Locator study of neutron and light inelastic scattering and infrared absorption in disordered solids

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(Received 15 June 1984; revised manuscript received 27 February 1985)

A unified approximate theory of the one-phonon phenomena in disordered solids [neutron inelastic scattering (NIS), first-order Raman scattering (FOR), and infrared absorption (IRA)] is formulated, under the assumption that different atoms couple to external probes in the same way. The spectra are expressed in terms of the function $\langle \overleftrightarrow{G}_Q(\omega) \rangle$, the Fourier transform (with respect to time and atomic position vectors) of the displacement-displacement Green's function (GF). To derive $\langle \overleftrightarrow{G}_Q(\omega) \rangle$ a mean-field approximation is applied to the Dyson equation based on the locator GF. In the ω-Q plane the poles of $\langle \overleftrightarrow{G}_Q(\omega) \rangle$ occur at two "dispersion curves," L and T, where $\hbar\omega$ and $\hbar Q$ are the energy and momentum transfers. These curves can be expressed in terms of the two universal functions of Q. Disorder can also manifest itself in the appearance of frequency gaps in the curves. The NIS provides information on the L curve. The IRA spectrum is predicted to consist of isolated peaks situated at the gap edges. For multiatomic systems, the mass-averaged frequency spectrum is shown to be a linear combination of the FOR and IRA spectra. Experimental data and computer-simulation results for vitreous GeO_2 and SiO_2 confirm this prediction. The nearest-neighbor axial-symmetry model for amorphous Ge and Si is shown to lead to dispersion curves that are compatible with the corresponding Raman spectra.

This paper is an extension of the local Green's-function (GF) approach, used previously to study the dynamics of substitutional crystalline alloys,[1] to cover fully disordered solids. The locator GF, carrying information on the dynamics of an atom as it moves with respect to its frozen environment, and the isotropy of a disordered macroscopic system, are the basic notions being considered here.

We consider the interaction of an external probe with a solid, with an energy transfer $\hbar\omega$ and a momentum transfer $\hbar Q$, which excites or de-excites normal modes of vibration in the solid. Our aim is to compare the experimental spectra measured with neutron inelastic scattering (NIS), first-order Raman scattering (FOR), and infrared absorption (IRA) within a unified, if approximate, theoretical framework. These spectra depend on the correlation between displacements u_R of atoms from their mean positions R. Relevant correlation functions may be expressed[2] by the Green's function

$$\overleftrightarrow{G}_{RR'}(t-t') = \langle\langle u_R(t), u_{R'}(t') \rangle\rangle .$$

It turns out that expressions describing experimental spectra involve sums over R and R' which have the form of products of the GF's and the factors describing coupling of the probe to atoms. In the NIS case, they are scalars, $B_R B_{R'}$, where B_R is the neutron scattering length times the Debye-Waller factor for the Rth atom. In the IRA case, they are of the form $\overleftrightarrow{M}_R^{(1)} \overleftrightarrow{M}_{R'}^{(1)}$, where $\overleftrightarrow{M}_R^{(1)}$ is the coefficient in the expansion of the electric dipole moment with respect to u_R. In both cases, one can safely substitute their averages and put them before the sum.

The Raman case is different. Here one deals with the electronic polarizability tensor and its expansion with respect to u_R. Taking into account isotropy of the system, one ends up with the dyadic $P_R P_{R'}$. But the same isotropy requires that any macroscopic vector vanishes: $\sum_R P_R = 0$. Obviously, it does not make sense to average P_R over R, as was done for the first two cases.

The P_R cancellation condition means that there is a certain correlation between the vectors P_R, which must be accounted for in our treatment of the FOR cross sections. We find it reasonable to assume that the cancellation takes place in some atomic clusters rather than in the whole solid. Let the average number of atoms in the clusters be n_c and their average radius, R_c. Using these values, the following seems to be the simplest nontrivial averaging procedure:

$$P_R^\alpha P_{R'}^\beta \implies P^2 \delta^{\alpha\beta} \left[\delta_{R,R'} - \frac{1}{n_c} \Theta(R_c^2 - (R-R')^2) \right] , \tag{1}$$

where $\Theta(x)$ is the unit step function. One can easily check that the cancellation property is contained in this form. Moreover, it is convenient to choose n_c large enough so that it is characteristic to all correlations we may deal here with, including the displacement-displacement correlations.

