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Phonon dispersion in metallic glasses: A simple model

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Analytic expressions for the dispersion of longitudinal and transverse phonons are obtained for one-component metallic glasses and amorphous materials on the basis of a simple model. The model assumes a central force, effective between the nearest neighbors, and a volume-dependent force due to conduction electrons. The expressions reproduce chief characteristic features of the dispersion curves both for the longitudinal and transverse phonons (e.g., oscillatory behavior in one and lack thereof in the other, etc.) obtained by neutron scattering and computer-simulation techniques. The model, within its framework, also illustrates that the results may depend on the starting structure from which the glass is made. The special cases of a liquid and forces that are entirely central are also discussed.

I. INTRODUCTION

In recent years there has been considerable interest in the phonon dispersion (frequency ω versus wave number q) curves for metallic glasses. Experimentally, dispersion curves for longitudinal phonons have been determined for several glasses by measuring the dynamical structure factor $S(q,\omega)$ using neutron scattering.[1-5] Theoretically computer-simulation (experiments) and recursion techniques have provided dispersion curves for both longitudinal and transverse phonons in a variety of cases.[6-10] For further references and excellent reviews we refer the reader to papers by Hafner,[11] Suck and Rudin,[12] and Nagel *et al.*[13]

The dispersion curves show certain broad features. For example, the dispersion of longitudinal phonons exhibit oscillatory behavior, the position of the first minimum roughly coinciding with the first peak in the static structure factor. In contrast, the ω-q curve for transverse phonons reaches its maximum at a higher q than the longitudinal-phonon curve and any oscillatory behavior beyond that is quite insignificant. The main purpose of this paper is to report a simple analytic model which reproduces these results. Additionally, it is of interest since—without claiming to be fully quantitative because of its very simplicity—it provides clues to questions such as what is the difference between dispersion in a metallic and nonmetallic glass (all forces central) or how results might depend on the starting structure from which the glass is made.

Section II of the paper describes the model and derives the dispersion relations. The $q\rightarrow 0$ limit of these is discussed in Sec. III. Section IV calculates the dispersion curves for a number of cases—substances interacting with Lennard-Jones potential, a central-force model of iron, a hypothetical one-component metallic glass,[14] and $\mathrm{Ca_{70}Mg_{30}}$ glass. The comparison with experimental and computer-simulation results, as appropriate, is also given here. A brief comment on the change in the shear modulus on crystallization expected from the model is made in Sec. V, and Sec. VI discusses the dispersion in a liquid.

II. THE MODEL OF A METAL AND BASIC EQUATIONS

A. Formulas for cubic metals

The starting point of our work is a phenomenological model, suggested by one of us[15] nearly 30 years ago, for calculating the frequency spectrum of a simple metal with cubic symmetry taking into account the effect of conduction electrons. The model assumes, firstly, that the ions interact with a central pairwise potential $W(r)$ which is effective between the nearest neighbors only. Secondly, it assumes that the force on an ion due to volume-dependent energies in the metal (kinetic and exchange energies of the conduction electrons, the ground-state energy of the electron, etc.) could be calculated using the Thomas-Fermi method (see below). Under these assumptions the equations determining ω-q relations may be written as[15,16] (note the small difference in notation)

$$\rho\omega^2\mathbf{l}=\frac{4}{a^2}\sum_n\{(\sin^2\tfrac{1}{2}\mathbf{q}\cdot\mathbf{r}_n^{(0)})\times[(\delta/a^2)(\mathbf{r}_n^{(0)}\cdot\mathbf{l})\mathbf{r}_n^{(0)}+\beta\mathbf{l}]\}+\frac{(4\pi n_i n_e z e^2)\mathbf{q}(\mathbf{q}\cdot\mathbf{l})}{(q^2+K_{\mathrm{TF}}^2)}\,, \tag{1}$$

where ρ ($=n_iM$, M denotes mass of the ion) is the mass density of the metal, $\mathbf{l}$ is the unit vector along the displacement of the wave, $\mathbf{r}_n^{(0)}$ is the vector joining the atom at origin to one of its nearest neighbors, the sum (n) is over all the nearest neighbors, a ($\equiv|r_n^{(0)}|$) is the nearest-neighbor distance, and β and δ are related to the first and second derivatives of $W(r)$ at $r=a$ as

$$\beta=\frac{\rho a^2}{2M}\left[\frac{1}{r}\frac{dW}{dr}\right]_{r=a},\quad \delta=\frac{\rho a^3}{2M}\left[\frac{d}{dr}\left[\frac{1}{r}\frac{dW}{dr}\right]\right]_{r=a}. \tag{2}$$

Finally n_e is the electron density, z the valence, e the electron charge, and $K_{\rm TF}$ the reciprocal of Thomas-Fermi screening length:

$$K_{\rm TF}^2=(4me^2/\hbar^2)(3n_e/\pi)^{1/3} . \tag{3}$$

We note that $\beta\ [\propto(dW/dr)_{r=a}]$ is in general not zero since the metal is not in equilibrium under the forces arising from $W(r)$ alone. We may mention also that if we set $\beta=\delta=0$, Eq. (1) gives for the velocity of sound $V=\omega/q$, in the limit of $q\rightarrow 0$, the expression

$$V=(\tfrac{1}{3}mv_F^2z/M)^{1/2} , \tag{4}$$

which is the celebrated Bohm-Staver formula[17] for the velocity of sound in a liquid metal. [In Eq. (4) v_F is the Fermi velocity.]

