COULOMB EFFECTS IN GLASSES

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Numerical simulation techniques were used to study the vibrational properties of random networks. The networks, containing up to 1500 ions, were generated by the introduction of a large number of defects in regular crystals. Periodic boundary conditions were imposed. Long-range Coulomb effects were included for the first time. Our simulations reveal the existence of long-wavelength optic-type excitations which exhibit LO-TO splitting similar to crystalline solids. The LO-mode has a negative dispersion, whereas almost no dispersion is observed for the TO-mode. In the density of states, the TO-mode shows up as a peak, whereas the LO-mode defines the high frequency band edge.

1. INTRODUCTION

Almost a decade ago Galeener and Lucovsky \(^1\) argued that in glasses, such as vitreous silica and germanium dioxide, it is necessary to include long-range Coulomb interactions to account for the observed vibrational spectra. They argued that the long-range Coulomb interactions give rise to longitudinal and transverse optic excitations with wavelengths much larger than the nearest neighbor spacing. These can be observed as separate peaks in the optical spectra of these materials.

On the other hand it can be argued that long wavelength optic excitations require structural coherence over a large region in the material, which is generally not present in a glass. Alternative explanations have been put forward ascribing some of the peaks in the Raman spectra to localized modes involving oxygen ions on interior surfaces in the glass. \(^2\)

In this paper we present the results of numerical simulations of a random network containing 512 cations and 1024 anions. Periodic boundary conditions were imposed on our network. The results show unambiguously that optic excitations with wavelengths much longer than the nearest neighbor separation can propagate in amorphous media. Moreover an LO-TO splitting is observed similar to crystalline materials.

2. METHODOLOGY

A cube, containing 512 atoms of silicon on a diamond lattice, was made amorphous by the introduction of large numbers of topological defects of the kind suggested by Wooten and Weaire. \(^3,4\) We continued to introduce these
defects until a Fourier analysis of the density showed that all Bragg reflections of the original diamond lattice had merged into the background.\textsuperscript{5} Periodic boundary conditions were imposed on the system, so that an infinite periodic network with 512 atoms per unit cell was produced. Oxygen atoms were placed between each pair of silicon atoms and the network was relaxed with a potential of the form:

$$ V = V_0 + V_R + V_k $$

$$ V_c = \frac{1}{2} \sum_{i,j} \frac{q_i q_j}{r_{ij}^2} $$

$$ V_R = \sum_{(i,j)} \text{exp}(-r_{ij}/\sigma) $$

$$ V_k = \frac{3q}{8d^2} \sum_{k \alpha} \left( \frac{r_{k \alpha} - d}{2} \right)^2 + \frac{3}{8d^2} \sum \frac{\theta}{\rho} \left( \frac{r_{k \alpha} - r_{k \alpha'}}{2} \cos \theta \right)^2 $$

Here $V_c$ describes the Coulomb interactions between the ions; $q_i$ is the charge of ion $i$ in units of $e$; $r_{ij}$ is the distance between ions $i$ and $j$. An exponential repulsion $V_R$ acts between unlike ions to prevent them from collapsing into each other. The brackets $\langle \ldots \rangle$ denote that the sum is over pairs of unlike ions only. The parameter $\Lambda$ measures the strength of the repulsion and $\sigma$ its steepness. The Keating potential\textsuperscript{8} $V_k$ describes the change in energy due to bond stretching and angular forces. Here $k$ refers to an ion and $\alpha$ to a near neighbor vector. The angular brackets $\langle \ldots \rangle$ denote that each pair or triple of ions is only counted once.

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**TABLE I. PARAMETERS IN THE POTENTIAL**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>85 N/m</td>
</tr>
<tr>
<td>$d$</td>
<td>1.65 Å</td>
</tr>
<tr>
<td>$\Lambda$</td>
<td>635 eV</td>
</tr>
<tr>
<td>$q_+$</td>
<td>4</td>
</tr>
<tr>
<td>$\beta_+$</td>
<td>30 N/m</td>
</tr>
<tr>
<td>$\beta_-$</td>
<td>30 N/m</td>
</tr>
<tr>
<td>$\theta_+$</td>
<td>109.5°</td>
</tr>
<tr>
<td>$\theta_-$</td>
<td>156°</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>0.3 Å</td>
</tr>
<tr>
<td>$q_-$</td>
<td>-2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>0.6 e</td>
</tr>
</tbody>
</table>

The parameters in the potential were adjusted to reproduce the LO-T0 splitting observed in $\alpha$-quartz\textsuperscript{7}: $\omega_{LO}^{\alpha}$ 1235 cm\textsuperscript{-1} and $\omega_{T0}^{\alpha}$ 1072 cm\textsuperscript{-1}. Values of the parameters are collected in Table I. It should be noted that our potential does not reproduce other parts of the vibrational spectrum of $\alpha$-quartz very well. It appears to be difficult to reproduce both the LO-T0 pair of branches in $\alpha$-quartz and the other branches,\textsuperscript{8} mainly because of the large ionic charge required to produce a splitting of 163 cm\textsuperscript{-1}.