When the factors due to the probe-atom coupling are extracted, it turns out that in all three cases the observable quantities are given in terms of the imaginary part of the function $\langle \overleftrightarrow{G}_Q(\omega+i\epsilon) \rangle$, where

$$\langle \overleftrightarrow{G}_Q(\omega) \rangle = \frac{1}{N} \sum_{R,R'} \overleftrightarrow{G}_{RR'}(\omega) e^{iQ\cdot(R-R')} \tag{2}$$

[this formula also gives one a recipe for determining quantities of the type $\langle(\cdots)_Q\rangle$ from the quantities $(\cdots)_{RR'}$, which we use later]. When light is involved, one has to put $Q \to 0$. It should be emphasized that, on summing over a uniform distribution of the Q points and extending the volume of summation to infinity, one obtains

$$\text{Im Tr}\left[\sum_Q \langle \overset{\leftrightarrow}{G}_Q(\omega+i\epsilon)\rangle\right] \sim \sum_R \text{Im Tr}[\overset{\leftrightarrow}{G}_{RR}(\omega+i\epsilon)]$$

$$\sim \omega^{-1}\gamma(\omega) , \qquad (3)$$

where $\gamma(\omega)$ is the frequency distribution for the system with identical (average) masses: $M = \sum_R M_R$. For monoatomic systems $\gamma(\omega)$ turns into usual frequency spectrum $g(\omega)$. Having expressed the experimental spectra in terms of the same GF, we can compare them with each other. One finds that if the FOR and IRA spectra are properly reduced, then we may combine them to arrive at

$$\gamma(\omega) \sim \gamma^{\text{FOR}}(\omega) + \alpha\gamma^{\text{IRA}}(\omega) , \qquad (4)$$

where α is an unknown parameter.

This rule has been applied to the experimental results of Galeener, Leadbetter, and Stringfellow[3] and the computer results of Bell and Dean[4] for vitreous GeO_2 and Sio_2 (see Fig. 2). Despite some shifts in some peak positions, which may be due to deficiencies of the model used for computer simulations, the general similarity and a coincidence of the main features in the mass-averaged frequency spectrum $\gamma(\omega)$ set up with formula (4), and in the computed $g(\omega)$, is striking. The choice of $\alpha = 1$ assumed here is rather arbitrary; a reliable estimate for this parameter should come from the microscopic theory of polarization phenomena.

The validity of formula (4) does not depend on which particular approximation for the $\langle \overset{\leftrightarrow}{G}_Q(\omega)\rangle$ we may take. However, to make further predictions on experimental spectra, and to gain some insight into the nature of the vibration modes in disordered solids, we shall derive this function using some specific approximations.

We shall adopt here the average local-information transfer approximation (ALITA), developed earlier to study NIS in substitutional crystalline alloys.[1] As an auxiliary system we introduce the system of Einstein oscillators described by the local GF (see Fig. 1)—the locator

$$\overset{\leftrightarrow}{L}_{RR'} = [M_R\omega^2\overset{\leftrightarrow}{1} - \overset{\leftrightarrow}{\Psi}_R]^{-1}\delta_{RR'} , \qquad (5)$$

where $\overset{\leftrightarrow}{\Psi}_R$ is the self-force constants matrix, obeying the translational invariance condition

$$\overset{\leftrightarrow}{\Psi}_R = -\sum_{R'}{}' \overset{\leftrightarrow}{\Phi}_{RR'} .$$

$\overset{\leftrightarrow}{\Phi}_{RR'}$ is the force constants matrix (of the harmonic theory of small vibrations) between atoms at R and R', and M_R is atomic mass. With the perturbation matrix