The above model predates pseudopotential methods and more sophisticated expressions for electron screening. To make the electronic term in the model more realistic without losing its essential simplicity, we make the following modification in the light of some of these developments.

First, as is well known, the Thomas-Fermi expression for the screening length ($K_{\rm TF}^{-1}$) or the corresponding dielectric function $\epsilon_{\rm TF}(q)$ $(=1+K_{\rm TF}^2/q^2)$ is a valid approximation for $q\rightarrow 0$ limit only. A more appropriate $\epsilon(q)$ to use is that calculated by the self-consistent-field method or random-phase approximation (Lindhard[18] and Langer and Vosko[19]). The effect of using this $\epsilon(q)$ is simply to replace $K_{\rm TF}^2$ in Eq. (1) by $K_{\rm TF}^2\tilde{g}(q)$, where

$$\tilde{g}(q)=\frac{1}{2}\left[1+\frac{k_F}{q}\left[1-\frac{q^2}{4k_F^2}\right]\ln\left|\frac{q+2k_F}{q-2k_F}\right|\right][1-f(q)] , \tag{5}$$

where the factor $[1-f(q)]$ has been added to incorporate correlation effects. We take $f(q)$ to be of the form[20]

$$f(q)=\tfrac{1}{2}q^2/(q^2+k_F^2+\tfrac{1}{2}K_{\rm TF}^2) . \tag{6}$$

In (5) and (6) $k_F=(3\pi^2n_e)^{1/3}$ is the Fermi wave number. Note that as $q\rightarrow 0$, $\tilde{g}(q)\rightarrow 1$.

Secondly, since the electronic term is derived using free electrons in a jellium background, it does not take into account the cancellation effects which occur between kinetic and potential energies inside the core of the ions making the effective potential weak in the core. Several authors[21–24] have considered this cancellation in different contexts, and the effect of it is to multiply the electronic term in Eq. (1) by a "shape factor" which we take to be[25]

$$[G(qr_s)]^2=\left[\frac{3[\sin(qr_s)-(qr_s)\cos(qr_s)]}{(qr_s)^3}\right]^2 , \tag{7}$$

r_s $(=[3/(4\pi n_i)]^{1/3})$ being the radius of the Wigner-Seitz sphere. We note that $G(qr_s)\rightarrow 1$ for $q\rightarrow 0$ and dwindles to zero for large q.

Thirdly, to compensate for the fact that electrons are not entirely "free," we take in Eq. (1) the prefactor, namely $4\pi n_e n_i z e^2$, or κ_e defined as

$$\kappa_e=4\pi n_e n_i z e^2/K_{\rm TF}^2 , \tag{8}$$

as a parameter.[15] The full Eq. (1) then contains three parameters, β, δ, and κ_e, which may be determined using the observed elastic data as discussed below.

Finally we mention that the electronic term in Eq. (1) is not periodic with the period of the reciprocal lattice. Modifications of it in this light can be made by adding appropriately the umklapp terms.[23,26] However, this makes the calculations quite complex and, moreover, because of the $G(qr_s)$ factor and because we will be making a transition of Eq. (1) to amorphous materials (where there is no periodicity), we believe that its incorporation does not modify results appreciably for our problem.

Returning to the parameters β, δ, and κ_e, they can be related to the elastic constants of the material by comparing the $q\rightarrow 0$ limit of Eq. (1) with the Christoffel's equations of the elasticity theory. The relations depend on the crystal structure. For a body-centered-cubic lattice, for which $\mathbf{r}_n^{(0)}$ are $a\,(\pm 1/\sqrt{3},\ \pm 1/\sqrt{3},\ \pm 1/\sqrt{3})$, one has[15]

$$\begin{aligned} c_{11}&=\tfrac{8}{3}\beta+\tfrac{8}{9}\delta+\kappa_e\ ,\quad \nu=8\\ c_{12}&=-\tfrac{8}{3}\beta+\tfrac{8}{9}\delta+\kappa_e,\quad \nu=8\\ c_{44}&=\tfrac{8}{3}\beta+\tfrac{8}{9}\delta\ ,\quad \nu=8 \end{aligned} \tag{9}$$

where for later convenience we have given also the value of ν, the number of nearest neighbors of an atom in the lattice. For face-centered-cubic structure one has[15]

$$\begin{aligned} c_{11}&=4\beta+2\delta+\kappa_e\ ,\quad \nu=12\\ c_{12}&=-4\beta+\delta+\kappa_e,\quad \nu=12\\ c_{44}&=4\beta+\delta\ ,\quad \nu=12\ . \end{aligned} \tag{10}$$