The network was relaxed with the method of conjugate gradients.\textsuperscript{9} Ewald's sum\textsuperscript{10} was used to evaluate the Coulomb energy of the network. The energy was monitored as a function of the density $\rho$ and found to be minimal at
\[ \rho = 2.20 \text{ gm/cm}^3, \text{ which agrees well with the experimental density of } \nu\text{-SiO}_2. \]

The mean nearest neighbor separation came out to be 1.65 \pm 0.04 \text{ Å}. Mean values of 109.5^\circ \text{ and } 151.0^\circ \text{ were obtained for the O-Si-O and Si-O-Si angles respectively}. The spread in the oxygen angles was reasonable with r.m.s. \Delta \theta = 12.5^\circ. \text{ The angular deviations at silicon, with r.m.s. } \Delta \theta = 9.8^\circ, \text{ were considerably larger than observed experimentally. This seems to be a general problem with networks constructed in this manner.}^{3,4} \text{ The radial distribution function was rather insensitive to the addition of Coulomb forces.} \]

We have used the equation of motion technique \textsuperscript{11} to compute the relevant response functions. The principle of the method is as follows. The potential of eq. 1 is expanded to second order in the displacements of the ions from their equilibrium positions in the relaxed network. The ions are given initial displacements \( \bar{u}_i^0 \) and the displacements \( u_i(t) \), resulting from the harmonic equations of motion, are computed with the method of molecular dynamics. The initial velocities \( \bar{u}_i^0 \) are set to zero. Verlet's \textsuperscript{12} algorithm was used for the integration of the equations of motion. Having obtained the ionic displacements \( u_i(t) \) up to \( t = T \) we calculate the spectral function:

\[ G(\omega) = \frac{2}{\pi} \int_0^T dt \ e^{-3(t/T)^2} \cos \omega t \sum_{i=1}^N A_i \cdot u_i(t) \]  \hspace{1cm} (2)

The choice of the quantities \( A_i \) and \( u_i^0 \) is determined by the response function one seeks to compute. For example, if we choose random phase factors for the \( z \)-components \( u_{1z}^0 \) and \( A_{1z} \):

\[ u_{1z}^0 = A_{1z} = \sqrt{2} \cos \theta_{1z} \]  \hspace{1cm} (3)

\( \theta_{1z} \) being a random angle, \( G(\omega) \) is the density of states. Similarly if we choose:

\[ u_1^0 = q_1 \hat{E} / m_1 ; \ A_1 = q_1 \hat{E} \]  \hspace{1cm} (4)

where \( \hat{E} \) is a unit vector in the direction of polarization of incident light, \( G(\omega) \) is related to the infrared absorption coefficient \( \alpha_i(\omega) \) of the sample. A derivation of these equations is given by Bear and Alben. \textsuperscript{11} The generalization to fields of wavevector \( \vec{k} \) and frequency \( \omega \) is immediately obvious. Setting

\[ u_1^0 = q_1 \hat{E}_k / m_1 \ e^{-i \vec{k} \vec{r}_1^0} ; \ A_1 = q_1 \hat{E}_k / e^{-i \vec{k} \vec{r}_1^0} ; \ \hat{E}_k^2 = 1 \]  \hspace{1cm} (5)
we compute the transverse \( G_{\parallel}(k, \omega) \) and longitudinal \( G_{\perp}(k, \omega) \) response functions. The periodic boundary conditions impose the usual restrictions on the wave vectors \( k \).