$$\overset{\leftrightarrow}{C}_{RR'} = (1-\delta_{RR'})\overset{\leftrightarrow}{\Phi}_{RR'} .$$
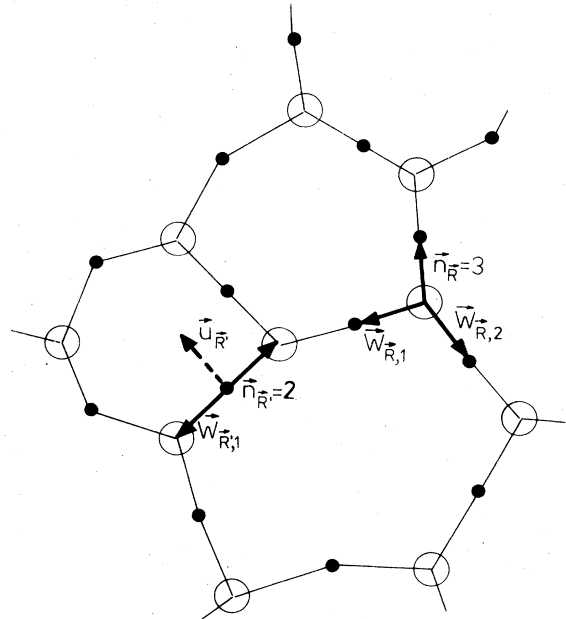

FIG. 1. A two-atom disordered system in two dimensions. Atomic neighborhoods about the atoms at R and R' have been distinguished: It is clear that the relevant locators $\overset{\leftrightarrow}{L}_R, \overset{\leftrightarrow}{L}_R'$ are different [see Eq. (5)]. n_R is the number of the nearest neighbors of the Rth atom. $W_{R,1}$ is one of the bond vectors for the Rth atom; $u_{R'}$ marks a displacement of the R' atom.

the Dyson equation $\langle \overset{\leftrightarrow}{G}\rangle = \langle \overset{\leftrightarrow}{L}\rangle + \langle \overset{\leftrightarrow}{L}\cdot\overset{\leftrightarrow}{C}\cdot\overset{\leftrightarrow}{G}\rangle$ [see Eq. (2) for the meaning of the brackets] can be solved with the decoupling[1,5]

$$\langle \overset{\leftrightarrow}{L}\cdot\overset{\leftrightarrow}{C}\cdot\overset{\leftrightarrow}{G}\rangle = \langle \overset{\leftrightarrow}{L}\cdot\overset{\leftrightarrow}{C}\rangle\langle \overset{\leftrightarrow}{G}\rangle .$$

Such a step is exact for the crystal because of its translational symmetry. Its use in the present problem probably imposes certain extra ordering on our final conclusions. It turns out, however, that in the so-constructed GF there is still enough information on the consequences of disorder to make the present approach valuable.

The momentum transfer $\hbar Q$ distinguishes the direction Q in our isotropic system. Therefore the second-order tensor $\langle \overset{\leftrightarrow}{G}_q(\omega)\rangle$ must be of the form

$$\langle \overset{\leftrightarrow}{G}_Q(\omega)\rangle = \frac{\hat{Q}\hat{Q}}{\omega^2 M^{\text{eff}}(\omega) - \Phi_Q^L(\omega)} + \frac{\overset{\leftrightarrow}{1} - \hat{Q}\hat{Q}}{\omega^2 M^{\text{eff}}(\omega) - \Phi_Q^T(\omega)} ,$$

$$(6)$$

where $\hat{Q} = Q/Q$, $Q = |Q|$. The effective mass function

$$M^{\text{eff}}(\omega) = \sum_R M_R \text{Tr}\overset{\leftrightarrow}{L}_R \bigg/ \sum_R \text{Tr}\overset{\leftrightarrow}{L}_R$$

has poles about the eigenvalues of the matrices $\overset{\leftrightarrow}{\Psi}_R/M_R$—the squared Einstein frequencies. One can show that the functions $\Phi_Q^{L,T}(\omega)$ are

$$\Phi_Q^L(\omega) = \sum_W [H_0^L(W)h_0(\tfrac{1}{2}QW) + H_2^L(W)h_2(\tfrac{1}{2}QW)] ,$$

$$\Phi_Q^T(\omega) = \tfrac{1}{2}\sum_W \{[H_0(W) - H_0^L(W)]h_0(\tfrac{1}{2}QW) \qquad (7)$$

$$- H_2^L(W)h_2(\tfrac{1}{2}QW)\} ,$$

where **W** stands for a vector joining the two atoms—the bond vector and $W = |\mathbf{W}|$. The parameters $H(W)$ depend on the locators and are therefore singular versus ω. The Q dependence is entirely given by the two functions $(p = QW/2)$

$$h_0(p) = \frac{1}{2}\left[1 - \frac{\sin(2p)}{2p}\right],$$

$$h_2(p) = \frac{1}{6}\left[1 - \frac{3}{2p^2}\left[1 - \frac{\sin(2p)}{2p}\right]\right.$$

$$\left. + 3\frac{\sin p}{p}\frac{\sin p - p\cos p}{p}\right]. \tag{8}$$

One can show that $\Phi_Q^L \to \Phi_Q^T$ for $Q \to \infty$.

