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Bethe lattice studies in glasses

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Abstract

The Bethe lattice has been extensively used to study amorphous and glassy solids, due to the abundant and easily obtainable analytical results. However, not much attention has been paid to the unphysical and spurious features that make the calculations difficult to interpret. In this paper, some of the results extracted from Bethe lattice studies are critically reviewed and their most serious drawbacks are discussed, particularly the effects of an unphysical surface on local and long range correlations. A study of the localization of states in the Bethe lattice is also included.

1. Introduction

The most important difficulty when studying glasses, or amorphous solids in general, is the absence of long range translational symmetry. However, as discussed by Frank L. Galeener [1], one usually finds local chemical order and some type of intermediate range order in these, otherwise, disordered solids. Covalent amorphous semiconductors and AX_2 glasses, for instance, present nearest neighbour fixed geometry and regular coordination. This fact makes the Bethe lattice an appropriate network to simulate these glassy structures, since, as we shall see below, it is possible to define a local unit (or effective site) preserving the local short range order, and construct an infinite random network without long range order. This method is sometimes more convenient than building disordered clusters with free ends or periodic boundary conditions, since it is

free from unwanted finite size effects and artificial periodicities, although care must be taken when interpreting the results due to the unphysical properties of the Bethe lattice. The main advantage of Bethe lattice models is that most results are obtained analytically.

In this paper we present a new discussion of the properties of the Bethe lattice and revise a series of Bethe lattice models for glasses made in collaboration with Galeener in the past ten years, and referred to in the following text.

2. Properties of the Bethe lattice

Suppose one is interested in calculating the magnetic properties of a large system, and one approximates it by a small cluster. The difficulty in doing so is that the magnetization of the atoms in the surface of the cluster differs from those in the interior. One can impose periodic boundary conditions, but one is likely to obtain spurious results due to the artificial periodicity. The idea then is to attach to the surface

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atoms some effective medium imposing the condition that the magnetization of the surface should be equal to the atoms in the interior of the cluster. This is called the Bethe–Peierls approximation [2].

If one asks the question whether there is a network in which the Bethe–Peierls approximation is the exact result, the answer is the Bethe lattice [3]. If one studies the vibrations of a tetrahedron with five atoms and devises an imaginary impedance attached to the four surface atoms, imposing the condition that the amplitude of vibration for any atom in the cluster should be the same, one is talking about the ‘structural potential approximation’ [4] which, not surprisingly, turns out to be the Bethe lattice again.

Topologically, the Bethe lattice is the Cayley tree [3], which can be visualized as a simply connected network of identical units with constant coordination, Z , and without closed loops of paths. From this point of view, the Bethe lattice is a first approximation to any regular network, in which all connected diagrams without closed loops are summed exactly. There are two important observations: the first is that there is no long range order or periodicity in the Bethe lattice, and second is that there is only one path from one given site to another.

The first observation has been used as a justification to simulate amorphous infinite networks and calculate electronic [5], vibrational [6] and magnetic [7] properties. The second is responsible for the drawbacks and non-physical features of the results. If there is only one way to transit from one place to another, one should expect that the network is very similar to the linear chain; in fact, some of the properties of the Bethe lattice are as for a one-dimensional system, and a linear chain can be considered as a Bethe lattice of coordination $Z = 2$. However, as we see below, the linear chain is singular and different from the other Bethe lattices. If one chooses a given site in the Bethe lattice as being the center, the number of steps, n , to go to another site defines a shell shared by $Z(Z - 1)^{n-1}$ sites. Then, as the lattice grows, the number of sites in the surface, or the last shell, grows exponentially. The total number of sites in a Bethe lattice with n shells is $1 + Z \sum_{i=0}^{n-1} (Z - 1)^i = [Z(Z - 1)^n - 2]/(Z - 2)$. Therefore, as the number of shells tends to infinity, the proportion of surface sites tends to $(Z - 2)/(Z - 1)$.

Except for $Z = 2$, in the infinite Bethe lattice, the number of sites in the surface is not negligible, as it is in any other physical network. More than half of the sites belong to the surface and, as we see below, this unphysical fact is responsible for *all* the undesirable properties of the Bethe lattice.

In order to illustrate the procedure to solve analytically a problem in the Bethe lattice, let us take the simplest possible Hamiltonian

$$\mathcal{H} = V \sum_{i,j} |i\rangle\langle j|, \quad (1)$$

where sites i and j are nearest neighbours. The equations of motion for the Green’s function $g = (E - H)^{-1}$ are explicitly

$$Eg_{00} = 1 + Vg_{01}, \quad (2)$$

$$Eg_{01} = Vg_{00} + (Z - 1)Vg_{02},$$

$$\vdots$$

$$Eg_{0n} = Vg_{0(n-1)} + (Z - 1)Vg_{0(n+1)},$$

$$\vdots$$

where g_{0n} is the correlation between the central atom and any of the atoms in shell n . The usual way of solving this set of equations is by defining a transfer function $g_{0n} = tg_{0(n-1)}$, which is obtained by substituting it in the equations of motion and solving for a quadratic equation to give

