

## Vibrational Bethe Lattice with Random Dihedral Angles

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We report an analytical solution for the vibrations of a Bethe lattice having a random and uncorrelated set of dihedral angles  $\{\phi_i\}$ . The resultant  $\phi$ -averaged Bethe lattice provides a very good fit to the Raman spectra of vitreous  $\text{SiO}_2$ , and is a powerful tool for the treatment of network and defect vibrations in this and other amorphous solids.

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The Bethe lattice<sup>1</sup> is an infinite simply connected network of points, which has proven useful as an approximate structure on which to calculate the elementary excitations of certain amorphous solids.<sup>2-8</sup> It has the ability to model exactly the highly ordered nearest-neighbor environment of each atom, while imposing no long-range translational symmetry. Unlike the real network, however, the tree-like Bethe lattice contains no closed rings of bonds, and this greatly simplifies the calculation of elementary excitations.

Vibrational calculations generally involve two kinds of forces: central (or bond-length restoring) and noncentral (or intrinsic angle restoring) forces. Sen and Thorpe<sup>7</sup> have shown that vibrations on the  $AX_2$  tetrahedral Bethe lattice are easily calculated when the noncentral forces are set to zero. In recent years, their central-forces-only approach has been exploited to investigate selection rules,<sup>9-11</sup> and then generalized to cover several different topologies.<sup>12,13</sup> However, the central-forces-only model fails completely at low (and intermediate) vibrational energies, since it drives the acoustic (and rocking) modes to zero frequency<sup>7,11</sup>; it occasionally causes serious error even at high frequencies.<sup>13</sup>

The inclusion of noncentral forces in Bethe lattice calculations has been difficult<sup>4</sup> because it has required specification of the *exact* positions of atoms on successive "branches" of the tree-like lattice. This greatly complicates the mathematics and requires a knowledge of intermediate range order including dihedral angles  $\phi_i$  that is not available for any real amorphous solid.<sup>14</sup> We circumvent this problem by performing an *analytical* average of the dynamics over a random distribution of the dihedral angles at the successive branches.

Consider the local geometry for an  $AX_2$  glass depicted in Fig. 1, where every atom of type  $A$  is at the center of a tetrahedron of  $X$  atoms. The relative position of two neighboring tetrahedra is determined by the intertetrahedral angle  $\theta$  and the dihedral angle  $\phi$ . Disorder in real glasses, like  $\text{SiO}_2$ ,

is associated with variations in *both* angles, although the typical spread in  $\phi$  is thought to be much larger than in  $\theta$ .<sup>15</sup> To approximate this, we take  $\theta$  to have a single value (its most probable one) and assume  $\phi$  to be uniformly distributed<sup>15</sup> over the range  $-\pi \leq \phi \leq \pi$ . More specifically, we will develop a solution for arbitrary  $\theta$ , on the assumption that the particular value of  $\phi$  at a given pair of bonds is uniformly distributed *and* independent of the value of  $\phi$  at any other pair of bonds: In other words, the  $\{\phi_i\}$  are *random and uncorrelated*.

The nature of our solution is shown schematically in Fig. 2, where the cones represent averaged mean fields due to the rest of the lattice. Note that every  $A$  atom is now *on the average* at a site of perfect tetrahedral symmetry, the pair of bonds arriving at any  $X$  atom still make an angle  $\theta$ , and all restoring force fields are cylindrically symmetric about each  $A-X$  bond. This means that the network looks isotropic to the  $A$  atom through any one of its bonds, as one expects in real life—*on the average*.

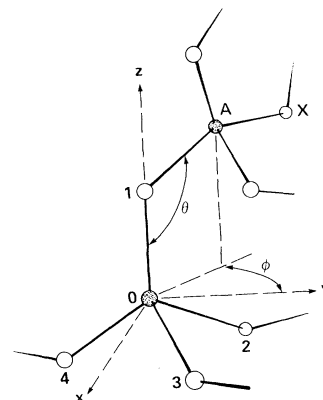


FIG. 1. The local geometry of a 4-2 connected tetrahedral  $AX_2$  glass, like  $\nu\text{-SiO}_2$ . The "intertetrahedral" angle is  $\theta$  and the "dihedral" angle is  $\phi$ . For any particular value of  $\phi$ , the  $A$  atom at the origin sees an *anisotropic* mechanical impedance at the bridging  $X$  atom.

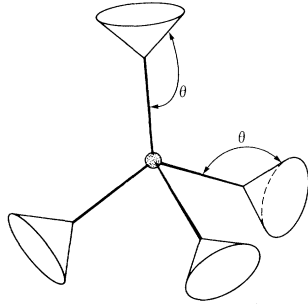


FIG. 2. The nature of our  $\phi$ -averaged solution to vibrations on the Bethe lattice. Each  $A$  atom is *on the average* at a position of *tetrahedral* symmetry; the restoring force field at an  $X$  atom is cylindrically symmetrical about the  $A$ - $X$  bond (although its strength depends on  $\theta$ ). The rest of the network looks *isotropic* to the  $A$  atom through any one of its  $A$ - $X$  bonds.