The NIS cross section is proportional to

$$\mathbf{Q}\mathbf{Q}\,\mathrm{Im}\langle \overleftrightarrow{G}_Q(\omega + i\epsilon)\rangle \sim \delta(\omega - \omega_Q^L),$$

where the $\omega_Q^{L,T}$ are the roots of the equation

$$\omega^2 M^{\mathrm{eff}}(\omega) = \Phi_Q^{L,T}(\omega).$$

These "dispersion curves" are fully expressible in terms of the functions $h_0(p), h_2(p)$. Locator singularities manifest themselves as frequency gaps in the curves. It should be emphasized that the NIS spectra depend solely on ω_Q^L, i.e., they are basically unable to provide all the information necessary to determine the frequency spectra, see Eqs. (3) and (6). The ω_Q^L curve can be determined with a constant-Q scan. A long-wave-vector transverse external probe should be invented to look for ω_Q^T.

We should think of the dispersion curves as only a convenient means of interpreting scattering experiments. However, their connection to the frequency spectra $\gamma(\omega)$, displayed in Eq. (3) (we will omit discussion of the convergence of the **Q** summation and the problem of the NIS peak broadening), indicates that they have direct relevance to the normal modes in disordered systems. Let us remember that the NIS cross section involves correlation functions, $\langle \mathbf{Q}\cdot\mathbf{u}_R\mathbf{Q}\cdot\mathbf{u}_R\rangle$, i.e., that only a projection of normal modes in the direction of the scattering vector **Q** is sensed by neutrons. On the other hand, if in a certain ω range there are no normal modes, they cannot show up in dispersion curves, so the information on frequency gaps is reliable at least.

The present theory predicts that one of the gap edges coincides with a root of $M^{\mathrm{eff}}(\omega)$. The IRA spectrum should consist of isolated δ-function-like peaks, also at the frequencies corresponding to the above roots. Indeed, assuming some broadening, this is the structure of the experimental IRA spectrum for GeO_2 and SiO_2 (see Fig. 2). Remarkably, the IRA peaks turn out to be good gap markers.

For monoatomic systems $M^{\mathrm{eff}}(\omega) = M$ and one-phonon infrared absorption should be absent: $\gamma^{\mathrm{IRA}}(\omega) = 0$. Taking this result together with formula (4), we get for monoatomic systems

$$g(\omega) \approx \gamma^{\mathrm{FOR}}(\omega). \tag{9}$$

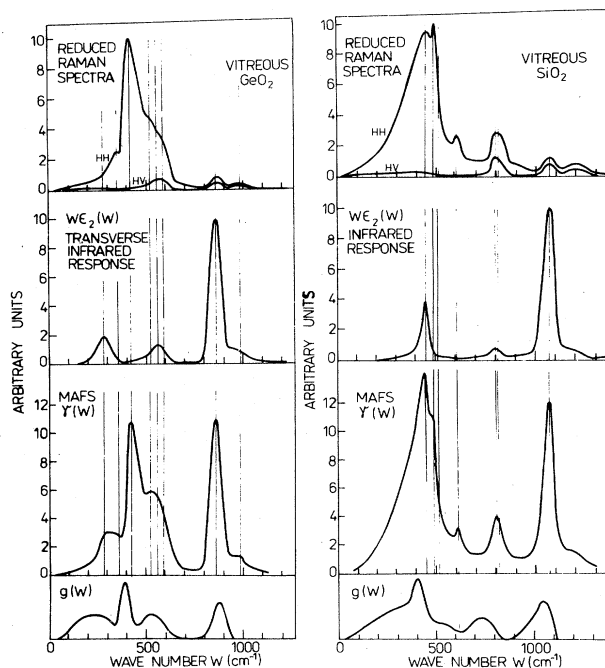This approximate result is obtained here under assumptions stronger than Eq. (3) and the more complicated and