B. Transition to amorphous material

We now assume that in an amorphous material, the nearest-neighbor atoms around each atom may be regarded as continuously distributed over a spherical surface of appropriate radius a. This is, of course, an idealization and there are deviations in local positions and in local stresses[27] which may affect also the values of the force constants. But within the aim of the present paper these effects, which are at best an order of magnitude more difficult to take into account, can be neglected. Then, with the above assumption, the dispersion equations for an amorphous material are obtained by replacing, in Eq. (1), the sum over neighbors by an integral over the surface of a sphere

$$\sum_n\cdots=\frac{\nu}{4\pi}\int\cdots d\Omega . \tag{11}$$

For the frequencies ω_L of the longitudinal waves ($\mathbf{l}\,||\,\mathbf{q}$), use of Eq. (11) in (1) gives

$$\rho\omega_L^2=\frac{2\nu}{a^2}(\beta\mathscr{I}_0+\delta\mathscr{I}_2)+\frac{\kappa_e K_{\rm TF}^2q^2[G(qr_s)]^2}{q^2+K_{\rm TF}^2\tilde{g}(q)} , \tag{12}$$

where in writing the electronic term we have incorporated the modifications embodied in Eqs. (5)—(8). For frequencies ω_T of the transverse waves ($\mathbf{l}\perp\mathbf{q}$), one has

$$\rho\omega_T^2 = \left[\frac{2\nu}{a^2}\right][\beta\mathscr{I}_0 + \tfrac{1}{2}\delta(\mathscr{I}_0 - \mathscr{I}_2)] \ . \tag{13}$$

In Eqs. (12) and (13),

$$\mathscr{I}_n = \int_0^\pi \sin\theta\cos^n\theta[\sin^2(\tfrac{1}{2}qa\cos\theta)]d\theta \ , \tag{14}$$

so that $\mathscr{I}_0$ and $\mathscr{I}_2$ are, with $x \equiv qa$,

$$\mathscr{I}_0(x) = 1 - \sin x/x \ , \tag{15}$$

$$\mathscr{I}_2(x) = \tfrac{1}{3} - \sin x\left[\frac{1}{x} - \frac{2}{x^3}\right] - \frac{2\cos x}{x^2} \ . \tag{16}$$

Equations (12) and (13) are the dispersion relations we wished to derive. It is next instructive to consider their long-wavelength ($q \rightarrow 0$) limit.

III. LONG-WAVELENGTH LIMIT OF PHONON VELOCITIES (IN A GLASS) AND ELASTIC CONSTANTS OF A CUBIC MATERIAL

For $q \rightarrow 0$, $x \rightarrow 0$, and hence, to leading term in x, $\mathscr{I}_0(x) \simeq \frac{1}{6}x^2$ and $\mathscr{I}_2(x) \simeq \frac{1}{10}x^2$. Substituting these in Eqs. (12) and (13), we have for the velocities $V_L(0)$ $(=\omega_L/q)$ and $V_T(0)$ $(=\omega_T/q)$ in the $q \rightarrow 0$ limit the expressions

$$\rho V_L^2(0) = \nu(\tfrac{1}{3}\beta + \tfrac{1}{5}\delta) + \kappa_e \ , \tag{17}$$

$$\rho V_T^2(0) = \nu(\tfrac{1}{3}\beta + \tfrac{1}{15}\delta) \ . \tag{18}$$

Remembering that in terms of the elastic modulii $c_{11}^{(g)}$, etc. of the glassy material,

$$\rho V_L^2(0) \equiv c_{11}^{(g)} = B^{(g)} + \tfrac{4}{3}G^{(g)} \ , \tag{19}$$

$$\rho V_T^2(0) = c_{44}^{(g)} = \tfrac{1}{2}(c_{11}^{(g)} - c_{12}^{(g)}) = G^{(g)} \ , \tag{20}$$

where $B^{(g)}$ and $G^{(g)}$ are the bulk and shear moduli, we can express $c_{11}^{(g)}$, etc. in terms of c_{11}, etc. of the cubic materials using Eq. (9) or (10). One sees that for both the case of the body-centered-cubic structure ($\nu=8$) and of the face-centered-cubic structure ($\nu=12$), use of (9) and (10), respectively, in Eqs. (17)— (20) leads to

$$c_{11}^{(g)} = c_{11} - \tfrac{2}{5}\mathscr{P}_a \ , \tag{21}$$

$$c_{44}^{(g)} = c_{44} + \tfrac{1}{5}\mathscr{P}_a \ , \tag{22}$$

where $\mathscr{P}_a = c_{11} - c_{12} - 2c_{44}$ is the elastic anisotropy of a cubic material. For an elastically isotropic solid $\mathscr{P}_a = 0$. The right-hand side of Eqs. (21) and (22) may be recognized as just the average values $\langle c_{11}\rangle$ and $\langle c_{44}\rangle$ appropriate to a polycrystalline material in which the individual crystallites are all randomly oriented (for example, see Bhatia[28]). Thus, in our model, the $q \rightarrow 0$ limit of the velocities in the glass are given by just enough as though it was a polycrystalline material. This is not unexpected since as mentioned earlier we have neglected the effects of local stress relaxation, etc.

