(0)}, \dots, \mathbf{x}_N^{(0)})$ to another nearby minimum $\mathbf{M}^{(1)} \equiv (\mathbf{x}_1^{(1)}, \dots, \mathbf{x}_N^{(1)})$ following a two-step process mimicking a physical activated processes:

- i) the **activation** during which a configuration is pushed from a local minimum to a nearby saddle-point;
- ii) the **relaxation** which brings the configuration from this saddle-point to a new local minimum.

The details of how the saddle point is reached, and other technical points concerning the implementation may be found in the literature²⁵.

ART has already been applied with success to a series of static problems in metallic glasses, a -Si²⁵ and a -GaAs^{27,28}. A slightly different version of the algorithm was also developed independently by Doye and Wales and applied to map the full energy landscape of a 13-atom Lennard-Jones cluster²⁹.

Because it necessitates only the calculation of the force, ART is fully scalable with the size of the systems studied. In general, about a 1000 force evaluations per event are necessary. This means that ART will be useful for activated processes with barriers significantly larger than the temperature of the material studied. In this case, though, it provides a unique tool for the description of rare events such as diffusion and relaxation mechanisms in disordered materials.

2.4 *Alternate Dynamics*

Allen and Tildesly¹⁷ discuss methods to perform Lagrangian constrained dynamics (or relaxations) of systems such that a particular symmetry is enforced through the simulation.

The simplest approach to MD simulation is to work in the microcanonical (constant NVE) ensemble. Other, perhaps more realistic ensembles are the canonical (NVT), isothermal/isobaric (NPT) and even the grand canonical (μ VT). Allen and Tildesly¹⁷ also give a complete discussion of these alternate ensembles. The most sophisticated approach to a canonical simulation³⁰ is to introduce a new degree of freedom to represent the “heat bath” and allow heat flow between the physical degrees of freedom (eg the atomic coordinates and velocities) and the fictitious heat bath. A “Nose’ thermostat” faithfully produces a trajectory which samples from the canonical distribution function.

Virtually all *ab initio* MD simulations are carried out at constant volume (or some crude “adiabatic” volume shift from liquid volume to glass volume in the course of a simulated quench to form a glass). The state of the art for isobaric simulation is the work of Parrinello and Rahman, who also enable a changing box shape³¹. An exception to this rule is the work of Wentzkovitch and coworkers³².

Vashishta³³ has fully implemented these more physical ensembles in simulations of glasses, and simulations of phase changes such as amorphization and densification, with impressive results which fully exploit the possibility of performing *very* large scale MD simulations with empirical potentials. This is a reminder that the most accurate method (an *ab initio* method) is not necessarily the right choice, in this case, if the choice of ensemble is important to the final structure obtained.

2.5 *Modeling Infinite Systems: Periodic boundary conditions*

To model a bulk topologically disordered system, it is usually not a reasonable approach to simply study a cluster, terminated by vacuum. For example, if one was studying a tetrahedral semiconductor like a -Si, this would produce *many* electronic states in the optical gap due to the dangling bonds at the surface. Since some of these states would be occupied

in general, this would change the energetics, forces and topology of the system especially near the surface: an unphysical boundary. One way out is to passivate the dangling bonds with hydrogen, although this is not so easy in practice as it sounds for surface structures which are not near ideal dangling bonds. Of course if one is interested in the surface of an amorphous material, the truncation to vacuum is physical (we describe a calculation on an amorphous C surface later in this article).

The usual choice to avoid truncation effects is to apply Born-von Karman (periodic) boundary conditions. All such models are then technically crystals, albeit with a large unit cell. An essential part of the analysis of any MD simulation is determining how the periodic boundary conditions manifest themselves in predictions of physical quantities. Vashishta³⁴ has studied this point, and there is plenty of discussion of size and boundary condition artifacts in the classical MD literature. We¹⁴ have observed in a 63 atom model of g-GeSe₂ that the static structure factor is modulated by an unphysical “ringing” presumably connected with the relatively small box size used. When the calculation was repeated in a 216 atom cell (at the same density), the ringing virtually disappeared¹⁵. The “first sharp diffraction peak” (near $k = 1\text{\AA}^{-1}$) also agreed much more closely with experiment for the larger cell. Clearly, low \mathbf{k} features are most affected by small box sizes. In a similar way, periodic boundary conditions enable meaningful studies of spatial correlations only up to half the box size.

More subtle problems also arise with periodic boundary conditions for calculations based on an electronic structure calculation (either tight-binding or *ab initio*); to compute the electronic contribution to the total energy and forces one needs to approximately integrate over the first Brillouin zone and sum over the occupied energy bands. It is usual to neglect this and pretend that there is no \mathbf{k} dispersion in the energy bands and evaluate the energy bands only at $\mathbf{k} = 0$. The validity of this approximation, *particularly for forces* needs to be checked in small (roughly speaking less than 100 atom) cells. We have discussed this in more detail elsewhere³⁵. Related issues arise in calculations of the vibrational states; we discuss this later.

3 The interatomic Interactions

3.1 Overview

It is obvious that any attempt to perform MD simulations requires an interatomic potential in some form. In this article I will concentrate on potentials useful for realistic simulations of particular materials, rather than “generic” potentials for studies of the glass transition or other network order-disorder transitions.

For glasses the interatomic potential $\Phi(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N)$ arises from the chemical bonding (in the general case including important covalent and ionic contributions) between the various constituent atoms. The chemical bond is an intrinsically spatially non-local entity, the details of which depend critically on the local topology. This complexity makes simple

partitions of Φ into two-body, three-body and higher multi-body interactions only approximately valid. In effect, one is attempting to model the subtle physics of chemical bonding in a disordered environment with some relatively simple assumed form. Depending on the problem this can meet with varied degrees of success.

The most reliable approach to modeling Φ is to acknowledge the origin of the complexity (multi-atom forces originating in complicated electronic effects), and start with an attempt to model the electronic structure of the system. From this, one can proceed to compute interatomic forces. As I will describe below, there is a mature and highly successful approach to approximately solving the electronic structure problem: the local density functional method; now implemented in a variety of forms. Such accuracy comes at a high price: even with clever algorithms and fast computers, these computations are limited usually to a few hundred atoms and a few picoseconds (1ps=10⁻¹² sec) of time evolution, which is inadequate for many problems.

It is important to note that amorphous and glassy materials pose a formidable challenge to an assumed potential, because the disorder implies a wide range of bonding environments. For any empirical potential, including empirical tight-binding formulations, there is inevitably a “memory” of the database used to fit the potential in the first place. This means that the assumed potential will typically be reliable for structures topologically similar to what was included in the fitting database, but increasingly unreliable for topologies that are “new” to the potential. In the interatomic potential lore, the ability of a potential to properly describe a broad range of local bonding environments is called *transferability*. One can expect that an assumed functional form which includes the underlying chemistry/physics of the interatomic potential will be more transferable than a generic ansatz which fits large numbers of free parameters with little or no *a priori* information about the electronic structure included.

In the following subsections, I will review some of the more popular approaches to modeling Φ .

3.2 Empirical Classical Potentials

A venerable potential which has been heavily used (and misused) as a tool to investigate disordered phases of Si is the Stillinger-Weber (SW) potential⁵, which consists of a two-body part, plus a three-body term given by:

$$\Phi_3(R_i, R_j, R_k) = Cf(R_{ij})f(R_{ik})[\cos(\theta_{ijk}) + 1/3]^2 \quad (2)$$

where θ_{ijk} is the angle at atom i subtended by atoms j and k. Here, $Cf(R_{ij})f(R_{ik})$ is positive definite, and quite obviously, the sensible underlying idea is to favor tetrahedral bonding (the triplet term vanishes for $\theta_{ijk} = 109.47^\circ$, the tetrahedral angle). In fact, there is such an overwhelming propensity for tetrahedral (sp³) bonding in *solid* phases of Si, that this very simple potential is a respectable “zeroth order” approximation to the interatomic interactions. It is worth pointing out that liquid Si is presumably poorly described by this

functional form (where the topology is highly non-tetrahedral); it is also apparent that non-tetrahedral network defects are poorly described. As an indication of how much care is needed when considering the appropriateness of a potential to a given problem, I have seen published studies of Si surface reconstructions and adatom adsorption energetics which use the SW potential, even though it gives the wrong surface reconstructions! Despite this warning, I emphasize that the SW potential has been a very valuable tool in the hands of researchers that understand what it can and cannot accomplish⁶.