Because of the long-ranged interactions between the displacement dipoles we have computed the dipolar energy by summing over all periodic replicas of our network. Following de Leeuw et al. \(^{10} \) we find that the dipolar part of the energy can be written as the sum of two parts:

\[
V_{dd} = V_{EW} + V_{SE} \quad \quad (6)
\]

Here \( V_{EW} \) is the well-known result of Ewald for the Coulomb energy of dipoles in a lattice. \(^{13} \) The second term \( V_{SE} \) in (6) contains the influence of the shape and surroundings of our periodic system, as discussed fully in ref. 10 and 14. By suitably adjusting \( V_{SE} \) we can obtain the transverse or longitudinal optic response at \( k = 0 \). In particular, setting \( V_{SE} = 0 \) (which corresponds to an infinite isotropic system) yields the transverse optic response function. For a slab geometry, with the slab perpendicular to the \( z \)-direction, we have:

\[
V_{SE} = 2\pi \left( \sum \frac{1}{1} \right)^2 \quad \quad (7)
\]

where \( V \) is the volume of the supercell. In this case the prescription (4) yields the longitudinal optic response at \( k = 0 \) for \( k = (0,0,1) \).

3. RESULTS

We have computed the transverse \( G_{\parallel}(k, \omega) \) and longitudinal \( G_{\perp}(k, \omega) \) response functions with the prescription (5) for \( k = 2\pi (0,0,n)/L \); \( n = 1,2,3,5 \). Two simulations are necessary for each response function, corresponding to respectively the real and imaginary parts of the complex exponent in (5). The duration of our simulation was 300 time intervals of \( 0.2 \times 10^{-14} \) sec, leading to a broadening of about 50 cm\(^{-1}\). The results are shown in Fig. 1. The transverse optic response function \( G_{\parallel}(k, \omega) \) in Fig. 1a shows a well-defined optic excitation at \( \omega = 1080 \) cm\(^{-1}\), essentially at the same position as in \( \alpha \)-quartz. Furthermore the peaks occur at the same frequency irrespective of the wave-number \( k \) and the width remains approximately constant (FWHM = 75 cm\(^{-1}\) after deconvoluting the broadening function). The intensity of the peak around 1080 cm\(^{-1}\) decreases with increasing wave number in favor of a larger participation of modes in the broad band \( \omega < 1000 \) cm\(^{-1}\). Similarly a well-defined longitudinal optic excitation is observed for \( \omega > 1000 \) cm\(^{-1}\) for \( G_{\perp}(k, \omega) \) in Fig. 1b. Again the intensity decreases with increasing wave number. A negative dispersion is observed, the peak frequency decreasing from \( \omega = 1220 \) cm\(^{-1}\) at \( k = 0.22 \) Å\(^{-1}\) to \( \omega = 1095 \) cm\(^{-1}\) at \( k = 1.10 \) Å\(^{-1}\). At the same time the FWHM increases from \(-50 \) cm\(^{-1}\) to 100 cm\(^{-1}\) (after deconvolution).
Fig. 1  Transverse (a) and longitudinal (b) optic responses for wave vectors $k = 2\pi (0, 0, k)/L$ where L is the boxtight. The resolution is marked in the top right-hand side of the figure. In (c) the $k=0$ responses are shown for the slab geometry and in (d) we show the density of states.

In Fig. 1d and h we display the density of states for our model together with the response functions $G_k(k, \omega)$ as $k \neq 0$. They were calculated from simulations of 600 time intervals. $G_k(0, \omega)$ is obtained by setting $V_s = 0$ in Eq. 6, whereas $G_k(0, \omega)$ is obtained by choosing $V_s$ corresponding to slab geometry. We have checked that both forms of $V_s$ lead to the same density of states and the same response functions at $k \neq 0$. Clearly an LO-TO splitting similar to crystalline materials is observed. The frequencies are close to the values observed in α-quartz: $\omega_{LO} = 1230 \text{ cm}^{-1}$, $\omega_{TO} = 1080 \text{ cm}^{-1}$. $G_k(0, \omega)$ is seen to be very sharp with a FWHM of 35 cm$^{-1}$ (after deconvolution). Its peak frequency coincides with the band edge in the density of states. This position and the sharpness of the response agree well with the experimentally observed features of the dielectric function.$^1$ The transverse optic frequency $\omega_{TO}$ falls in the middle of the band. Because of the strongly negative dispersion of the LO-modes the splitting does not lead to a double peak in the density of states as is observed experimentally.$^{16}$ Other modes must contribute to the band at $\omega > 1000 \text{ cm}^{-1}$ and it is the relative position of these modes which determines
the shape of the band. We intend to study this further by varying the
terms in the potential.

The density of states does not resemble the measured spectrum very well.
This is due to the excessively large point-charge necessary to reproduce the
LO-TO splitting in α-quartz. Presently efforts are under way to improve this.

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