In the special case where the system is in equilibrium under central forces alone [no electronic term ($\kappa_e = 0$) and $\beta = 0$], the ratio of the longitudinal- to transverse-wave velocities from Eqs. (17) and (18) is just[29] $V_L/V_T(0) = \sqrt{3}$, which is almost exactly the value for $V_L(0)/V_T(0)$ obtained by Grest *et al.*[8] by computer simulation for a glass in which the atoms interact with the Lennard-Jones potential. For a metallic material $V_L(0)/V_T(0)$ would not have in general this value.

In the opposite limit, namely $q \rightarrow \infty$, Eqs. (12) and (13) give

$$\omega_L^2(\infty) = \omega_T^2(\infty) = (2\nu/a^2\rho)(\beta + \tfrac{1}{3}\delta) \ . \tag{23}$$

IV. DISPERSION RELATIONS FOR A FEW SPECIAL CASES

We now consider the form of the dispersion relations (12) and (13) for a few special cases.

A. Central forces

As mentioned earlier when a system is in equilibrium under central forces alone and when this force is effective for nearest neighbors only, $\kappa_e = \beta = 0$. Hence the dispersion relations (12) and (13) reduce to

$$\rho\omega_L^2 = (2\nu/a^2)\delta\mathscr{I}_2(qa) \ , \tag{24}$$

$$\rho\omega_T^2 = (\nu/a^2)\delta[\mathscr{I}_0(qa) - \mathscr{I}_2(qa)] \ . \tag{25}$$

First, in order to be able to compare our results with the computer-simulation results of Grest *et al.*,[8] we take, as there, $W(r)$ to be the Lennard-Jones potential

$$W(r) = 4\epsilon\left[\left[\frac{\sigma}{r}\right]^{12} - \left[\frac{\sigma}{r}\right]^{6}\right] \ . \tag{26}$$

By making the approximation that $W(r)$ is effective up to nearest neighbors only, the equilibrium nearest-neighbor distance a is given by $(dW/dr)_{r=a} = 0$, so that $a = 2^{1/6}\sigma$. One then finds from (26) and (2) that $\delta/\rho = (36/M)\epsilon$. Hence, if one expresses ω in units of τ^{-1}, as in Grest *et al.*, where $\tau^2 = \sigma^2 M/\epsilon$, the dispersion relations (24) and (25) become

$$\omega_L^2\tau^2 = 72\nu(\sigma/a)^2\mathscr{I}_2(qa) \ , \tag{27}$$

$$\omega_T^2\tau^2 = 36\nu(\sigma/a)^2[\mathscr{I}_0(qa) - \mathscr{I}_2(qa)] \ . \tag{28}$$

Equations (27) and (28) contain just the coordination number ν as an unknown which occurs as a simple multiplicative factor. To set its value we note that the computer-simulation results of Grest *et al.*[8] were obtained for the density n_i such that $n_i\sigma^3 = 0.95$ or $n_i a^3 = 1.344$. If the structure were face-centered cubic where $\nu = 12$, $n_i a^3 = 1.414$, whereas for a body-centered-cubic lattice where $\nu = 8$, $n_i a^3 = 1.299$. This suggests $\nu = 10$ as an appropriate choice and Fig. 1 plots ω_L and ω_T as a function of $q\sigma$. In computer simulation the longitudinal and transverse dynamical correlation functions are calculated at each q and the results are depicted on ω-q plot as vertical bars—the height of a bar representing the width of the peak in the corresponding correlation function at that q. These are also depicted in Fig. 1 for comparison.

We remark that the curves based on Eqs. (27) and (28) reproduce all the central features of dispersion. In particular, the longitudinal-mode frequency ω_L shows oscillatory behavior and the position of the first peak and the next