Where empirical potentials are concerned, we have performed explicit comparisons between several proposed empirical potentials and an *ab initio* calculation for a-Si³⁵. This work illustrates the high degree of mutual inconsistency between the various potentials themselves and more sophisticated methods.

It is worth noting that some systems are much harder to model than others. For example, carbon is especially difficult since it can form almost degenerate tetrahedral sp^3 bonds (as for diamond), and trigonal sp^2 bonds (as for graphite). Thus, in this extreme case, it is very difficult for a carbon potential to properly differentiate different topologies which are possible in amorphous carbon. Silicon is easier, but still quite difficult to construct a *generally applicable* potential form. For either C or Si, it is not difficult to construct a potential which is accurate for a single topology, and small variations about that ideal. In some ways SiO_2 is easier to handle, since the basic unit of the glass (the crystals, or even the *liquid*³⁶) is the $Si(O_{1/2})_4$ tetrahedron, rather than *atoms*, which are all too “flexible” in their bonding attributes. The ionicity of silica forbids “wrong” (homopolar) bonds, which is another key constraint which can be built into a reliable SiO_2 potential; no such information is available for elemental Si or C. Vashishta³⁷ has proposed a successful silica potential which is very useful, particularly since *ab initio* plane wave calculations are almost non-competitive because of tremendous demands on computer power to properly represent oxygen bonding.

3.3 Potentials from Electronic Structure

A very sensible and relatively successful approach to modeling the interatomic potential is to take an electronic structure viewpoint, and then determine approximate potentials based on the foundation of some electronic structure scheme (for example, a tight-binding Hamiltonian), and then develop functional forms extracted from the approximate version of the electronic structure calculation. An excellent review on this type of approach is that of Anders Carlsson³⁸. I begin with a brief tutorial on the tight-binding total-energy method, with no approximations (beside the choice of tight-binding Hamiltonian).

3.3.1 The tight-binding method

In the “empirical tight-binding (ETB) approximation”, we imagine that the electronic eigenstates can be represented by a linear combination of atomic orbitals: $|\psi_i\rangle = \sum_{\mu} a_{\mu}^i |\mu\rangle$ where μ is a site-orbital index and i indexes the band or state. This method enables the calculation

of an approximate one-body Hamiltonian matrix, whose eigenvalues are taken to approximate the allowed electronic energies and the eigenvectors are the states. In the usual implementation of ETB calculations, the basis is taken to be orthonormal: $\langle\mu|\nu\rangle = \delta_{\mu\nu}$. Also, most ETB Hamiltonians include interactions only with near neighbors and include only two-center contributions. The sum of the occupied eigenvalues is the (attractive) electronic contribution to the total energy. To compute the system (ions + electrons) energy a repulsive interaction must be added to the electronic part. This is obtained from some fitting procedure. ETB is the simplest approach enabling an estimate of the many-body forces characteristic of covalently bonded materials. I outline here how an ETB calculation is implemented, since it is simple and is illustrative of many of the concepts of electronic structure calculations in amorphous solids.

(1) We begin by considering a supercell model (large unit cell with periodic boundary conditions) of an amorphous solid with N atoms and atomic coordinates $\{\mathbf{R}_i\}_{i=1}^N$ and three lattice vectors specifying the periodic boundary conditions. We can view the $\{\mathbf{R}_i\}_{i=1}^N$ as specifying a set of “basis vectors” for a crystal with a very large and topologically complex unit cell. Such a large unit cell possesses a band structure, as does any periodic system, but since the cell is supposed to represent an *amorphous* system, it must be large to have credibility. We will suppose that the \mathbf{k} dispersion is negligible because of the large cell size. In calculations *this point must be checked*. The significance of this is discussed further in Section 4.2.1. We limit our discussion here to the $\mathbf{k} = \mathbf{0}$ point of the Brillouin zone, valid for a large enough model.

(2) Next, we set up the Hamiltonian matrix $H_{\mu\nu} = \langle\mu|\hat{H}|\nu\rangle$ where \hat{H} is the Hamiltonian operator and $|\mu\rangle$ are a set of orbitals (typically s, p_x , p_y , and p_z for a column IV material) centered on each atom. As the matrix elements in this representation depend in detail on the network topology, it is convenient to work with “molecular coordinates” specifying the interatomic hopping. These are V_{ss} , $V_{sp-\sigma}$, $V_{pp-\sigma}$, $V_{pp-\pi}$, in the usual chemistry nomenclature for an sp^3 model. Explicit forms for the distance dependence of these interactions (see for example Harrison³⁹) plus simple rules⁴⁰ connecting the molecular and $|\mu\rangle$ representation enables the calculation of \hat{H} in the $|\mu\rangle$ representation. The H matrix eigenvalue problem then reads $H|\psi_i\rangle = \epsilon_i|\psi_i\rangle$, the usual orthogonal eigenvalue problem, where the electronic eigenvalues are supposed to be approximated by ϵ_i . The electronic or “band structure” energy is given by

$$E_{BS} = 2 \sum_{i \text{ occ}} \epsilon_i = 2 \sum_{i \text{ occ}} \langle\psi_i|\hat{H}|\psi_i\rangle \quad (3)$$

For electronic state density calculations or questions of the spectral signature of a defect, an exact diagonalization of H is sufficient. (3) The calculation of forces is easy when we possess the exact eigenvalues and eigenvectors; then the Hellmann-Feynman theorem can be employed in the form:

$$\mathbf{F}_\alpha^{BS} = -\partial E_{BS}/\partial \mathbf{R}_\alpha = -2\partial \sum_{i \text{ occ}} \langle\psi_i|H|\psi_i\rangle/\partial \mathbf{R}_\alpha = 2 \sum_{i \text{ occ}} \langle\psi_i|-\partial H/\partial \mathbf{R}_\alpha|\psi_i\rangle \quad (4)$$

Here, the sum on i is restricted to occupied states. Since total energies, forces, charge densities and other ground state properties depend upon the *occupied* eigenfunctions and

eigenvalues, it is natural at this point to introduce the single-particle density operator $\hat{\rho} = 2 \sum_{i \text{ occ}} |\psi_i\rangle\langle\psi_i|$, which is just the projector onto the occupied subspace at zero temperature. In a particular representation $|\mu\rangle$, this is just the usual density matrix:

$$\rho_{\mu\nu} = 2 \sum_{i \text{ occ}} \langle\mu|\psi_i\rangle\langle\psi_i|\nu\rangle \quad (5)$$

giving the usual expression for the electronic energy, $E = \text{Tr}(\rho H)$, and the forces are:

$$\mathbf{F}_\alpha = - \sum_{\mu\nu} \rho_{\mu\nu} \partial H_{\nu\mu} / \partial \mathbf{R}_\alpha \quad (6)$$

Note that this form assumes that the overlap matrix remains exactly the unit matrix through any atomic motions, which is suggestive of why forces in particular are sensitive to the assumption of orthogonality. It is also important to remind the reader that Eq. (6) prescribes only the (purely attractive) electronic part of the force; *an additional empirical repulsive pair potential must be added to the electronic energy to specify a system energy*; the derivative of this term contributes likewise to the forces, and a dynamical simulation is a complicated balancing act between the electronic and repulsive terms. Atomic trajectories are obtained by integrating the (classical) equations of motion for the atoms using one of many schemes for performing numerical integrations as we discussed above.