$$t = \frac{E \pm [E^2 - 4V^2(Z - 1)]^{1/2}}{2V(Z - 1)} \quad (3)$$

and

$$g_{00} = (E - ZVt)^{-1}. \quad (4)$$

The reason for assuming that t does not depend on n is that one has neglected the surface atoms at shell N , which obey a different equation:

$$Eg_{0N} = Vg_{0(N-1)}. \quad (5)$$

This neglect is wrong, because there are as many atoms in the surface as there are in the interior. There is an elegant and computationally efficient way of solving the system with a surface, which is considering the shell-dependent transfer functions $g_{0n} = T_n g_{0(n-1)}$ and using the Tschevicheff functions of the second kind $U(X/2)$, where $X =$

$E/(V\sqrt{Z-1})$ [8]. Eq. (5) shows that $T_N = 1/(X\sqrt{Z-1})$ and iterating one finds

$$T_1 = U_{N-1}(X/2)/(U_N(X/2)\sqrt{Z-1}).$$

In this case the self-correlation function is written as $g_{00} = [E - ZVT_1]^{-1}$. As the lattice tends to infinity,

$$\begin{aligned} \lim_{N \rightarrow \infty} T_1 &= \frac{(Z-1)^{-1/2}}{X - [1/X - (1/X - \dots)]} \\ &= \frac{X \pm (X^2 - 4)^{1/2}}{2\sqrt{Z-1}} = t \end{aligned} \quad (6)$$

which means that for a large enough Bethe lattice the effect of the surface on the self-correlation is very small.

One could say that properties involving only the density of states, $\rho(E)$, are not strongly affected by the surface, since

$$\rho(E) = -(1/\pi) \operatorname{Im}[E - ZVt]^{-1} \quad (7)$$

is the same for an infinite lattice with or without a surface, giving a band of width $W = 4V\sqrt{Z-1}$, according to Eq. (3). However, there is a subtle point: if one neglects the surface, one finds that perfectly coherent states (constant and equal amplitude in all sites) at $E = \pm ZV$ exist *out* of the band, since they are eigenstates of Eq. (2), their weight being inversely proportional to the total number of atoms. If one takes into account the surface, $\pm ZV$ is *not* an eigenstate; thus, the presence of an ever-growing surface prevents the existence of coherent states and the band shrinks. One may say that even the very local properties of the Bethe lattice are affected by the surface.

The case is even worse when one attempts to calculate properties that depend on long range correlations, for instance, the infrared, Raman and inelastic neutron cross-sections [9] are related to the imaginary part of quantities like

$$\sum_N = \sum_{j=1}^N g_{0j} \quad (8)$$

which can be calculated in the Bethe lattice [10]

$$\sum_N = (1 - ZV(Z-1)^N g_{0N})/(E - ZV). \quad (9)$$

This equation shows that the result is entirely domi-

nated by the surface for $Z > 2$ because of the very large factor $(Z-1)^N$. Again, if one incorrectly neglects the surface (i.e., $g_{0N} = 0$), there appears a δ -function response at $E = ZV$, but if the surface is taken into account the weight of the δ function is zero because $g_{0N}(E = ZV) = 1/[ZV(Z-1)^N]$.

As a final point, let us say some words about the effects of the surface in the localization of states of the Bethe lattice. Let the amplitude of the wave function of a site in shell n be ϕ_n , and define a transfer matrix

$$\mathbf{T} = \begin{pmatrix} \frac{E}{(Z-1)V} & \frac{1}{(Z-1)} \\ 1 & 0 \end{pmatrix}$$

such that $\mathbf{T}\mathbf{c}_{n-1} = \mathbf{c}_n$, where $\mathbf{c}_n = (\phi_n, \phi_{n-1})$. The eigenvalues of \mathbf{T} are

$$\lambda_{\pm} = |\lambda| e^{\pm i\beta},$$

where $|\lambda| = (Z-1)^{-1/2}$ and $\beta = \arctan \sqrt{4(Z-1) - E^2}/E$. From here one defines the localization distance, ξ , through

$$|\phi_n| = |\lambda|^n = e^{-n/\xi}$$

or $\xi = 2/\ln(Z-1)$. In the linear chain the states are extended ($\xi = \infty$) but in any other Bethe lattice the states are localized, explaining the ‘discreteness’ of the continuum discussed elsewhere [11]. The same result is obtained defining the localization distance as the inverse of the Lyapunov exponent calculated with the norm of the transfer matrix. One could say that the shrinking of the band is due to this localization of states, that prevents the existence of coherent states in the Bethe lattice. The energies of the states in the band can be written as $E = 2V e^{-1/\xi} \cos \beta$ and the energy gap, Δ , between the edge of the band and ZV is

$$\Delta/V = (e^{1/\xi} - 1)^2 \geq 1/\xi^2, \quad (10)$$

which can be understood in general if one considers that for long wavelengths $E \sim p^2$, and $\xi p \geq 1$, therefore $E \geq 1/\xi^2$.