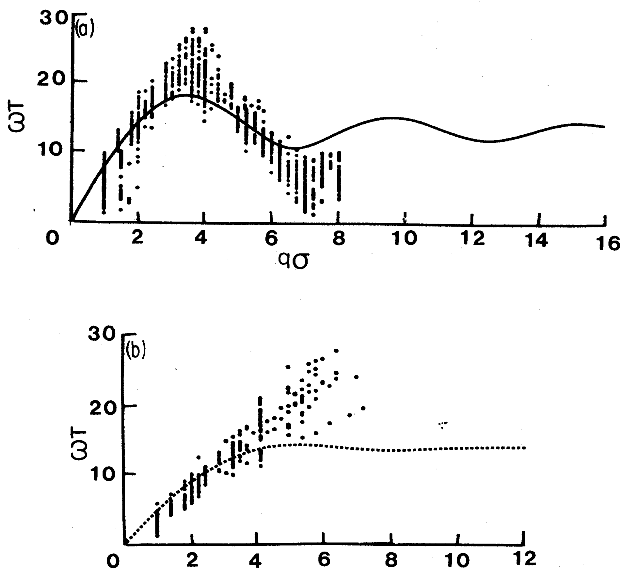

FIG. 1. Dispersion of (a) longitudinal modes and (b) transverse modes for central force (Lennard-Jones) according to Eqs. (27) and (28) with $\nu=10$. $\tau^2=\sigma^2 M/\epsilon$ as in Grest *et al.* (Ref. 8). Vertical bars represent computer-simulation results of Grest *et al.* (Ref. 8).

minimum are in good agreement with the computer-simulation results. Also the position of the first minimum occurs at $q\sigma=6.6$, which is about the value at which the static structure factor $S(q)$ has its first maximum—a feature which has been experimentally (or in computer simulation) found for other materials also.[30] In contrast to ω_L, the transverse-mode frequency ω_T shows barely any oscillations, again in agreement with computer-simulation results. Finally as noted in Sec. III, according to Eqs. (24) and (25),

$$\omega_L(q\to 0)/\omega_T(q\to 0)=\sqrt{3}\ ,$$

which is almost exactly the value in computer-simulation results of Grest *et al.*

We note that for the central-force case discussed in this section, substantially similar results have been recently obtained by Schwartz[31] in another manner.

Another case where a central-force model has been used to computer simulate dispersion relations is that of amorphous iron by Yamamoto *et al.*[9] They work with iron of density $n_i=7.56\times 10^{22}$ cm^{-3} and use Pak-Doyama[32] potential ($\equiv W_{\rm PD}$) with a cutoff distance between the second- and third-nearest neighbors—the parameters in the potential being determined from the observed lattice constant and elastic constants in the crystalline phase. To compare their results with those based on Eqs. (24) and (25), we again make the approximation that the potential, now $W_{\rm PD}$, is effective up to nearest neighbors only. Setting $(dW_{\rm PD}/dr)_{r=a}=0$ gives $a=2.62$ Å, and then use of $W_{\rm PD}$ in (2) gives $\beta=0$ and $\delta=0.82\times 10^{12}$ ergs/cm^3. Finally we choose $\nu=8$ corresponding to the coordination number of body-centered-cubic iron in the crystalline phase. This choice of ν together with the above values of δ and n_i yield, from (17) and (18) (with $\beta=\kappa_e=0$), for the velocities $V_L(0)$ and $V_T(0)$ in $q\to 0$ limit, the values $V_L(0)=4.31\times 10^5$ cm/sec and $V_T(0)=2.45\times 10^5$ cm/sec compared to the values 4.3×10^5 and 2.5×10^5 cm/sec, respectively, given by Yamamoto *et al.*[9]

The dispersion curves calculated from (24) and (25) are compared with the results of Yamamoto *et al.*[9] in Fig. 2. We see that the two are in surprisingly good agreement with one another both for the longitudinal and transverse phonons. In particular, unlike the case of Fig. 1, the agreement regarding the depth of the first minimum for the longitudinal waves is striking. In regard to its position $q_{\rm min}$ ($=2.9$ Å^{-1}), it, as for the Lennard-Jones case, lies close to the first maximum in $S(q)$. It may be noted that the positions of the second and the third minima in the ω_L-q curve also lie close to the second and third maxima in $S(q)$, respectively.

B. Influence of starting structure on dispersion curves of an amorphous metal

Unlike the case of central forces discussed above, in a metal, in general, all the three force constants β, δ, and κ_e will be nonzero in the dispersion relations (12) and (13). These force constants can be determined from the three elastic constants of the material in the crystalline phase. Referring to Eqs. (9) and (10), this requires also the knowledge of the crystalline structure, i.e., whether it is face-centered cubic (fcc) or body-centered cubic (bcc). Thus in our model the dispersion curves obtained from (12) and (13) depend on the crystalline structure from which the glass had originated. Since, as mentioned earlier, phonon data on a pure amorphous metal are not available, we take elastic constants corresponding to silver to illustrate the difference between the dispersion curves of an amorphous material originating from the fcc and bcc structures. The results, which are displayed in Fig. 3, were computed using

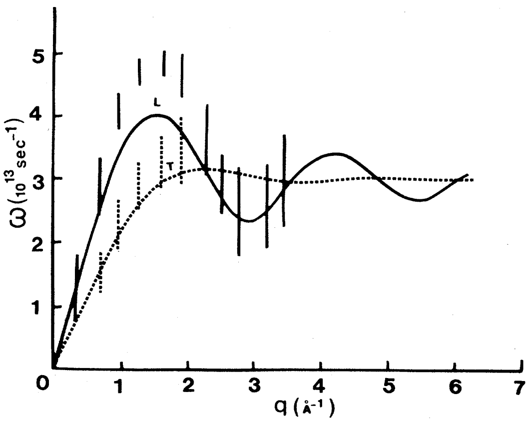

FIG. 2. Dispersion relations for longitudinal (——) and transverse (· · ·) modes for amorphous iron. Curves represent our results and vertical bars from Yamamoto *et al.* (Ref. 9).

