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Effect of second-nearest-neighbor forces on the vibrations of amorphous SiO_2

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A method is presented of solving for the vibrational Green's function of a silicon-dioxide Bethe lattice when it contains second-nearest-neighbor interactions. The method is used to find the density of states of a Bethe lattice constructed with a Keating Hamiltonian. The primary effect of the second-nearest-neighbor interactions is a softening of the rocking bands below 450 cm^{-1}.

In a recent publication,[1] we showed how a continued-fraction technique could be used to calculate the vibrational Green's function of a silicon-dioxide Bethe lattice constructed using a nearest-neighbor Born[2] force law. In this publication we show how a similar technique can be used when the force law involves second-nearest-neighbor interactions as well.

The inclusion of non-nearest-neighbor interactions into a Bethe lattice increases its complexity considerably by introducing rings of interactions into the Hamiltonian. For example, two oxygen atoms bonded to the same silicon atom can now interact with each other, as well as with the silicon atom to which they are bonded, to form a threefold ring. It is ordinarily the absence of rings of interactions in the Bethe lattice which facilitates its solution, rather than the absence of rings of bonds. There is no distinction between these two when only nearest-neighbor interactions are included. Even though it contains rings of interactions, however, such a system may generally be solved,[3] provided the atoms are consolidated into larger units which interact only when they are adjacent. This procedure regularly produces an intractable numerical problem. In silicon dioxide, however, the twofold coordination of the oxygen atoms makes a solution with second-nearest-neighbor interactions practical.

In Fig. 1 we show the silicon-dioxide Bethe lattice partitioned into units which we will henceforth refer to as bubbles. Each bubble interacts only with itself and with its nearest neighbors. Interaction in this case means an atom in one unit interacting with any atom in the other one. If one now thinks of a bubble as a site with 12 degrees of freedom, then the system transforms into an ordinary tetrahedrally coordinated Bethe lattice with the exception that there are now *four* distinct kinds of *directed* sites. The four oxygen atoms in a tetrahedron are distinguishable, causing there to be four distinct kinds of bubble. The bubbles also point outward in a way that is evident in Fig. 1.

In Fig. 1 there is a central bubble which is different from all the rest. The inclusion of a central bubble is necessitated by the artificial directionality induced by the partitioning. The atoms in the central bubble are not physically distinguishable from the atoms in the periphery, and it is important to emphasize that the solution to the vibration problem is independent of the location of the central bubble. The physical system, in this case, has more symmetry than the formalism would indicate.

Since the bubbles are basically tetrahedra, we assign to them local coordinates as discussed previously.[1] As before, we number the bond directions in a tetrahedron 1–4, and pick an outward bond-matching convention $\nu \rightarrow \sigma(\nu)$, where ν runs from 1 through 4 and σ is a cyclic permutation. We now number the four kinds of bubble by the direction of the bond which points into them. For example, if the cyclic permutation is $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$, then a bubble which is missing a 2 oxygen atom is a 1 bubble, one that is missing a 3 oxygen

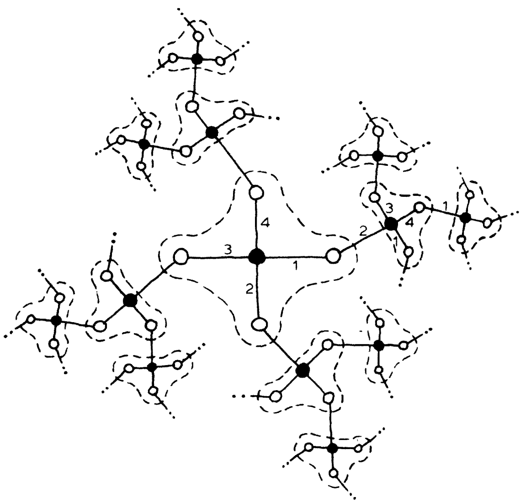

FIG. 1. Diagram of silicon-dioxide Bethe lattice showing how it can be partitioned to remove second-nearest-neighbor interactions.

atom is a 2 bubble, and so on.

