Coulomb Splittings in Glasses

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The equation-of-motion technique has been used to study the optic response functions of a computer-generated periodic random network containing 1536 ions. Long-range Coulomb effects were included for the first time. Our results show unambiguously the existence of an LO-TO splitting. The long-wavelength LO response function peaks at the band edge in the density of states and is very sharp, whereas the long-wavelength TO response function peaks at a lower frequency and is much broader.

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The vibrational properties of glassy materials, such as v-SiO$_2$ and v-BeF$_2$, have been the focus of a number of investigations, experimental as well as theoretical,[1] in recent years. The bonding in these materials has a partially *ionic* character, so that we may expect that long-range Coulomb effects play an important role in their vibrational properties. This was first stressed by Galeener and Lucovsky[2] almost a decade ago. They argued that Coulomb interactions lead to a splitting between long-wavelength longitudinal (LO) and transverse (TO) optic modes similar to that observed in crystalline materials. These can be observed as separate peaks in the infrared and Raman spectra of these materials.

Earlier numerical studies[3] on large random clusters did not give evidence for the separated peaks observed in the optical spectra of these materials because Coulomb interactions were not included. More recently Pick and Yvinec[4] studied the vibrational properties of a random system containing *polar molecules* and claimed an LO-TO splitting. Their results are misleading and at variance with ours, because they ignored the infinite range of the Coulomb force.

We have used the equation-of-motion technique to investigate the vibrational properties of a random network with chemical formula unit AX_2.[5] Our results provide the first unambiguous evidence for an LO-TO splitting in these systems. Further, we show that in the long-wavelength limit the LO response peaks at the *band edge* in the density of states, as observed experimentally[2,6] in vitreous silica (v-SiO$_2$).

A diamond cubic crystal, containing 512 atoms, was made amorphous by the introduction of topological defects of the kind suggested by Wooten and Weaire.[7] We continued introducing these defects until all Bragg reflections of the original lattice were reduced in intensity to the general noise level in the static structure factor $S(\mathbf{k})$ of the system. An additional 1024 twofold-coordinated atoms were then placed along the bonds connecting the original atoms. Periodic boundary conditions were maintained throughout this procedure. The atoms were relaxed with a potential

$$U=\frac{3}{8}\frac{\alpha}{d^2}\sum_{\langle l\Delta\rangle}[\mathbf{r}_l(\Delta)^2-d^2]^2+\frac{3}{8}\sum_{\langle l\Delta\Delta'\rangle}\frac{\beta_l}{d^2}[\mathbf{r}_l(\Delta)\cdot\mathbf{r}_l(\Delta')-d^2\cos\Theta_l]^2 + \sum_{\langle lm\rangle}A_{lm}\exp\left(-\frac{|\mathbf{r}_{lm}|}{\rho}\right)+\frac{1}{\epsilon_\infty}\sum_{\langle lm\rangle}\frac{q_l q_m}{|\mathbf{r}_{lm}|}. \tag{1}$$

The first two terms in Eq. (1) describe the energy change due to bond stretching (α) and angular forces (β) and have the form suggested by Keating.[8] Here $\mathbf{r}_l(\Delta)$ is a vector from an ion l to a near neighbor Δ. The third term describes the repulsion between the ions l,m separated by $\mathbf{r}_{lm}$ and is necessary for stability when the Coulomb forces are included. The last term describes the Coulomb interactions between ions with charges q_l screened by the high-frequency dielectric constant ϵ_∞ due to the electronic response of the system. Values of the parameters are given in Table I and were chosen to correspond roughly to v-SiO$_2$. The structural features of the network are collected in Table II.

TABLE I. Parameters in the potential.

$\alpha=8.5\times10^4$ dyn/cm	$A_{++}=A_{--}=0$
$\beta_+=\beta_-=3\times10^4$ dyn/cm	$A_\pm=1.0174\times10^{-9}$ erg
$d=1.65$ Å	$\rho=0.3$ Å
$\theta_+=109.5°$	$q_+=-2q_-=3.67e$
$\theta_-=155°$	$\epsilon_\infty=2.10$