A useful local quantity that it very easy to extract in a tight binding calculation is the local electron charge projected onto a site (or orbital). This quantity is not uniquely defined, but a suitable definition (the ‘‘Mulliken’’ charge⁴¹):

$$q_A = Z_A - \sum_{\mu \in A} \rho_{\mu\mu}, \quad (7)$$

where Z_A is the charge of the atomic nucleus A ; the sum is over basis functions centered on atom A .

As to the question of specific ETB Hamiltonians ‘‘on the market’’, there are several, and their transferability is variable. In particular, some are designed for producing good band structures⁴², but are at the same time quite inappropriate for total energies and forces. As with the empirical potential methods, these Hamiltonians are most reliable for conformations ‘‘near’’ what the Hamiltonian was fit to in the first place. The entire underlying idea of an orthogonal TB model is the notion that there exist some underlying set of generalized Wannier functions with the property that these are mutually orthonormal in real-space. This is a justified point of view, which, however is valid only for a particular topology – if a different structure is considered, another set of Wannier functions emerge, and the justification for an orthogonal basis fails (unless the Hamiltonian is refit to the new structure). To be fair, it is probable that the failure is not serious until significant distortions are introduced; such is sometimes the case in amorphous insulators. The most widely used ETB Hamiltonians for force calculations are those of Goodwin-Skinner-Pettifor⁴³ type. The original⁴³ was for Si; this was adapted by Xu *et al.*⁴⁴ to carbon systems. The difficulties with the orthogonal Hamiltonians seem to emerge most dramatically in *force* calculations

[a universal feature of simulations is that the forces are more sensitive to approximations than quantities like the energy]^{45,46}.

More consistently reliable results can be obtained from a variety of non-orthogonal Hamiltonians. Menon⁴⁷ has proposed an empirical, nonorthogonal TB Hamiltonian which has been applied widely to clusters and recently has been generalized to bulk systems. Also in this category is a Hamiltonian whose form is motivated by density functional theory, explicitly using squeezed atomic orbitals as basis functions⁴⁸. This Hamiltonian has been tested extensively on total energies and equilibrium structures of simple structures⁴⁹, and neglects three-center integrals. Both of these methods seem to provide reasonably faithful descriptions of the chemistry while paying only a slightly higher price than the orthogonal Hamiltonian (the only computational difference is that the “generalized eigenvalue problem”: $H|\psi\rangle = \epsilon S|\psi\rangle$, where H, S are the Hamiltonian and basis positive-definite overlap matrix, respectively, and ϵ is the energy eigenvalue). The equations of this section must be modified to accommodate a non-orthogonal basis. One key factor is that “Pulay corrections”⁵⁰ must be added, since the derivative of the matrix elements is no longer the matrix element of the derivative in Equation 4.

3.3.2 Approximate methods based on Tight-Binding

The tight-binding prescription for total energies and forces is useful in its own right, as we saw above. It still is a demanding procedure to implement without additional approximations for large model systems, since the method requires the diagonalization of a matrix of dimension $N_{atoms} \times N_{basis}$. Some discussion of alternatives to diagonalization are discussed in Section 3.5 below.

A major industry of materials theory has involved extracting simpler approximate interatomic potentials from tight-binding models. Carlsson³⁸ has written a very useful review of this field and shows that even some potentials like the “embedded atom method” (applicable for certain metals) are most easily understood from tight-binding theory, and low-order moment expansions of the density of states (appropriate partial integrals of which provide the Fermi level and band energy). This work provides convincing evidence that an accurate description of the interatomic potential and forces *must* be based upon an electronic structure framework of some kind; well considered approximations can then be made with that starting point. Merely compelling a function with huge numbers of parameters to conform to a large number of (perhaps slightly discrepant) experimental parameters is unlikely to ever produce accurate results.

Many examples of successful empirical potentials and their origin is reviewed³⁸; some selected recent developments include the work of Ercolessi⁵¹ for Al, and that of Kaxiras and coworkers for Si⁵². Vashishta³⁷ has also proposed empirical potentials for binary systems.

3.4 First Principles

As we discussed above, the complexity of electronic structure and force calculations arises from the many-body nature of the interactions between the electrons. Currently, it would seem that direct attacks on the many-electron problem is too difficult to have direct impact on amorphous systems, requiring as they do a large number of atoms to provide a model worth investigating. Thus, all the successful electronic structure calculations salient to amorphous insulators have involved some kind of mapping of the many-body problem into an effective one-electron problem. Historically, the Hartree and Hartree-Fock approaches were the first success in this direction; descendants of these methods are widely used today, particularly in quantum chemistry. The ETB work captures some of the many-body effects, albeit in an approximate fashion, and the exact connection between the ETB model and the real many-body problem is obscure.

Of course, the true many-body Hamiltonian treats both the ions and electrons on a quantum mechanical basis. Because of the large mass difference between the electrons and nuclei, it is standard to decouple the nuclear and electronic degrees of freedom with the adiabatic or Born-Oppenheimer approximation⁵³, in which the electrons are assumed to respond instantly to motions of the ions (the electrons are taken to be in their ground state for all instantaneous ionic conformations). Moreover, the nuclei are treated as classical particles which move in a potential determined by the electrons in their ground state (computed for the given ionic coordinates). For most studies of amorphous solids, this is a reliable approximation, and I am unaware of any such calculation which has not started with the Born-Oppenheimer approximation.

The key breakthrough for good approximate solution of the ground state many-electron problem came in the sixties: the density functional method of Hohenberg, Kohn and Sham⁵⁴. In a nutshell, these workers showed that the electron charge density $\rho(\mathbf{r})$ determines the *ground state* energy (and related quantities, such as forces) for an interacting many-electron system *exactly*. Then, it was shown that the ground state energy satisfied a variational principle; if one possessed the exact energy functional, and could consider all possible charge densities as input to the functional, that density which minimized the energy would be the physical charge density and E would be the exact ground state. Moreover, the variational optimum density is unique.

Beside the fact that density functional methods provided (within some approximations) explicit computational recipes which work surprisingly well, it also gave researchers a solid and simple way to think about the extremely complex problem of a large number of interacting fermions. Clearly, density functional methods share much in philosophy with simpler “charge density based” theories of total energies such as the Gordon-Kim⁵⁵ scheme (applicable only for closed-shell systems - non-bonded interactions) and of course the Thomas-Fermi theories⁵⁶. The density functional methods underlie practically every first principles calculation in glasses or amorphous materials. It is an unfortunate fact that $E[\rho]$ is not exactly known. Some rather good and relatively simple approximations *are* available, such as the “local density approximation”, (LDA) (which is loosely an approximation that the charge

density is slowly varying in the solid or molecule). The LDA is more reliable than its derivation would suggest⁵⁷, and is often very reliable for structural and vibrational calculations. For well understood reasons, it is poor at estimating energy gaps (the band gap is typically underestimated by 50% - 100%). It is an area of intense development to improve the LDA, and there have been some successes⁵⁸. Self-energy corrections⁵⁹ largely fix the gap problem, but are extremely computationally demanding. There are even promising developments toward fixing the excitation energies in a density functional framework.⁶⁰

I will not develop the well-known density functional equations in this article. I will instead summarize the “mathematical strategy” needed for approximately implementing density functional theory. One would guess from the dependence of E on ρ that the object subject to variation would be ρ . However, it turns out that in order to obtain a good estimate for the electronic kinetic energy, it is better to work with a set of $n_{elec}/2$ orbitals, $|\chi_i\rangle$ (we have made the assumption that the orbitals are all doubly occupied). It is necessary that these $|\chi_i\rangle$ should form an orthonormal set $\langle\chi_i|\chi_j\rangle = \delta_{ij}$, with the connection $\rho = 2\sum_{iocc}\chi_i^*\chi_i$. This then specifies E as a functional of the $|\chi_i\rangle$ subject to the orthogonality constraint. To the extent that the basis set upon which the $|\chi_i\rangle$ is expanded on is *complete*, one can expect to get a reliable estimate of the energy and other ground state properties.