Given that the displacements of the atoms in a bubble are expressed in the bubble's local coordinates, the dynamical matrix elements are well defined and can presumably be obtained. The part of the dynamical matrix connecting the central bubble with itself we denote A. The part connecting the central bubble with its nearest neighbor in the ν_1 direction we denote D_{ν_1}. The part connecting this nearest-neighbor bubble with itself we denote A_{ν_1}. The part connecting this bubble with its nearest neighbor in the ν_2 direction we denote $D_{\nu_1\nu_2}$. Since the Bethe lattice repeats from this point out, there are no more independent matrix elements. Note that ν_2 cannot be $\sigma(\nu_1)$, so that there are only twelve matrices $D_{\nu_1\nu_2}$. A is a 15×15 matrix, the D_ν are 15×12 matrices, and all the rest are 12×12.

As before, we index the submatrices of the vibrational Green's function by the sequence of directions $\nu_1, \nu_2, \ldots, \nu_n$ used in traveling from the central bubble to the one in question. G_0 denotes the part of the Green's function connecting the central bubble with itself. $G_1^{\nu_1}$ denotes the part connecting the central bubble to its neighbor in the ν_1 direction. $G_2^{\nu_1,\nu_2}$ denotes the part connecting to a second-nearest neighbor, and so on. G_0 is a 15×15 matrix, and all the rest are 12×15.

We now have the following sequence of equations:

$$(\omega^2 - A)G_0 = 1 + \sum_{\nu_1} D_{\nu_1} G_1^{\nu_1}, \tag{1}$$

$$(\omega^2 - A_{\nu_1})G_1^{\nu_1} = D_{\nu_1}^t G_0 + \sum_{\nu_2 \neq \sigma(\nu_1)} D_{\nu_1\nu_2} G_2^{\nu_1,\nu_2}, \tag{2}$$

$$(\omega^2 - A_{\nu_2})G_2^{\nu_1,\nu_2} = D_{\nu_1\nu_2}^t + \sum_{\nu_3 \neq \sigma(\nu_2)} D_{\nu_2\nu_3} G_3^{\nu_1,\nu_2,\nu_3} \tag{3}$$

$$\begin{matrix} \cdot & & \cdot \\ \cdot & & \cdot\ , \\ \cdot & & \cdot \end{matrix}$$

$$(\omega^2 - A_{\nu_n})G_n^{\nu_1,\ldots,\nu_n} = D_{\nu_{n-1}\nu_n}^t G_{n-1}^{\nu_1,\ldots,\nu_{n-1}} + \sum_{\nu_{n+1} \neq \sigma(\nu_n)} D_{\nu_n\nu_{n+1}} G_{n+1}^{\nu_1,\ldots,\nu_{n+1}}. \tag{4}$$

This sequence has a solution of the form

$$G_{n+1}^{\nu_1,\ldots,\nu_{n+1}} = \Phi_{\nu_{n+1}\nu_n} G_n^{\nu_1,\ldots,\nu_n}, \tag{5}$$

provided that 12 transfer matrices $\Phi_{\mu\nu}$ satisfy

$$(\omega^2 - A_\nu)\Phi_{\nu\rho} = D_{\rho\nu}^t + \sum_{\mu \neq \sigma(\nu)} D_{\nu\mu} \Phi_{\mu\nu} \Phi_{\nu\rho} \tag{6}$$

or

$$\Phi_{\nu\rho} = \left(\omega^2 - A_\nu - \sum_{\mu \neq \sigma(\nu)} D_{\nu\mu} \Phi_{\mu\nu}\right)^{-1} D_{\nu\rho}^t\ . \tag{7}$$

These equations may be solved as before by integrating the continued fraction starting at $\Phi_{\mu\nu} = 0$. Note that the quantity in parentheses depends only on ν. There are thus only four independent quantities, these corresponding physically to the Green's function of a terminated Bethe lattice restricted to the bubble at the terminus. If we let

$$F_\nu = \left(\omega^2 - A_\nu - \sum_{\mu \neq \sigma(\nu)} D_{\nu\mu} \Phi_{\mu\nu}\right)^{-1}, \tag{8}$$

then we have

$$F_\nu = \left(\omega^2 - A_\nu - \sum_{\mu \neq \sigma(\nu)} D_{\nu\mu} F_\mu D_{\nu\mu}^t\right)^{-1}. \tag{9}$$