Let $G_{\alpha\beta}(l,l';\omega)$ denote the usual thermal Green's function[9]:

$$G_{\alpha\beta}(l,l';\omega)=\langle\langle u_\alpha(l);u_\beta(l')\rangle\rangle_\omega, \tag{2}$$

where α is a Cartesian component of the displacement $\mathbf{u}$ of atom l from its equilibrium position $\mathbf{R}_l$, so that $\mathbf{r}_l = \mathbf{R}_l + \mathbf{u}_l$. We assume that the polarizability is due entirely to the ionic charges, so that the longitudinal, $\epsilon_L(\mathbf{k},\omega)$, and transverse, $\epsilon_t(\mathbf{k},\omega)$, dielectric functions can be written as

$$\epsilon_L(\mathbf{k},\omega) = \epsilon_\infty - \frac{4\pi}{\Omega} \sum_{mn\,\alpha\beta} q_m q_n \hat{k}_\alpha^{\parallel} \hat{k}_\beta^{\parallel} G_{\alpha\beta}(m,n;\omega) \exp(i\mathbf{k}\cdot\mathbf{R}_{mn}), \tag{3}$$

$$\epsilon_t(\mathbf{k},\omega) = \epsilon_\infty - \frac{4\pi}{\Omega} \sum_{mn\,\alpha\beta} q_m q_n \hat{k}_\alpha^{\perp} \hat{k}_\beta^{\perp} G_{\alpha\beta}(m;n;\omega) \exp(i\mathbf{k}\cdot\mathbf{R}_{mn}), \tag{4}$$

Here $\hat{k}_\alpha^{\parallel}$ is the α component of a unit vector *parallel* to the wave vector $\mathbf{k}$, whereas $\hat{k}_\alpha^{\perp}$ denotes the α component of any unit vector *perpendicular* to $\mathbf{k}$. In a macroscopically isotropic solid, all choices of $\hat{k}^{\perp}$ lead to the same $\epsilon_t(\mathbf{k},\omega)$. The volume of the system is $\Omega = L^3$.

The equation-of-motion technique allows us to compute the imaginary parts $\epsilon_l''(\mathbf{k},\omega)$ and $\epsilon_t''(\mathbf{k},\omega)$ directly by integrating the equations of motion of the system in the harmonic approximation with suitable initial conditions. Details of this technique are described elsewhere.[10] The real parts $\epsilon_L'(\mathbf{k},\omega)$ and $\epsilon_t'(\mathbf{k},\omega)$ can be calculated through the Kramers-Kronig relation.[9]

The integration of the harmonic equations of motion requires the evaluation of the long-range dipolar interactions. Following de Leeuw, Perram, and Smith[11] we find that the dipolar energy of our periodic system [i.e., the last term in Eq. (1)] can be written as

$$U_{dd} = U_{\mathrm{EK}} + \frac{2\pi}{\epsilon_\infty \Omega} \sum_\alpha B_\alpha \Big[\sum_l q_l u_\alpha(l)\Big]^2. \tag{5}$$

Here U_{EK} is the usual Ewald-Kornfeld result.[12] The second term describes the depolarizing field and varies according to shape and surroundings of the system through the depolarizing factors B_α.[11,13] In particular, for slab geometry we have that $B_\alpha = 1$ if the slab is perpendicular to the α direction, and zero otherwise. For a general ellipsoid $\sum_{\alpha=1}^{3} B_\alpha = 1$.

For *finite* wave vectors we find that the results obtained for the dielectric function are independent of the magnitude of the depolarizing field because the net dipole moment is almost zero for these displacement patterns.

The variation of the longitudinal and transverse dielectric functions with wave number is shown in Fig. 1. The frequency is in units of the bare plasma frequency ω_p, defined by $\omega_p^2 = (4\pi e^2/\Omega)\sum_i (q_i^2/m_i)$. With the parameters of our model we have $\omega_p = 939$ cm^{-1}. A noteworthy feature is the well-defined peak for $\omega > \omega_p$. The peak position at 1.16 ω_p is seen to be almost independent of wave number for the *transverse* dielectric function. The *longitudinal* dielectric function has a negative dispersion character in the optic peak similar to that in many crystals for the high-frequency modes. This peak in the region $\omega > 1.1\omega_p$ is sharp at long wavelength, but broadens and decreases in inten-

TABLE II. Details of the relaxed network.

No. of cations	512
No. of anions	1024
Box length	28.5 Å
Molar volume	27.2 cm^3
Mean nearest-neighbor distance	1.65 ± 0.04 Å
Mean angle at four-coordinated ion	109.5° ± 9.8°
Mean angle at two-coordinated ion	151.0° ± 12.5°
Mass of anion	16 amu
Mass of cation	28 amu