Consistent with chemical intuition, a minimal basis set of s and p functions is primarily responsible for the bonding and ground state electronic properties. The pseudopotentials are introduced so that only the really relevant electrons, namely the valence orbitals are *explicitly* treated in the calculation. Thus the valence electrons in the LDA solid are interacting with each other and with the ions via exotic potentials mimicking the nucleus dressed with the core electrons. This is an excellent approximation for most applications in the area of amorphous insulators. Pseudopotentials themselves have developed a considerable lore, and the classic modern work in the area is the paper of Bachelet, Hamann and Schlüter⁶¹. The choice of pseudopotential is governed partly by the basis used: for plane-waves special “soft” pseudopotentials are needed^{62,63}; plane-wave calculations also require a special “separable” form, enabling a factorization that saves considerable computational effort⁶⁴. Real space local basis functions are immune to the need for “softness”.

3.4.1 Local basis: “Ab initio Tight Binding”

Because of formal similarity to the ETB method of Section 2.2, I begin by describing a spatially local basis approach to construct the density functional orbitals $|\chi_i\rangle$. This is a program that was developed by Sankey⁶⁵, and his coworkers, and has been extensively applied to studies of amorphous materials.

The essential approximations are: (1) the LDA; (2) nonlocal (angular momentum dependent), norm-conserving pseudopotentials; (3) a minimal basis set of valence orbitals per site (this has recently been extended by Yang⁶⁶ to include d states in the basis). These basis functions are slightly excited (confined) pseudoatomic orbitals (PAO) (a PAO is a valence eigenfunction for a given atom type in free space, calculated self consistently within

the LDA using pseudopotentials to eliminate the core: in the case of Si, the PAO's can be thought of as approximate atomic 3s and 3p levels); (4) A linearized (non self consistent) version of density functional theory, the ‘‘Harris functional’’⁶⁷ is used which enables calculations without self consistent iterations. This approximation is best discussed by Foulkes and Haydock⁶⁸ and is quite remarkably good except in the most ionic glassy or amorphous systems like SiO₂. For additional discussion see the work of Smith⁶⁹.

The use of PAO's is appealing, because the chemistry is naturally built into the basis functions. The payoff is that for materials like Si and C, a minimal basis of four orbitals per site can be used, so that in a model with N atoms, the overlap and Hamiltonian matrix has dimension $n_b N$, for $n_b = 4$ or 10, the number of basis functions per atom (sp or spd) whereas $n_b \approx 100 - 1000$ for many plane-wave calculations (depending in detail on how carefully such a plane-wave calculation is implemented, and how ‘hard’ the pseudopotential is, which determines the number of plane-waves needed). Also the eigenvectors are expressed naturally in terms of the local PAO's, which is helpful in interpreting the physical meaning of the results. Finally, since the method is implemented entirely in *real-space*, no artificial periodicity is ever imposed, making the approach much more amenable to surface and cluster calculations, where desired.

Sankey and coworkers constructed this method to optimize performance for *ab initio* molecular dynamics simulations; the details are well beyond the scope of this paper. The method is able to handle systems with up to ≈ 500 atoms with exact diagonalization on a workstation, and has been extended recently to include quantum order N methods. The ability to perform exact diagonalizations (as opposed to ‘‘iterative minimization’’ schemes) is valuable for systems with states in the gap and particularly metallic systems. The limitation of non self consistency has been lifted recently by Demkov *et al*⁷⁰ and Ordejón *et al*.⁷¹

While this approach is relatively easy to understand, it is vastly more complex than the ETB method above. In particular, to make the scheme efficient, all the two and three-center matrix elements have to be tabled, so no integrals have to be computed during an electronic structure calculation or MD simulation; rather many calls are made to one and two dimensional interpolators. The calculations of forces, particularly with respect to the exchange correlation interaction, is tedious. Also, it is no longer correct to use the Hellmann-Feynman result (the derivative of the matrix elements is not the matrix element of the derivative, since the overlapping basis functions move with the atoms).

The formal expressions for matrix elements, forces etc. are substantially more complex than for plane-wave pseudopotential methods of the next Section. I refer the reader particularly to References^{65,70,71} for the details of the theory. This scheme has found considerable use in amorphous insulators.

A very recently developed method which appears to be very promising is the ‘‘SIESTA’’ code of Ordejón, Soler and Artacho⁷². This is a fully self-consistent implementation of Kohn-Sham LDA with a rich local basis (double zeta with polarization functions), post-LDA corrections (generalized gradient approximations) and local spin density (applicable to non-spin polarized systems).

3.4.2 Plane-waves: Car-Parrinello methods

The first *ab initio* molecular dynamics simulation was performed in 1985 by Car and Parrinello (CP). I begin with a comment on what “CP” means. Often a “CP simulation” refers to a molecular dynamics calculation using a plane wave basis and an iterative minimization scheme to solve the electronic structure problem (the self consistent LDA equations). More properly, “CP” refers only to a method for coupling the approximation of stationary states of giant basis eigenvalue problems with associated ionic dynamics, even for a basis other than plane-waves.

In the next paragraphs, I will discuss the basic CP equations of LDA on a plane-wave basis⁷³. To keep to the essentials I will write the expressions only for the Γ point of the Brillouin zone. As usual, the LDA equations take the form (for LDA Hamiltonian $\mathcal{H} = p^2/2m + V_{\text{eff}}$):

$$\mathcal{H}|\chi_i\rangle = \epsilon_i|\chi_i\rangle \quad (8)$$

where

$$|\chi_i\rangle = \sum_{\mathbf{G} \neq \mathbf{0}} A_{\mathbf{G}}^i |\mathbf{G}\rangle, \quad (9)$$

where $|\mathbf{G}\rangle = 1/\sqrt{\Omega} \exp(i\mathbf{G} \cdot \mathbf{x})$, Ω is the cell volume, and \mathbf{G} labels reciprocal lattice vectors (*a plane-wave basis restricts our studies to periodic systems*), so that the usual apparatus of reciprocal lattices is appropriate. The sum is cut off for $G = G_c$ large enough (“wavelength” small enough) that the smallest salient features in the problem are adequately described. An obvious advantage of this representation is that the kinetic energy operator is diagonal and therefore trivial. Matrix elements of V_{eff} are obtained by fast Fourier transforms, the existence of which makes the plane-wave approach tractable. The *problem* with Eq. (8) is that for systems large enough to interest us, the Hamiltonian matrix is too large to diagonalize with “classical” methods.

The key contribution of CP was to note that the diagonalization (Eq. 8) is unnecessary; it is adequate instead to consider the LDA expression for the total energy (a ‘partial trace’ over the occupied electronic subspace) and vary the χ_i :

$$E(\{\chi_i\}) = \sum_{i \text{ occ}} \langle \chi_i | \mathcal{H} | \chi_i \rangle \quad (10)$$

where two important facts must be emphasized: (1) the sum is over the *occupied* subspace and (2) $\langle \chi_i | \chi_j \rangle = \delta_{ij}$. Thus, using Eq. (9), E can be viewed as a function of an extremely large number of parameters $A_{\mathbf{G}}^i$ ($n_{pw} \times n_e/2$) for n_{pw} the number of reciprocal lattice vectors used and n_e the number of electrons (double occupancy assumed). The idea is that if a set of mutually orthogonal $|\chi_i\rangle$ can be found, adequate in number to accommodate the electrons in the problem, and minimizing the functional (Eq. 10), then the E so obtained is the LDA ground state energy, to the extent that the basis is complete (the plane wave cutoff is sufficiently large).