We treat dynamics on the Bethe lattice using the Born Hamiltonian.<sup>1-7:</sup>

$$V_{ij} = \frac{\alpha - \beta}{2} \{ [\bar{u}(i) - \bar{u}(j)] \cdot \hat{\delta}_{ij} \}^2 + \frac{\beta}{2} [\bar{u}(i) - \bar{u}(j)]^2. \quad (1)$$

Here,  $\bar{u}(i)$  is the displacement of the atom at site  $i$  from its equilibrium position  $\bar{\mathbf{R}}_0(i)$ ,  $\hat{\delta}_{ij}$  is a unit vector along  $\bar{\mathbf{R}}_0(i) - \bar{\mathbf{R}}_0(j)$  between nearest neighbors, and  $\alpha$  and  $\beta$  are the central and noncentral force constants, respectively. The Born noncentral force is a two-body force which Laughlin and Joannopoulos<sup>4</sup> have demonstrated can accurately simulate the more realistic Keating three-body noncentral force (except at the lowest frequencies).

The displacement-displacement Green's function for the atom with mass  $M$  at position 0 in Fig. 1, can be written in matrix notation as

$$G_{00} = [M\omega^2 - \sum_{i=1}^4 \langle K_i \rangle]^{-1}, \quad (2)$$

where  $\omega$  is the vibrational frequency and the  $\langle \dots \rangle$  means an *unweighted average over  $\phi$* . If, as in Fig. 1, the bond from 0 to 1 is along the  $z$  axis, then (after much algebraic manipulation<sup>16</sup>) the  $\phi$ -averaged self-energy due to that bond is found to be

$$\langle K_1 \rangle = -D_1 + D_1 \langle A_1^{-1} \rangle D_1 + \langle D_1^{\text{eff}} T_1 \rangle. \quad (3)$$

In this expression,

$$D_1 = \begin{bmatrix} -\beta & 0 & 0 \\ 0 & -\beta & 0 \\ 0 & 0 & -\alpha \end{bmatrix} \quad (4)$$

is the interaction matrix between atoms 0 and 1,

and is independent of  $\phi$ . Also,

$$A_1 = m\omega^2 + D_1 + \Phi^{-1} \Theta^{-1} D_1 \Theta \Phi, \quad (5)$$

where  $m$  is the mass of the bridging  $X$  atom and  $\Theta$  and  $\Phi$  are rotation matrices (by angles  $\theta$  and  $\phi$ , respectively) that create the geometry of Fig. 1 from an arrangement where the two neighboring tetrahedra coincide. And finally

$$D_1^{\text{eff}} = D_1 A_1^{-1} \Phi^{-1} \Theta^{-1} D_1, \quad (6)$$

while the transfer matrix  $T_1$  is defined as in Ref. 5 by

$$T_1 G_{00} = G_{01}, \quad (7)$$

where  $G_{01}$  is the correlation between atoms 0 and  $A$  (through the bridging atom 1 in Fig. 1). Note that  $A_1$ ,  $D_1^{\text{eff}}$ , and  $T_1$  are dependent on  $\theta$  and  $\phi$  and are *not* diagonal. Nevertheless, it is found that the  $\phi$ -averaged  $\langle A_1^{-1} \rangle$ ,  $\langle D_1^{\text{eff}} T_1 \rangle$ , and all  $\langle K_i \rangle$  have the same diagonal form as  $D_1$ . Their elements can then be obtained by a simple iterative procedure<sup>16</sup> involving only scalar equations. Having determined the  $\langle K_i \rangle$  one can calculate all the remaining elements of the full Green's function  $G$ .<sup>16</sup>

To illustrate the use and accuracy of the theory, we will apply it to vitreous  $\text{SiO}_2$  for which accurate infrared,<sup>17,18</sup> Raman,<sup>17</sup> and inelastic neutron scattering spectra<sup>11</sup> have been published.

The total vibrational density of states (VDOS) per  $AX_2$  unit is given by

$$\rho(\omega) = -(2\omega/3\pi) \text{Im} [M(\text{Tr} G_{00}) + 2m(\text{Tr} g_{11})], \quad (8)$$

where  $g_{11}$  is the autocorrelation at an oxygen site, easily derived<sup>16</sup> from the results already determined. Results for  $\nu$ - $\text{SiO}_2$  are shown in Fig. 3(a) for  $M = 28$  amu,  $m = 16$  amu,  $\theta = 154^\circ$ ,  $\alpha = 507$  N/m, and  $\beta = 78$  N/m.