3. Bethe lattice models for glasses

We first used the Bethe lattice to study electronic and vibrational excitations in amorphous silicon [12].

Then, when I met Frank we started trying to model a random network of AX_4 units to study glasses as SiO_2 , GeO_2 , GeS_2 , BeF_2 , etc. We obtained reasonable densities of vibrational states and, as Frank was an excellent experimenter, our aim was to compare the results of the theoretical model with Frank's infrared, Raman and neutron scattering experimental spectra. Consequently, we obtained analytical expressions with Bethe lattice models to simulate and compare the measurements. The results were in general quite satisfactory [13], except for one feature that became Galeener's obsession: there were sharp peaks in the Raman spectra of some glasses, like SiO_2 , which were too narrow to be expected in a disordered structure [3]. Galeener postulated [14] that these features were the signature of regular intermediate range order structures or local defects. Thus, we started using the cluster Bethe lattice method [15] to study local defects in a cluster, as broken bonds, wrong bonds, double bonds, and square rings [16], with the surface atoms linked to appropriate Bethe lattices. The results showed that, although some of the defects could produce peaks at the right frequencies, none were as sharp as in the experiment because it was impossible to disconnect the defect from the rest of the lattice. This failure is important, because some people were assigning the sharp Raman peaks to local defects based on cluster calculations, without taking into account that they should be connected to a network.

The experimental evidence supported the idea that the sharp peaks were due to regular and almost planar threefold and fourfold rings of bonds [14]. We were able to show that threefold rings could be detached from the rest of the lattice at the Raman active mode if the ratio between central and angular forces was in a range of values, perfectly reasonable for the real materials. We reproduced the experimental peaks for threefold [17] and fourfold rings [18] with our models.

Galeener was also interested in vitreous boron oxide B_2O_3 , which is supposed to contain large numbers of threefold planar rings [19]. Therefore, we built up a Bethe lattice of rings and obtained reasonable results for the density of vibrational states [20] and for the vibrational spectroscopies [21].

At this point it is worthwhile to mention that the expressions for the spectral responses have to be

taken with care, as there are problems with δ -function unphysical responses in the Bethe lattice. For instance, if one calculates the infrared response from a simple effective point charge $e(n)$ model in amorphous silicon, one obtains

$$I = \sum_{n,m} e(n) e(m) g_{\alpha\alpha}(n, m; \omega) \\ = e^2 g \left[1 + \frac{4}{3} \left(\frac{t_{\parallel}}{1 - t_{\parallel}} + \frac{2t_{\perp}}{1 - t_{\perp}} \right) \right]^{-1},$$

where g is the displacement–displacement autocorrelation and t_{\parallel} and t_{\perp} are the components of the transfer function parallel and perpendicular to the bond direction, respectively. It can be shown that this expression gives a δ function at the maximum frequency, ω_{\max} , where there is no mode.

The Raman scattering response from a bond polarizability model can be obtained

$$R = g \frac{1}{1 + \frac{4}{3} \left[\frac{t_{\parallel}}{1 - t_{\parallel}} + \frac{2}{3} \left(\frac{t_{\perp}}{1 - t_{\perp}} + \frac{2at_{\perp}}{1 - at_{\perp}} \right) \right]},$$

where $a = \cos 3\varphi$, and φ is the dihedral angle. For random angles ($a = 0$), this expression gives a broad response highly peaked towards the optic modes, which is qualitatively correct, but for the staggered case ($a = 1$) the response is again a δ function at ω_{\max} . The neutron scattering response is more complicated to obtain [9], but the result also predicts a δ function response, which is unreasonable.

All these problems are due to the significance of the enormous surface in the Bethe lattice, but they can be corrected if instead of t one uses qt (with $q \sim e^{-1/\xi} \leq 1$) in all the above expressions. This means that the coherence of the response is destroyed within a distance of the order of ξ , due to the localization of the states.

In the models for the vibrational responses for SiO_2 we used a bond polarizability model only in a local environment around the defect, based on the fact that in a disordered solid the coherent responses fade out fairly quickly. The results for the Raman response for SiO_2 , GeO_2 and B_2O_3 agree extremely well with the experimental results. Even a study of a disordered Bethe lattice with three-coordinated and

four-coordinated boron atoms in B_2O_3 to simulate Li-doped boron oxide gives satisfactory answers [22].

4. Conclusions

The Bethe lattice has been very helpful to study glasses and amorphous solids. The theoretical results agree extremely well with experimental probes and allow one to test hypotheses about some structural and physical properties of glasses. We have presented some examples of the use of these models, almost exclusively those made in collaboration with Frank, and we mentioned the main problem when interpreting the results. No attempt has been made to mention numerous works made by other people using the Bethe lattice.

We have discussed the unphysical features of the Bethe lattice from a new point of view that relates all these features to the existence of an enormous surface. In practice, when modeling disordered solids one can avoid the surface by arguing that there is a decay in the long range correlations due precisely to disorder; therefore, one can calculate responses locally and also deal with local defects with the Bethe lattice and be confident that the results are reasonable.

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