To perform the minimization, CP introduces a fictitious Lagrangian⁷⁴ which includes

both the electronic and ionic degrees of freedom:

$$\mathcal{L} = \sum_i \mu/2 \langle \dot{\chi}_i | \dot{\chi}_i \rangle + \sum_\alpha 1/2 M_\alpha \dot{\mathbf{R}}_\alpha^2 - E(\{\chi_i\}, \{\mathbf{R}_\alpha\}). \quad (11)$$

In this equation, $E(\{\chi_i, \mathbf{R}_\alpha\})$ is the same as that given in Eq. (10) (the expectation value for the electronic energy, viewed as a functional of the orbitals χ_i), and the quadratic terms involving time derivatives (dots) are for the electrons (χ_i) and ions (\mathbf{R}_α). Parameter μ is a fictitious mass assigned to the electron (it has nothing to do with the real mass, and is adjusted to make the calculation proceed efficiently). Note at this point that this method *does not* provide any information about electron dynamics in the usual quantum mechanical sense of time evolution. Rather it is just a trick to find the stationary states of the LDA Hamiltonian (approximate the occupied eigenstates from eigenvalue problem Eq. 8). Thus, the “dynamics” for the electrons has only the utility of helping to solve the eigenvalue problem, and in fact if the fictitious kinetic energy becomes significant compared to the physical ionic kinetic energy, the dynamics for the ions will be suspect. In the absence of the “fictitious electronic kinetic energy”, this Lagrangian would just generate the Newton equations of motion for the ions $M_\alpha \ddot{\mathbf{R}}_\alpha = -\partial E / \partial \mathbf{R}_\alpha$, as one would expect. The additional term adds an extra equation however: $\mu |\ddot{\chi}_i\rangle = -\delta E / \delta \langle \chi_i | + \sum_k \Lambda_{ik} |\chi_k\rangle$. Here, Λ_{ik} is a matrix of Lagrange multipliers required to maintain orthogonality $\langle \chi_i | \chi_j \rangle = \delta_{ij}$. In practical methods the Λ_{ik} are obtained by compelling the eigenvectors $|\chi_i\rangle$ to be orthonormal at each time step, and computing Λ_{ik} from $\Lambda_{ik} = \langle k | \mathcal{H} | i \rangle - \mu \langle \dot{\chi}_k | \dot{\chi}_i \rangle$. Then the ionic and fictitious electronic “forces” are completely specified, and the determination of the stationary states can proceed. Note that there are effectively two time scales in the dynamics so generated: one is determined by the artificial “mass” μ of the electrons; the physically salient time scale is set by the ionic masses M_α . This method generates unreliable dynamics for the ions if significant energy is transferred from the ionic (physical) degrees of freedom to the fictitious electronic degrees of freedom. That this must happen for long times is apparent from the equipartition theorem (Eq. (11) is a quadratic form, and asymptotically energy will reach equipartition at least if the ionic coordinates are near an energy minimum). It develops that the rate of transfer from the ions to the unphysical electron kinetic energy depends critically on the energy gap (rapid transfer for small gap), which makes the CP method difficult to apply to metals⁷⁵.

3.5 Efficient ab initio methods for large systems

The area of network glasses and associated dynamics is a challenge not only to transferability (which requires first principles methods, at least in cases like a-C or a-Si), but requires models with *many* atoms. Depending on the precise question being addressed it can be necessary to have thousands of atoms. This is beyond the reach of plane wave based density functional methods, and is quite difficult even for the local basis methods (by contrast, simulations with millions of particles are possible for empirical potentials and using special linear scaling methods there¹¹).

Several groups have been working on first principles total energy and even MD codes which have CPU and memory demand scaling *linearly* with the system size. These are dependent on two ideas: the existence of a real-space localized representation for the electron states, and a way to avoid explicitly keeping electron orbitals mutually orthogonal.

3.5.1 *The need for locality of electron states in real space*

The condition that a system should possess a localized real-space representation is connected closely to the idea of the “Wannier functions” in crystals. It has long been known⁷⁶ that an alternative to the space-filling Bloch representation (with band label n and quasicontinuous vector \mathbf{k}) is the Wannier function with labels (n, \mathbf{R}) , where \mathbf{R} specifies a lattice vector near where the electron is localized. It has been shown that idealized Wannier functions can exhibit exponential decay for insulators⁷⁶. In this representation, the overlap between Wannier functions becomes exponentially small (and therefore negligible) for sufficiently separated Wannier centers. This also justifies use of a similar truncation in the single particle density matrix^{77,78}, which can similarly be truncated for (local) basis functions sufficiently mutually remote. This ability to “cut off” the tails of the Wannier orbitals (with negligible harm done to the accuracy) is the key to efficient electronic calculations for insulators. In effect, it makes quantum mechanics a local theory (although there are fundamental bounds on *how* local it can be made). In a complicated way, the possibility for the real space local representation requires the existence of a significant optical gap; in a metal the density matrix (or Wannier orbitals) decay as a power law at zero temperature. A representation-independent measure of this spatial locality is the decay of the off-diagonal elements of the real-space single-particle density matrix $\rho(\mathbf{x}, \mathbf{x}')$; it seems clear that the Wannier orbitals cannot be *more* localized than the range of ρ . It is also possible^{10,79} to compute “generalized” Wannier functions for non-crystalline systems. Such generalized functions usually differ from the classical Wannier functions also by involving more than one band. Recently, “visualizations” of these functions have been published for diamond and discussed in detail for amorphous diamond⁷⁹. The applicability of quantum order-N methods to disordered insulators is a considerable boon for our community, and will enable studies that are currently unthinkable in metallic systems. Ordejón and Drabold⁸⁰ performed local basis *ab initio* order-N MD on a 512 atom model of amorphous diamond⁸¹, and Stephan and Drabold have recently applied *ab initio* methods to an a-C model with 4096 atoms⁸¹, and showed⁷⁹ using projection methods^{82,83} that the local representation works in a disordered insulator as well as for crystals.

3.5.2 *Avoiding explicit orthogonalization*

The second requirement for a linear scaling algorithm is to avoid explicitly orthogonalizing the electronic orbitals at each step through a variational minimization scheme. The most obvious (but notoriously unstable) Gram-Schmidt orthogonalization¹⁹ process has cpu demand scaling as N^3 . This problem has been solved by Vanderbilt for calculations in which

the density matrix is the object to be variationally determined⁷⁷ and independently by Ordejón *et al*¹⁰ and Mauri *et al*⁸⁴ for a “generalized Wannier orbital” based approach. I refer the interested reader to the original references.

4 Connecting Simulation to Experiment

4.1 Structure

Diffraction measurements (typically X rays or neutrons) provide information about the distribution of radial distances between atomic pairs. In particular, neutron diffraction experiments can measure the static structure factor:

$$S(Q) = 1 + \frac{1}{N\langle b^2 \rangle} \sum_i \sum_{j,j \neq i} b_i b_j \frac{\sin(Qr_{ij})}{Qr_{ij}} \quad (12)$$

The summations are over the atoms of the supercell, r_{ij} being the magnitude of the difference between the positions of atom i and atom j . The b 's are the scattering lengths for whatever atoms are present in the system. It is often more convenient to work with the pair-distribution function $g(r)$, related to $S(Q)$ according to⁸⁵:

$$g(r) = 1 + \frac{1}{8\pi^3 n_0} \int_0^\infty [S(Q) - 1] (\sin(Qr)/Qr) 4\pi Q^2 dQ \quad (13)$$

An essential requirement for any physically credible model is agreement on static structural measurements, especially from X-ray or neutron diffraction studies. It cannot be too strongly emphasized however that while sufficient agreement on radial distribution function $g(r)$ and closely related static structure factor $S(q)$, is *necessary*, it is *not sufficient*. That is, the literature is replete with calculations yielding models with “good” radial distribution functions, which are wholly unrealistic. Some especially revealing work along these lines is by Putszaf⁸⁶ for a-Si, who has shown that essentially perfect agreement for $S(q)$ can be obtained for models with a bond angle distribution at least twice as broad as what occurs in nature. For a complete discussion, see Wright’s contribution in this volume.

Other *local* probes like NMR, NQR, Mössbauer and certain electronic and vibrational experiments are also critically important, and discussed by experts elsewhere in this volume.