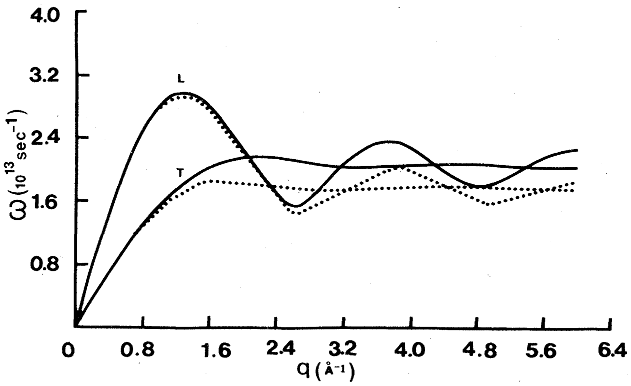

FIG. 3. Figure illustrating the difference between the dispersion curves on our model for an amorphous material originating from face-centered-cubic (fcc) structure and body-centered-cubic (bcc) structure (see text). ——, ω_L and ω_T for fcc previous structure; · · · ·, ω_L and ω_T for bcc previous structure. (Other input data, namely, elastic constants, density, etc. are the same for two cases.)

$$c_{11}=1.20\times10^{12},\quad c_{12}=0.90\times10^{12}\ ,$$

$$c_{44}=0.44\times10^{12}\ \text{dyn/cm}^2\ ,$$

and taking ρ and n_i ($=5.86\times10^{22}$ cm^{-3}) corresponding to silver.

We observe from Fig. 3 that for small q the dispersion curves (both for ω_L and ω_T) are almost the same for the two cases—$V_L(0)$ and $V_T(0)$ being identical for the two cases. However, as q approaches the value where ω_L has its first peak and for higher q, the difference between the dispersion curves becomes quite significant for the amorphous material originating from the fcc and bcc structures. In particular, note that the asymptotic value $\omega_L(\infty)[=\omega_T(\infty)]=2.07$ for the fcc case while $\omega_L(\infty)[=\omega_T(\infty)]=1.78$ for the bcc case. Although the detailed differences are naturally model dependent, our calculations seem to suggest that in computer-simulation technique the starting structure, the relaxation of which leads to the glass, may have a bearing on the dynamics of the amorphous system. Also, dispersion curves obtained from neutron scattering on an amorphous specimen (which is usually obtained from liquid quenching) may depend on the structural history of the specimen.

C. Dispersion curves for metallic glass $Ca_{70}Mg_{30}$

As a last application of the dispersion relations (12) and (13) to metallic glasses, we apply them to the glass $Ca_{70}Mg_{30}$, taking the mean atomic mass as the mass of each atom. This glass has been studied by Suck *et al.*[2,4] by neutron scattering, and Hafner[33] has made detailed theoretical calculations based on first-principles pseudopotential treatment of the interatomic potential and using cluster relaxation and recursion techniques for computations.

Since the elastic constants for the crystalline phase of $Ca_{70}Mg_{30}$ are not available, we fix the force constants β, δ, and κ_e in our equations as follows. First, we take the values of $V_L(0)$ and $V_T(0)$ for amorphous $Ca_{70}Mg_{30}$ as estimated by Hafner,[33] namely 4.67×10^5 cm/sec and 2.34×10^5 cm/sec, respectively. Secondly, we take $\kappa_e=14.2\times10^{10}$ dyn/cm^2, which may be compared with the free-electron value of 29.4×10^{10} dyn/cm^2, from Eq. (8), with $z=2$ and $n_i=2.69\times10^{22}$ cm^{-3}. (As discussed in Sec. II, κ_e should be taken as a parameter and not the free-electron value; in actual calculations a 50% variation of κ_e from the chosen value does not affect the results significantly.) Finally we take $\nu=12$, so that the relation $n_i a^3=\sqrt{2}$ corresponding to fcc lattice gives $a=3.746$ Å, in good agreement with the value $a=3.74$ Å computed by Hafner for amorphous $Ca_{70}Mg_{30}$. The use of (17) and (18) then enables one to determine β and δ, and hence all the quantities in the dispersion relations (12) and (13) become known.