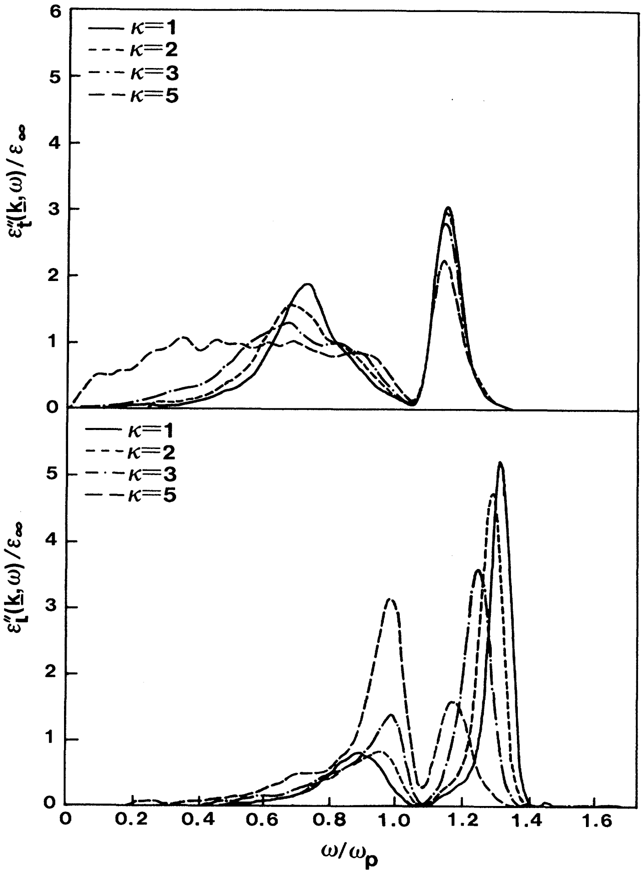

FIG. 1. Imaginary parts of the transverse and longitudinal dielectric functions for various wave vectors $\mathbf{k} = 2\pi(0, 0, \kappa)/L$. The resolution is $0.05\omega_p$.

sity with increasing wave number.

Although at finite wavelength our results are not dependent on the precise form of the depolarization field, this is no longer true in the limit of infinite wavelength. Consider a slab geometry in which the slab is perpendicular to the z axis, so that $B_z = 1$ in Eq. (5) and $B_x = B_y = 0$. We compute $\epsilon_L''(0,\omega)$ and $\epsilon_t''(0,\omega)$ where longitudinal and transverse now refer to the slab. It is clear then that the depolarizing field acts to *increase* the restoring force for longitudinal vibrations, but has *no effect* on transverse vibrations as is clearly shown in Fig. 2. Note that both $\epsilon_t''(0,\omega)$ and $\epsilon_L''(0,\omega)$ are *smooth* extrapolations of the results obtained at finite wavelength. The transverse dielectric function $\epsilon_t''(0,\omega)$ has a well-defined peak at $\omega = 1.17\omega_p$ with a width of 0.09 ω_p after deconvolution with the resolution width introduced by the finite-time truncation in the equation-of-motion method; $\epsilon_L''(0,\omega)$ has a remarkably sharp peak at $\omega = 1.33\omega_p$ with a width of only $0.04\omega_p$ after deconvolution. These results, in combination with the results at finite wavelength, provide unambiguous evidence for the existence of well-differentiated transverse- and longitudinal-optic responses in disordered networks.

In the limit of vanishing wave number the longitudinal and transverse dielectric functions are *not independent.* A straightforward electrostatic argument shows that we can identify $\epsilon_t(0,\omega)$ with the dielectric function $\epsilon(\omega)$,

$$\epsilon_t(0,\omega) = \epsilon(\omega), \tag{6}$$

whereas

$$\frac{\epsilon_L(0,\omega)}{\epsilon_\infty} = 2 - \frac{\epsilon_\infty}{\epsilon(\omega)}. \tag{7}$$

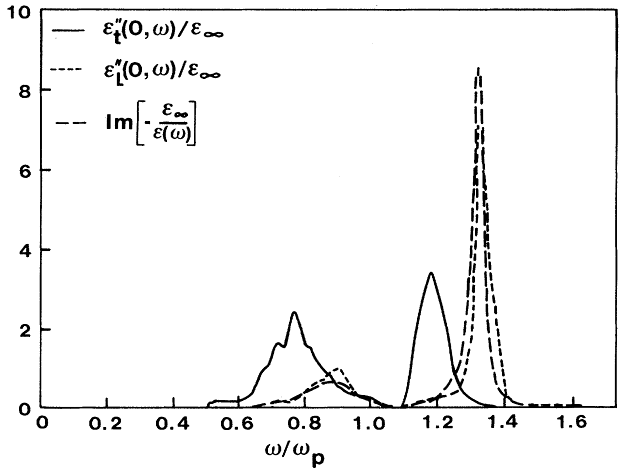

FIG. 2. Imaginary parts of the long-wavelength limit of the transverse and longitudinal dielectric functions and the loss function $\mathrm{Im}[-\epsilon_\infty/\epsilon(\omega)]$. The resolution is $0.03\omega_p$.

We have demonstrated Eq. (7) to be correct directly by using the fact that the depolarizing potential in Eq. (5) is separable.[14] The imaginary part of the right-hand side of Eq. (7) has been included in Fig. 2 and agrees well with $\epsilon_L''(0,\omega)/\epsilon_\infty$ within expected computational limits.