4.2 Network Dynamics

Inelastic neutron scattering offers the most direct probe of lattice dynamics experimentally available. For a proper discussion, see the article of Cappelletti in this volume. It can provide an accurate measure of the vibrational power spectrum, something easy to compute for a given structural model and interatomic potential (first principles or empirical). Other spectroscopies (such as Raman⁸⁷) also probe the vibrational density of states, albeit, modulated by matrix elements that are hard to compute very accurately. It is common to

compare the position of peaks in the Raman spectrum to peaks in the vibrational density of states, though this can be misleading if a particular sought after feature is not Raman active (symmetry forbidden). It would be rare to find a truly symmetry-forbidden feature in a glass, because of the lack of order. Certainly however, some modes are much more Raman active than others because of *local* order which certainly is present in all glasses.

4.2.1 Computing the harmonic modes

In the harmonic approximation, one models small oscillations of atomic positions about a local or global minimum of the potential energy function. In crystals with translational invariance, it is customary to label vibrational modes with band (branch) and \mathbf{k} indexes, where it is sufficient to consider only those \mathbf{k} in the first Brillouin zone. For a perfect crystal, all the vibrational modes are extended in real space.

In disordered systems the lattice vibrational excitations are not so easily categorized, since \mathbf{k} is no longer a suitable label. One can proceed to think about the vibrational modes in either of two ways: (1) The simplest approach is to view the harmonic modes as the normal excitations of a very large molecule (the model under consideration). It can be very instructive to visualize the time development of the atomic positions *executing a single vibrational eigenmode*⁸⁸. (2) If periodic boundary conditions are used, as is usually the case in modeling a glassy or amorphous material, then there is in fact a Brillouin zone, and technically the apparatus of crystalline solids should apply. From this point of view, the $\mathbf{k} \rightarrow 0$ (acoustic) modes are not properly reproduced by a $\Gamma(\mathbf{k} = \mathbf{0})$ point calculation, and the smallest frequencies in the density of states to be accurately represented by a Γ point calculations should be $\omega_{min} \approx 2\pi c/a$, where c is the speed of sound and a is the smallest dimension parameter of the supercell. One could of course compute the dynamical matrix as a function of \mathbf{k} and compute the dispersion curves, but this is of doubtful value, since the dispersion so computed originates from an unphysical (but convenient) periodicity. For a sufficiently large cell and ω , it is appropriate to limit oneself to $\mathbf{k}=\mathbf{0}$ modes.

The dynamical matrix D is the key ingredient to a calculation of the normal vibrational modes, and is easily obtained from a system *well* relaxed to equilibrium for which interatomic forces are available. In particular, $D_{\alpha I, \beta J}$ is defined as $D_{\alpha I, \beta J} = (M_I M_J)^{-1/2} \partial^2 E / \partial u_{\alpha I} \partial u_{\beta J}$, where E is the total energy of the system, α and β are Cartesian coordinates on atoms I and J , respectively, and the M 's are ionic masses, is computed by finite differences: atom I is displaced an amount $\Delta x_{\alpha I}$ in the α direction, and the forces on all the atoms $F_{\beta J}$ are computed. Then, $D_{\alpha I, \beta J} \approx (M_I M_J)^{-1/2} F_{\beta J} / \Delta x_{\alpha I}$, since the force on an atom is the derivative of the total energy with respect to the displacement of that atom: $F_{\beta J} = -\partial E / \partial x_{\beta J}$. In practical implementations, one usually has to symmetrize the dynamical matrix (it will not be *exactly* Hermitian unless the potential is exactly harmonic)⁸⁹.

If one is interested in a very large system, the dynamical matrix can be accurately approximated as a sparse matrix (a matrix with the vast majority of elements being zero), if the forces on atoms closer than a certain cutoff R_f from the displaced atom are computed,

the rest of the forces being set to zero. This approximation takes into account the fact that the forces on each atom depend only on its local environment, and not on the details of the structure in distant regions. This also reflects the fact that the dynamical matrix elements between distant atoms decreases rapidly with distance. Our approximation can therefore be put in terms of imposing a cutoff on the dynamical matrix:

$$D_{\alpha I, \beta J} = 0 \quad \text{if} \quad |\mathbf{R}_I - \mathbf{R}_J| > R_f \quad (14)$$

so that the resulting matrix is sparse. Its calculation and storage are both $O(N)^{90}$. With the dynamical matrix in hand one can exactly diagonalize D for small systems or use the Maxent spectral technique^{91,92} for large systems. In addition, a Lanczos method can be used for computing a limited number of vibrational eigenvectors in a user specified energy range⁹³. Of course this method also works for empirical potentials in which case the germain approximations are that D have finite range and one of the spectral techniques described in this paper.

It would be interesting to try these ideas on extremely large models of amorphous semi-conductors to study the floppy-rigid transition^{94,95} for a model with Keating⁹⁶ springs. The density of states would be easy to compute $O(N)$. Such an approach would not be as efficient or elegant as *The Pebble Game*⁹⁷, but it would also be more “realistic”, with relatively realistic interatomic interactions.

4.2.2 Dynamical Autocorrelation functions

Sometimes it is inconvenient or even impossible to implement a calculation of the dynamical matrix because the harmonic approximation is not valid (as for a liquid). One can still compute the vibrational power spectrum directly from the trajectory given by a thermal MD simulation. Of course this method can also be applied to a system in the solid state, though in practice, it should be inferior to the dynamical matrix calculation since it gives less information (only the vibrational power spectrum), and in practice requires at least as many times steps of MD as the $3N$ steps needed to compute the full dynamical matrix. The dynamical approach also requires a numerical Fourier transform, which requires a long time series (simulation) to produce good estimates for the vibrational spectrum for $\omega \rightarrow 0$.

In this approach, the vibrational density of states (VDOS) $g(\omega)$ of a model can be obtained from the Fourier transform of the velocity autocorrelation function $G(t)$:

$$G(t) = \frac{\langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle}{\langle \mathbf{V}(0) \cdot \mathbf{V}(0) \rangle}, \quad (15)$$

$$\langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle = \frac{1}{3N} \sum_i^N \sum_j^3 V_{ij}(0) V_{ij}(t), \quad (16)$$

$$g(\omega) = \frac{2}{\pi} \int_0^T G(t) \cos(\omega t) W(t) dt. \quad (17)$$

The values of N and T are the number of atoms and the total simulation time respectively. The summations in Eq. 16 are over the total number of atoms and the three components of each atom’s velocity. We use a standard Blackman window¹⁹ $W(t)$:

$$W(t) = 0.42 + 0.5 \cos\left(\frac{\pi t}{T}\right) + 0.08 \cos\left(\frac{2\pi t}{T}\right). \quad (18)$$

The spectral resolution of the Fourier transform depends on how much time series data can be generated and a rule of thumb is to simply check whether the spectral function is too broad to address the question of interest. Our experience is that the Blackman window gives the best results over the entire spectral range of our VDOS. Note that periodic boundary conditions introduce artifacts in $G(t)$ for times longer than $\tau \approx a/c$, where c is the speed of sound and a is the box size.¹⁷ For completeness, we should also mention that the diffusion constant can in principle be computed from velocity autocorrelations via the value of g at zero frequency:

$$D = (1/3) \int_0^\infty \langle \mathbf{V}(0) \cdot \mathbf{V}(t) \rangle W(t) dt. \quad (19)$$

A much more sophisticated and potentially more powerful approach to spectral estimation (eg to finding the “frequency content” of a time series) is to use the methods of Bayesian parameter estimation⁹⁸. Here, one can actually compute the probability that a given model (say a harmonic series with p distinct frequencies) describes a given data set (time series $G(t)$). I have applied this approach to carbon clusters⁹⁹ and it is easy to see that a shorter MD simulation is needed to get an estimate of the normal mode frequencies than one would obtain by Fourier transform with windows. For additional details I refer the reader to the Bayesian literature⁹⁸. While this approach is clearly useful for small molecules⁹⁹, the possibilities for this approach are uninvestigated to date in glasses.