Figure 4 gives ω_L and ω_T as a function of q as computed from (12) and (13), respectively. As in previous examples the transverse phonons show hardly any oscillatory behavior while the ω_L-q curve shows oscillations. The first minimum in the ω_L-q curve is again at a value of q close to where the static structure factor of a pure dense noncrystalline material may be expected to show first peak. The solid circles in the figure show the ω-q relation derived from the peak positions in $S(q,\omega)$ computed by Hafner[33] and the triangles correspond to the points from neutron scattering data on $S(q,\omega)$ by Suck *et al.*[2,4] [For clarity the widths of the peak in $S(q,\omega)$ are not depicted—these, of course, become quite large as q increases—cf. Figs. 1 and 2.] It is to be remembered also that $S(q,\omega)$ here is an average of three dynamical structure factors, appropriately weighted by the neutron form factors of Ca and Mg, so that the ω-q plot derived from $S(q,\omega)$ is not entirely a property of just the dynamical correlations between the atoms, and an exact comparison between these and those derived from (12) is not significant (see also below). Bearing this in mind it is apparent from the figure that there is reasonably good agreement between our ω_L-q calculations and the dispersion derived from the experimental and theoretical $S(q,\omega)$. It may be noted that the position of the first peak in our ω_L-q curve

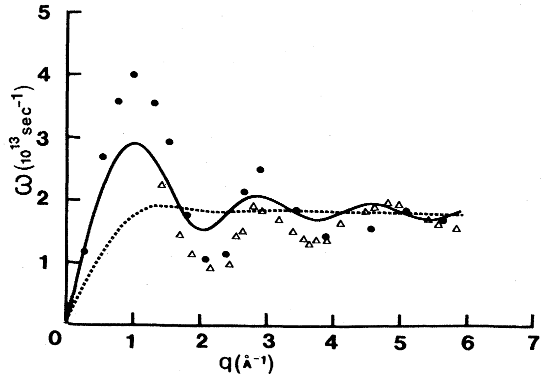

FIG. 4. Dispersion relations for $Ca_{70}Mg_{30}$. ω_L (——) and ω_T (· · ·) on the basis of Eqs. (12) and (13); ●, those due to Hafner (Ref. 33) from calculations of $S(q,\omega)$; △, experimental points from neutron scattering [Suck *et al.* (Refs. 2 and 4)].

coincides with that of Hafner's calculations, while the positions of the subsequent minima and maxima in our curves differ from the positions of the corresponding minima and maxima in Hafner and Suck *et al.* results by only a few percent. The difference in the values of ω at any q is not more than about 30%.

The dispersion near the first minimum (which occurs at approximately the wave number q_s where the static structure factor has its first peak) and subsequent minima has been explained by Hafner[34] in terms of the diffuse umklapp scattering similar to that occurring in a polycrystalline material. According to this picture near these q values most of the contribution to $S(q,\omega)$ comes from the transverse phonons of wave number $q_p < q_s/2$, so that [in ω-q plot from $S(q,\omega)$] near the minima an ω essentially corresponds to a transverse phonon of some appropriate wave number q_p. In contrast, in our unsophisticated picture, the minima in the ω_L-q curve seem to occur in a natural way around q values where $S(q)$ peaks to maxima. Note that as Figs. 1—4 show, shear waves do not exhibit this oscillatory behavior either in computer simulation or on our model.

V. CHANGE IN ELASTIC CONSTANTS ON CRYSTALLIZATION

It is well known[35] that when an amorphous material crystallizes, the shear modulus G increases by about 30—40%, while the corresponding increase in the bulk modulus B is only 4 to 6%. Although a full explanation of these changes is quite complex,[36,37] and lies outside the scope of our work, it may be of interest to mention that the present model does imply that $\Delta G/G$ may be expected to be greater than $\Delta B/B$.

First we observe that if the system is in equilibrium under the nearest-neighbor central force alone ($\beta=\kappa_e=0$), then Eqs. (17)—(20) imply that $\Delta B/B=\Delta G/G$; here we omit the suffix g on B and G for simplicity. On the other hand, from the full expressions (17) and (18), remembering (19) and (20), one may readily derive

$$\frac{\Delta G}{G}=\frac{n}{5}\left[3\frac{\Delta B}{B}-\frac{1}{m}\frac{\Delta\Omega}{\Omega}3y(1+2/y)\right] , \tag{29}$$

where $n=B/G$, $m=B/\kappa_e$, and $\Delta\Omega/\Omega$ is the fractional change in volume. In deriving (29) we have assumed that $\kappa_e=A\Omega^y$, A being a constant, and have used the equilibrium condition that the sum of the ionic pressure P_i ($=-\nu\beta/3$) and electronic pressure p_e $[=-\int(\kappa_e/\Omega)d\Omega]$ must be zero. If we take the free-electron expression, Eq. (8), for κ_e, $y=-\frac{5}{3}$ and (29) reduces to

$$\Delta G/G=\tfrac{1}{5}n[3(\Delta B/B)-m^{-1}(\Delta\Omega/\Omega)] . \tag{30}$$

As an example, by taking $m=1.5$, $\Delta\Omega/\Omega\simeq-0.02$, a typical decrease of volume on crystallization, and $\Delta B/B\simeq0.06$, one has from (30), $\Delta G/G\simeq0.04n$. As n ranges from 2 to 5 for different systems,[35] this change is of the correct order of magnitude although the model is too crude for a detailed comparison.