FIG. 2. Optical spectra, FOR and IRA, for vitreous GeO and SiO, according to Galeener, Leadbetter, and Stringfellow (Ref. 3). The mass-averaged frequency spectrum $\gamma(\omega)$ has been combined from the above spectra, using formula (4), with $\alpha = 1$. Frequency spectra obtained numerically for large clusters of atoms by Bell and Dean (Ref. 4) are shown below. $\omega = 2\pi cW$, where c is the velocity of light.

more exact formula of Shuker and Gammon.[6] For a long time, relation (9) was expected to be approximately true on intuitive grounds.

The structure of the dispersion curves is related to the structure of the frequency spectrum. To see this point clearly, let us examine an example. We can use axial
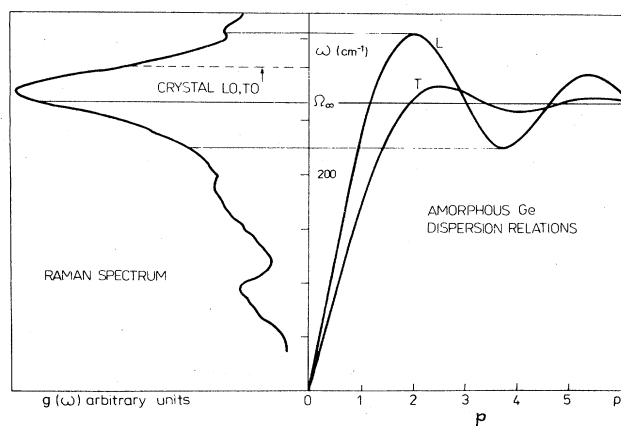

FIG. 3. Experimental Raman spectrum for amorphous Ge, according to Alben et al (Ref. 7), and calculated dispersion curves (11), corresponding to the nearest-neighbor axial-force model, with $t/l = \frac{2}{9}$. The highest frequency in the L curve has been matched with the high-frequency kink in the Raman spectrum. No locator effects have been allowed.

forces to describe interatomic coupling in amorphous Ge:

$$(\hat{\mathbf{W}}_\mathbf{R} = \mathbf{W}_{\hat{\mathbf{R}}}/|\mathbf{W}_{\hat{\mathbf{R}}}|)$$

$$\Phi^{\alpha\beta}_{\mathbf{R},\mathbf{W}_\mathbf{R}} = -l\hat{\mathbf{W}}^\alpha_\mathbf{R}\hat{\mathbf{W}}^\beta_\mathbf{R} - t\delta^{\alpha\beta} \tag{10}$$

Upon neglecting the locator effects ($\overleftrightarrow{\mathbf{L}} = \overleftrightarrow{\mathbf{1}}$), and assuming a fixed number n of nearest neighbors, we obtain the dispersion curves

$$M\omega^2_L = 2n[th_0(p) + lh_2(p)]$$

$$M\omega^2_T = n[(l+2t)h_0(p) - lh_2(p)] \tag{11}$$

The curves are shown in Fig. 3, together with the Raman spectrum of Alben et al.[7] We have assumed $n = 4$ and, following Thorpe,[8] $t/l = \frac{2}{9}$. The value of the coupling parameter l has been fixed by adjusting the maximum frequency in the L curve to the position of the shoulder kink in the Raman spectrum at $\omega = 360$ cm^{-1}. One finds

$l_{Ge} = 164$ kg/s, which is $\sim 70\%$ longer than the corresponding value for crystalline Ge. Similarly, for amorphous Si one finds $l_{Si} = 165$ kg/s^2. Remarkably, within experimental error, $l_{Ge} = l_{Si}$.

There is a high degree of internal agreement between the Raman spectra and the dispersion curves. The accumulation of frequencies about 280 cm^{-1}, especially in the T branches, should lead to a peak in $g(\omega)$ just in the vicinity of this value, and indeed, this is the main feature of the Raman spectrum. A much weaker structure at about cm^{-1} is probably due to some locator effects, neglected here.

A more detailed version of this work, along with a fuller discussion and reference list, will be published elsewhere.[9]

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