4.2.3 Dynamical Structure Factor

An additional advantage to the dynamical matrix calculation (which gives the normal modes eigenvectors) is that one can easily compute the dynamical structure factor $S(\mathbf{Q}, E)$ (See R. L. Cappelletti’s paper elsewhere in this volume). I refer the interested reader to the discussion given there.

4.3 Electronic Structure

A very important and sensitive probe of structure is the nature of the electronic states and the electronic density of states in disordered systems. Since electron states near the gap are always significantly localized due to disorder, one can link an electronic signature (defect state) with a finite (usually small) collection of atoms upon which the state is localized (where the state’s charge is located). In this way, electronic information can directly imply structural information. The nature of the electronic states in the vicinity of the optical gap is of key interest, since these states are responsible for conduction and are undoubtedly

of key importance to light-induced defect creation and more exotic forms of light-induced effects.

Now it must be admitted that the experimental determination of the electronic density of states can be a challenge. In particular, since any imaginable experiment involves *transitions* in electronic states one naturally measures something like a *joint* density of states involving a convolution of the valence and conduction band tails (note however the impressive “total yield photoelectron spectroscopy” experiments of Aljishi and coworkers¹⁰⁰, which are able to sort out the valence and conduction tails separately). In principle, transport measurements depend upon the electronic density of states (and, unfortunately, on many other things too); so that it is extraordinarily difficult to infer the density of states given information about transport (for some progress on this interesting problem see the article of Adriaenssens¹⁰¹).

A key point which is only now coming to be appreciated^{102,103}, is that informative calculations of anything but the most localized (midgap) states requires models which are extremely large by usual standards. This is because the *bandtail* states are not compactly exponentially localized as midgap defect states are (for example in a-Si). A proper (atomic) theory of transport within linear response in disordered systems is under development, and one (of several) essential features is to have models large enough to properly describe the states (eg. without much effect from finite size artifacts and periodic boundary conditions) responsible for the conduction.

4.3.1 Density of States

It is clear that to get accurate eigenstates, either electronic or vibrational, one needs *large* – in many cases several *thousand* atom models. The most natural way to compute the density of states of a large Hermitian matrix (either the electronic Hamiltonian in a selected representation or the dynamical matrix for lattice vibrations) is to exactly diagonalize it with standard iterative methods (usually Householder tridiagonalization followed by a “QR” algorithm)¹⁰⁴. This approach is extremely numerically reliable and it provides all the eigenvalues and eigenvectors to machine precision. The problem is that the cpu demand for this scales like the dimension of the matrix *cubed*. Practically speaking (for 1997 workstations) this means that a 2000×2000 matrix is quite tractable with these full diagonalization methods, but 5000×5000 is both a cpu and memory challenge.

Fortunately there are efficient alternatives to full diagonalization if one seeks only the density of states. These schemes can have cpu and memory cost that scales *linearly* with the dimension of the matrix. One simple and effective approach is the maximum entropy approach^{91,105}, and the closely related recursion methods¹⁰⁶. These methods apply for local basis representations of the Hamiltonian or the dynamical matrix, and fully exploit sparseness (when properly implemented, all matrix-vector operations are constructed to involve *only* the non-zero elements of the matrix. For a detailed discussion of methods to extract the DOS in “order N” fashion, I refer the reader to the literature.^{91,105}

For the calculation of eigenvalues and eigenvectors “in a gap” (again, either in the

electronic or vibrational DOS), eg, where the spectrum is not very dense, Lanczos or inverse iteration methods are very efficient. We have recently used a Lanczos method¹⁰⁷ to compute 500 states around the optical gap in a 4096 atom model of a-Si, which enabled some new insight into the Anderson transition¹⁶ in a real amorphous material (rather than for the Anderson model with its diagonal-only disorder). Knowledge of such states is critical to the optical and transport properties of disordered materials.

4.3.2 Thermal modulation of the electron states

Since our focus in this article is *dynamics*, we also consider here the time evolution of electron energy eigenvalues and associated eigenvectors due to their modulation by lattice vibrations, eg. we study the electron-phonon interaction in a quasi-classical approximation in which the atomic positions are modified from their ideal $T = 0$ positions by thermal disorder (superposed on the existing structural or topological disorder); this thermal motion induces a time dependence in the energy eigenstates and eigenvalues with experimentally observable consequences.

To illustrate these ideas, I consider the case of amorphous Si, for which we are motivated by the temperature-dependent photoemission measurements of Aljishi et al.¹⁰⁰. We have studied the modulation of the electronic energy levels due to thermal motion, as characterized by LDA simulations at different moderate temperatures in a WWW 216 atom cell.¹⁰⁸ In Fig. 1, we illustrate the time evolution of the band-tail and deep trap eigenvalues. Several points bear comment: (1) The thermal modulation of the gap states is very large (the lowest energy unoccupied state fluctuates by *several tenths of a volt*, an effect *much* larger than thermal energies), and the RMS fluctuation of twelve states in the vicinity of the gap (out of 864 states total) is larger than 0.03 eV. Naturally, the structure of the LDA eigenvectors conjugate to these eigenvalues is changing too. This variation reflects the large electron-phonon coupling between the lattice vibrations and a localized (defect or band tail) electronic state. (2) If one computes the inverse participation ratio (IPR) for the states illustrated in Fig. 1, there is considerable correlation between the RMS time fluctuation (a dynamical property) and the IPR (a static property) [more local, more fluctuation]¹². (3) For the conductivity, the thermal modulation of the electronic states is critical, most particularly for the states near the middle of the gap, as they fluctuate most strongly (and are also the key states for transport in the intrinsic material). (4) The conduction tail states fluctuate more than the valence tail states; this immediately suggests that electron transport should exhibit a more pronounced temperature dependence than holes in the valence tail. This is seen in drift mobility measurements¹⁰⁹. (5) By making the (remarkably crude) identification of the RMS fluctuation of the highest occupied electronic eigenvalue with the (temperature dependent part) of band-tailing, we obtained semi-quantitative agreement¹⁰⁸ with the temperature dependent band tail experiments of Aljishi *et al*¹⁰⁰. It must be admitted that much more work needs to be done along these lines, but I believe that it is a promising beginning. (6) Spectral analysis of the time series for each eigenvalue shows the influence of recognizable phonons. Highly localized states originate in a locally strained part

of the network, which usually also induces high frequency local vibrational modes¹¹⁰, the modulation of which has particular strength in the vicinity of the defect. These effects do not depend upon system size, at least for the most localized states. These thermal effects are rather well approximated by local basis LDA methods, as detailed tests on the phonon spectrum of c-Si, a-Si:H and a more complex glass like GeSe₂ reveal¹⁵.

The dynamics of the electronic properties as described in this way are an essential precursor to modeling the finite temperature transport properties of a-Si (or other disordered systems), and point the way to a theory more connected to microscopic models and consequently to a detailed understanding of the connection between transport and microstructure.

4.4 Transport

One of the most important probes of electronic, topological *and* vibrational structure is transport. In particular, interpreting experimental measurements of transport properties, particularly in the presence of disorder, is a challenging problem, precisely because the conductivity depends critically on *all* of these physical properties.

An emerging area of theory work in glasses and amorphous semiconductors is the formulation of a microscopic, indeed *atomistic* scale approach to modeling conduction. The idea is to explicitly connect the conductivity to electronic wave functions, doping (the position of the Fermi level), etc. This is based on a famous result from statistical mechanics, the “Kubo formula”^{111,112} for the electrical conductivity (the name is actually generic and refers to a variety of related correlation functions which give the linear response of a system to a weak external perturbation). The Kubo formula for the AC electrical conductivity can be expressed in many different but equivalent forms; one convenient form is:

$$\sigma(\omega) = \frac{2\pi e^2}{3m^2\Omega\omega} \sum_{i,k} [f_i - f_k] |\mathbf{M}_{i,k}|^2 \delta(E_k - E_i - \hbar\omega) \quad (20)$$

where $\mathbf{M}_{i,k} = -i\hbar\langle\psi_i|\nabla|\psi_k\rangle$ is the momentum operator matrix element between eigenstates ψ_i and ψ_k , Ω is the cell volume, and E_i is the energy of state i . f_i is the Fermi-Dirac distribution function evaluated at energy E_i . This result can also be obtained¹¹³ from a Fermi Golden rule¹¹⁴ argument. Equation (20) describes conductivity in terms of quantum transitions of electrons near the Fermi level. By inspection of the Kubo formula, it is clear that the localization of the states, overlap (and momentum matrix elements), and proximity in energy to each other and to the Fermi level, are primary determinants of the DC conductivity.