For the central bubble we have

$$G = \left(\omega^2 - A - \sum_\mu D_\mu F_\mu D_\mu^t\right)^{-1}. \tag{10}$$

In order to illustrate the validity of the method we have constructed and solved a Bethe lattice for silicon dioxide using a Keating[4] Hamiltonian. The Keating Hamiltonian assigns a quadratic potential energy to bond-length and bond-angle distortions, rather than to bond-length and bond-*direction* distortions, as does the simpler Born[2] Hamiltonian. For this reason it is rotationally invariant, and therefore more realistic than the Born Hamiltonian. For a bond-length distortion Δr we have

$$\Delta U = \tfrac{1}{2} K_r (\Delta r)^2, \tag{11}$$

while for every O-Si-O angle distortion $\Delta \cos\theta$ we have

$$\Delta U = \tfrac{1}{2} K_s (b \Delta \cos\theta)^2, \tag{12}$$

where b is the bond length. Following Kleinman and Spitzer,[5] we set the Si-O-Si angle distortion energy to zero as a fitted parameter. We use Kleinman and Spitzer's value for K_r, 4.32×10^5 dyn/cm, and a value for K_s of 0.27×10^5 dyn/cm. This value, slightly lower than the 0.29×10^5 dyn/cm suggested by Kleinman and Spitzer, was picked to make the frequency of the third A_1 mode of quartz agree with experiment.

In Fig. 2, we compare the density of states of the Keating Bethe lattice with that of quartz constructed using the same Hamiltonian, and with previous calculations performed using the Born Hamiltonian.[1] The distinctions between the crystal and Bethe-lattice densities of states are again due to the presence of 12-fold rings in the crystal. The

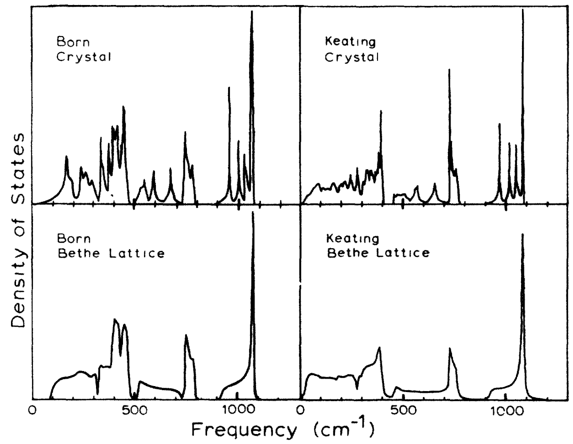

FIG. 2. Comparison of Keating Bethe-lattice density of states against that of α-quartz constructed with the same Hamiltonian, and against similar calculations performed using a Born Hamiltonian.

high-frequency band peaking at 1080 cm^{-1} is virtually identical to that produced by the Born Hamiltonian. These vibrations are dominated by the bond-stretching forces, which are the same in both models. The siliconlike states at 750 cm^{-1} are unchanged for the same reason. On the other hand, the low-frequency bands are broadened and shifted downward slightly in the Keating Bethe lattice. These bands are predominantly angle-distorting vibrations[1] and are sensitive to changes in the angular force constants. The fact that they move downward when the Keating Hamiltonian is substituted for the Born Hamiltonian indicates that the SiO_4 units in the glass tend to be rigid at these frequencies and that the bond directions tend to vary without distorting O-Si-O angles. The Keating model agrees more closely with experiment at these frequencies.[5] Overall, however, the Keating and Born Bethe lattices are remarkably similar, and it is clear that in most respects the simpler theory is an excellent approximation to the more realistic one. The overall similarity of the predictions of the two Hamiltonians has also been observed by Alben *et al.*[6] in calculations performed for silicon.

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[1] R. B. Laughlin and J. D. Joannopoulos, Phys. Rev. B 16, 2942 (1977).

[2] M. Born, Ann. Phys. (Leipz.) 44, 605 (1914).

[3] J. D. Joannopoulos, Phys. Rev. B 16, 2764 (1977).

[4] P. N. Keating, Phys. Rev. 145, 637 (1966).

[5] D. A. Kleinman and W. G. Spitzer, Phys. Rev. 125, 16 (1962).

[6] R. Alben, D. Weaire, J. E. Smith, and M. H. Brodsky, Phys. Rev. B 11, 2271 (1975).