In addition we can show from the definitions in Eqs. (3) and (4) that

$$\pi^{-1}\int_0^\infty d\omega^2\,\epsilon_L''(0,\omega) = \pi^{-1}\int_0^\infty d\omega^2\,\epsilon_t''(0,\omega) = \omega_p^2, \tag{8}$$

whereas a combination of Eqs. (3)–(5) yields

$$\pi^{-1}\int_0^\infty d\omega^2\,\omega^2[\epsilon_L''(0,\omega) - \epsilon_t''(0,\omega)] = \omega_p^4/\epsilon_\infty. \tag{9}$$

These two equations are conveniently combined and become

$$\langle\omega^2\rangle_L - \langle\omega^2\rangle_t = \omega_p^2/\epsilon_\infty, \tag{10}$$

where $\langle\omega^2\rangle_L$ and $\langle\omega^2\rangle_t$ are the second moments of the transverse and longitudinal responses. Relations between higher moments and moments at finite **k** can also be derived.[14] A sum rule similar to Eq. (9) has been derived earlier for crystals containing several ions per unit cell.[15] Both Eqs. (8) and (9) have been checked numerically. These relations can be used to extract effective charges (from ω_p^2) and ϵ_∞ in disordered systems and should be useful in processing experimental data.

If we regard dielectric response of the system as being due to the two ionic sublattices moving rigidly against each other, then we would expect a single sharp peak at $\langle\omega^2\rangle_t^{1/2} = 0.98\omega_p$ in the transverse

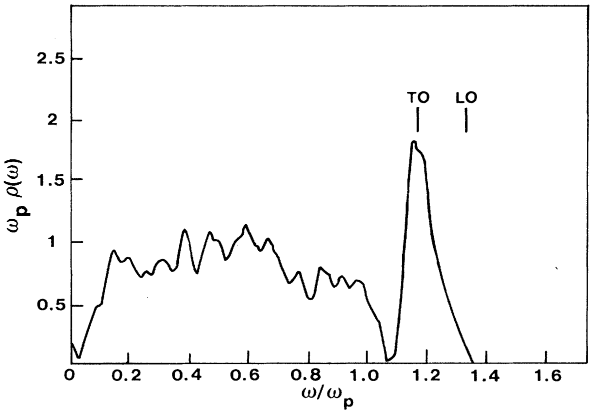

FIG. 3. Density of states with the peak frequencies in the transverse and longitudinal responses in Fig. 2 indicated by TO and LO. The resolution is $0.03\omega_p$.

response and a single sharp peak at $\langle\omega^2\rangle_L^{1/2} = 1.25\omega_p$ in the longitudinal response. This is clearly not the case as can be seen in Fig. 2.

In Fig. 3 we show the density of states $\rho(\omega)$ for the network:

$$\rho(\omega) = -\frac{2\omega}{3\pi N}\sum_{l,\alpha}\frac{1}{m_l}\operatorname{Im}G_{\alpha\alpha}(l,l;\omega), \tag{11}$$

where there are N terms in the l summation. It is characterized by a broad band for $\omega < \omega_p$ and a peak at $\omega = 1.15\omega_p$, i.e., close to the TO peak frequency.

The transverse modes produce a peak in the density of states but the longitudinal peak merely serves to define the upper band edge in the density of states[4] (see Fig. 3). These observations agree with experiments on v-SiO_2 and v-GeO_2.[2,6] The polarized spectrum resembles $\epsilon_l(0,\omega)$ but is distinct from it. Changes in the anisotropic bond polarizabilities that we have not considered probably make important contributions to both the polarized and depolarized Raman spectra. An *extra* peak is seen in v-SiO_2 and v-GeO_2 in the region between the LO and TO peaks. This is probably due to optically inactive modes in this frequency region of the kind found in crystalline quartz.[16] The parameters in the potential would have to be further refined to give this peak.[17]

Further comparison of the computed results with experimental data reveal inadequencies in the rigid-ion model. The experimental data[2] show *two* separate peaks in $\epsilon''(\omega)$ for $\omega < \omega_p$ rather than the broad peak at $\omega = 0.7\omega_p$ in our result. A simple ionic model is insufficient to account for the experimental results in this frequency region. This has been noted in connection with lattice dynamics of the various crystal modifications of SiO_2.[17] Also the charges q_l are expected to vary a little from site to site. This would lead to more of the density of states leaking through into the dielectric response.[18,19]

We hope that these numerical calculations will help to bridge the current gap between theory and experiment in disordered ionic materials and lead to the development of tractable effective-medium theories that will facilitate the interpretation of experiments. Some very preliminary attempts have been made in this direction.[20] The **k**-dependent dielectric response should be investigated with electron-energy-loss spectroscopy.[21]

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