The Kubo formula is quite correct and also deceptively innocent in its appearance. In particular it is nearly always the case for amorphous semiconductors that one is interested in the $\omega \rightarrow 0$ limit of σ , and this is tricky to evaluate for any finite system, since for any finite model the density of states is *discrete*, and therefore $\sigma(\omega = 0)$ is strictly zero! In fact, there are two key broadening mechanisms to the energy levels which must be considered in some fashion: (1) for finite temperatures, the electron-phonon interaction modulates

the position of the energy eigenvalues, especially those near the optical gap (since these are usually well localized); this can have a dramatic effect on some eigenvalues¹⁰⁸; causing them to fluctuate several *tenths* of an eV about their reference ($T = 0$) energy; also (2) in a supercell calculation there *is* a Brillouin zone associated with the supercell periodic boundary conditions, and thus there is a \mathbf{k} -space broadening which scales inversely with supercell volume. This latter effect is evidently important even for $T = 0$ and gives a properly continuous spectrum for the electronic eigenvalues. In Fig. 2, we show an early example of a theoretical calculation of the DC conductivity in amorphous Si¹⁰³. There is a developing literature on the proper ways to evaluate the Kubo formula and related results from linear response theory¹¹⁵.

To properly include thermal effects (eg the effects of thermal disorder superposed upon topological disorder) a necessary first step is to thermally average the expression 20 over a sufficiently long MD trajectory carried out at an appropriate temperature. This work is in progress¹¹⁶ and it is too early to say how effective this will be in predicting the *temperature dependence* of the conductivity, for example. One point that is already apparent to us however is that a “real MD” trajectory is needed to gain understanding of the (vibration-induced) time evolution of the electronic stationary states; an attempt to just make small *random* displacements of the atomic positions from their $T = 0$ conformation leads to modulations of the electronic energies much weaker than observed in experiments which directly probe the density of states.¹¹⁶

It is possible too that the most effective approach to understanding transport will involve a hybrid of atomistic electronic structure calculations in conjunction with a Monte Carlo or integral equation theory¹⁰¹ of transport which requires input such as the scattering cross section of a given electronic defect states, information about the localization of the trapping state (and therefore information about expected lifetimes in that state), etc.

5 Applications

In this section I will review a few applications of the MD method to amorphous or glassy materials, and again, provide pointers to published work.

5.1 *g-GeSe₂*

We have recently been modeling glassy chalcogenides, especially *g-GeSe₂*^{14,15,12}, using the methods of local basis *ab initio* MD. To summarize the principal results: (1) *ab initio* MD with supercells involving 216 or more atoms provides a rather faithful structural model of *g-GeSe₂*, including the first sharp diffraction peak (FSDP). In Fig. 1 of Ref. ¹² we show the total static structure factor for the liquid and glass. In the paper¹² we also elucidate the partial distribution functions, and make a connection between the rings and the FSDP; (2) by explicitly computing the dynamical matrix (Sec. 4.2.1), and studying the vibrational eigenmodes, we substantially justified the proposal of Suga¹¹⁷ that the A_{1c} mode is pre-

dominantly a tetrahedral breathing mode associated with corner-sharing tetrahedra, albeit with some mixing from network defects¹⁵; (3) the electronic structure of the liquid¹² has the interesting property that the electronic eigenvalues *cross* in the course of a thermal simulation, and by study of the electronic states conjugate to the crossing eigenvalues, one can see bond-forming and bond-breaking events. It is conjectured that these events are connected with the remarkable light-induced effects observed in the glass¹⁸. The time evolution of the LDA eigenvalues is given in the literature¹², and also discussed by Cappelletti in his contribution in this volume. There is a wealth of information in the “spaghetti” of this Figure, especially pertaining to transport and the electron-phonon interaction and its energy dependence.

5.2 *g-Ge_xSe_{1-x} Glasses*

A particularly interesting recent micro-Raman study was by Boolchand’s group¹¹⁹. A large collection of GeS and GeSe glasses with different mean coordinations were fabricated and a rather spectacular and abrupt shift in the frequency of the A₁ (tetrahedral breathing) mode was observed for mean coordination 2.46, very near the stiffness threshold predicted by Phillips⁹⁴ and Thorpe⁹⁵. Simulations are underway to probe the microscopic origin of this important experiment.

5.3 *Amorphous carbon surface*

As an indicator of another interesting frontier, only beginning to be explored, I describe our work on an amorphous diamond *surface*. There has been surprisingly little work done on the structure of surfaces for which the bulk material is topologically disordered. To the extent that the surface is always the “interface to the world” this seems like an interesting area for theory and experimental work. The first work we know of on this problem was on a-Si¹²⁰.

As a first example, we started with a 216 atom supercell model of amorphous diamond⁸¹, which we have studied previously¹²¹. This material is (by construction) entirely four-fold coordinated in the bulk, and is topologically very similar to amorphous Si. For this calculation, we simply maintained the periodic boundary conditions in only two dimensions (thus creating a slab geometry). This structure was then thoroughly relaxed, and naturally there were major rearrangements (the “amorphous analog of surface reconstruction”) near the surface, where the local bonding environment had changed dramatically. In Fig. 3, we illustrate the surface. Note the strong tendency to graphitization (hexagonal rings), even though the bulk structure is entirely sp³ (tetrahedral), and disordered. A similar graphitization effect is known in diamond; we establish here that it happens even for an amorphous system.

Beside the intrinsic interest of an “amorphous surface”, any microscopic approach to growth requires information about surface reactivity and microstructure, which this type of

calculation provides directly.

6 Where to get codes to get started

For many of the computational methods discussed in this paper, it is a considerable task to develop codes which implement the calculations from the beginning. Because of this, I would like to point out that some of the necessary codes are available for free from generous individuals who took the trouble to make “user friendly” versions of codes they developed in their research, or specifically for pedagogic purposes. In order to make these hyperlinks conveniently accessible, and also to keep them reasonable up to date, I am establishing a WWW page

“<http://www.phy.ohiou.edu/~drabold/software.html>”

which will have links to the software I describe below and other useful codes I encounter. Of course this service is provided with the stern injunction: *caveat emptor*; I do not vouch for these codes, although naturally I will not put up links if I doubt their quality. It must also be understood, of course, that some of these codes are very sophisticated and require *much* background work before the researcher new to the area can make much progress.

7 Acknowledgements

This work was supported in part by the National Science Foundation under grants DMR 96-18789, DMR 96-04921 and DMR 93-22412. I have benefited greatly from discussions and collaboration with Prof. R. L. Cappelletti, who first introduced me to glasses. I thank Prof. Normand Mousseau for providing the text on his activation relaxation technique. Peter Fedders, Otto Sankey, Pablo Ordejón, Richard Martin, Uwe Stephan, Mark Cobb and Jianjun Dong have contributed to many parts of the work I discuss here, and I thank them for all their insights and help.

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Figure 1: Thermal fluctuation of LDA eigenvalues in the gap. The dynamics are for the 216 atom WWW amorphous Si cell at 350K.

Figure 2: The density of electron states, localization and estimated DC conductivity (as a function of doping – the position of the Fermi level) for 4096 atom model of a-Si.

Figure 3: Topology of relaxed amorphous diamond surface from *ab initio* MD. Note the strong tendency to graphitization and ring formation at the surface. The lighter atoms are three-fold, to emphasize the graphite-like ring formation.