The polarized portion of the Raman response can be approximated<sup>10</sup> by

$$I_{\text{red}}^{\text{pp}}(\omega) \sim (-\omega) \text{Im} \sum_{i,j} \sum_{\mu,\nu} v_{\mu}^i G_{\mu\nu}(i,j) v_{\nu}^j, \quad (9)$$

where  $v_{\mu}^i$  is the  $\mu$ -Cartesian component of the sum of all unit vectors along each bond arriving to site  $i$ . This expression involves *infinite* summations which lead to incorrect results *on the Bethe lattice* because the number of distant sites is unphysically large.<sup>19</sup> On the basis that disorder "screens" longer range correlations in the real glass (and to avoid false response from the distance sites) we here restrict such summations to the  $\beta$  bonds associated with a five-atom  $AX_4$  cluster. The results for the parame-

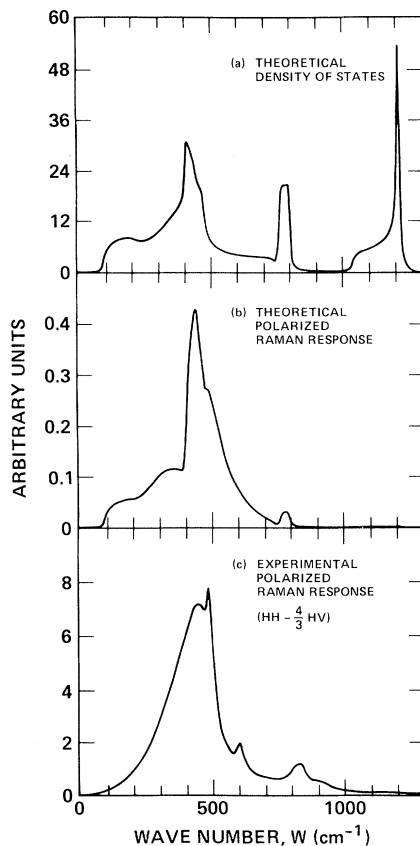


FIG. 3. (a) The theoretical density of states and (b) the calculated polarized Raman response for  $\nu$ -SiO<sub>2</sub>, using  $\theta = 154^\circ$ ,  $\alpha = 507$  N/m, and  $\beta = 78$  N/m. These parameters make an optimum fit of (b) to the broad features of (c) the experimental response. The two unpredicted sharp features in (c) are due to defects in the real glass structure (Ref. 14).

ters given earlier are shown in Fig. 3(b). All values of the  $\theta$ ,  $\alpha$ ,  $\beta$  parameter space were searched in order to achieve a "best fit" to the Raman data,<sup>17</sup> shown in Fig. 3(c). The parameters cited are those which best fitted the central frequencies of the broad experimental lines at 420 and 820 cm<sup>-1</sup> and the width of the 420 cm<sup>-1</sup> line. The values of  $\alpha$  and  $\beta$  are close to those deduced by other means.<sup>9,11</sup> The value of  $\theta = 154^\circ$  is remarkably close to the latest diffraction estimate<sup>20</sup> of  $152^\circ$ .

The overall shape of the Raman spectrum is reproduced rather well throughout the intermediate frequency range of Fig. 3(b) (100–800 cm<sup>-1</sup>). That the relative strength of the broad bands at 420 and 820 cm<sup>-1</sup> is approximately correct suggests that our truncation of Eq. (9) is a useful approximation. [This relative strength is slightly better when we include a second shell of bonds in Eq. (9).] Else-

where<sup>16</sup> we will show a significant reduction of the remaining differences, obtained by (1) averaging over a realistic distribution of  $\theta$ , and (2) adding a small imaginary component to the frequency  $\omega$  (to correct for the known tendency of the Bethe lattice to produce overly narrow bands<sup>2-6</sup>). These two refinements smooth the extra "bumps" in the theoretical spectra, and produce near-perfect agreement<sup>16</sup> of our VDOS with those of the large-cluster calculations of Bell and co-workers.<sup>21</sup> Our results (and those of the large-cluster calculations) are expected to be less accurate at low frequencies ( $< 100$  cm<sup>-1</sup>) because of certain deficiencies of the Born  $\beta$  forces<sup>4,7,11</sup> and at high frequencies ( $> 800$  cm<sup>-1</sup>) because of the neglect of Coulomb forces.<sup>9,11,17</sup>

The sharp peaks at 495 and 606 cm<sup>-1</sup> in the Raman data are *not* reproduced by the theory, because they arise from "defects" known to exist in the glass.<sup>14</sup> These "defects" may actually be regular rings embedded in the otherwise disordered glass structure,<sup>14</sup> and the present  $\phi$ -averaged Bethe lattice is being used to model the dynamics of such rings.

Because the scalar iterative calculations leading to Figs. 3(a) and 3(b) are so efficient, it has proved economical for us to investigate the vibrational natures of numerous broken bond, wrong bond, and regular ring defects in  $\nu$ -SiO<sub>2</sub>. We have also been able to extend the  $\phi$ -averaged Bethe-lattice technique to model amorphous materials having other network topologies, such as those listed in Refs. 13 and 14. The technique is powerful.

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