VI. AN APPLICATION TO A LIQUID

Although the dispersion relations (12) and (13) have been derived with specific reference to amorphous materials and the case of a liquid requires special considerations, it seems, nonetheless, tempting to see what sort of results they can give for a liquid. Since liquids cannot support static shear we can specialize (12) and (13) to the case of a liquid by requiring that the velocity V_T of the transverse waves in the long-wavelength limit ($q\rightarrow0$) be zero. By referring to Eq. (18), this means $\beta=-\frac{1}{5}\delta$, and Eqs. (12) and (13) reduce to

$$\rho\omega_L^2=\frac{2\nu\delta}{a^2}(\mathscr{I}_2-\tfrac{1}{5}\mathscr{I}_0)+\frac{\kappa_e K_{\mathrm{TF}}^2 q^2[G(qr_s)]^2}{q^2+K_{\mathrm{TF}}^2\tilde{g}(q)} , \tag{31}$$

$$\rho\omega_T^2=(\nu\delta/a^2)(\tfrac{3}{5}\mathscr{I}_0-\mathscr{I}_2) . \tag{32}$$

For $q\rightarrow0$, (31) and (32) give, retaining only the leading power of q ($qa\ll1$),

$$V_L^2=(1/\rho)(\tfrac{2}{15}\nu\delta+\kappa_e) , \tag{33}$$

$$V_T^2=(\nu\delta/\rho)\tfrac{1}{1050}q^2a^2 . \tag{34}$$

The dispersion of longitudinal waves according to (31) depends on the relative values of κ_e and δ. As an illustration, Fig. 5 depicts ω-q curves for two cases. First, $\delta=0$ so that pairwise interactions play no role and one has only the electronic term. [Actual value of κ_e was chosen to fit $V_L(0)$ for liquid rubidium.] We observe that $\omega_L(q)\rightarrow0$ as $q\rightarrow\infty$ for this case. Also, there are no shear waves for this case at any q. Secondly, δ was taken to be nonzero [with the value of δ chosen to fit $V_L(0)$ for rubidium, taking κ_e from the free-electron formula (8)]. For this case $\omega_L(q)$ oscillates about a nonzero value as q increases and has similar behavior as in an amorphous solid. For comparison, experimental data on rubidium obtained by Copley and Rowe[38] are also given in the figure.

When $\delta\neq0$, shear waves also exist for nonzero q and their dispersion is depicted in Fig. 5. It may be noted from (34) that for shear waves, for $qa\ll1$, $V_T\propto q$ or $V_T\propto\sqrt{\omega_T}$. This is the same proportionality as obtained for the velocity of the shear waves (or viscous waves as they are usually referred to) in a fluid on the basis of

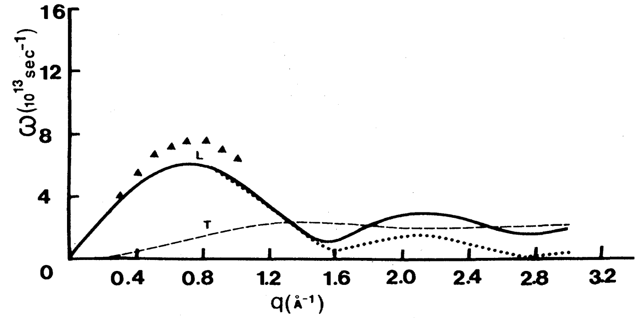

FIG. 5. Longitudinal and shear wave dispersion in a liquid for two choices of parameters: Case I, $\delta=0$; dotted curve gives ω_L and there is no shear wave for this case. Case II, $\delta\neq0$, ——, ω_L; — — —, ω_T. (For choice of parameters see text.) △, experimental on rubidium [Copley and Rowe (Ref. 38)].

Navier-Stokes equations of hydrodynamics.[39] Viscous waves are, of course, highly damped due to relaxation effects which are not taken into consideration in our work. As an illustration of the numerical values of V_T, taking $\kappa_e = 0$ and $V_L(0) \simeq 10^5$ cm/sec to fix δ, one obtains for $qa = 0.1$, $V_T \simeq 8.5 \times 10^2$ cm/sec or 1% of $V_L(0)$. For this value of qa, $\omega_T \simeq 5 \times 10^9$ sec^{-1} which is in the gigahertz range.

VII. SUMMARY AND OUTLOOK

Using a simple model of a metal, we have obtained in this paper analytic expressions for the dispersion of longitudinal and transverse phonons in an amorphous material. As all previous theoretical works seem to have involved intricate calculations and computer simulation, it was felt that a simple model such as presented here may provide useful insight. A perusal of Secs. IV and VI shows that the dispersion relations given here not only reproduce broad features of the dispersion in a variety of cases (Lennard-Jones interaction, central-force model for iron, metallic material, and liquid metal), but also give surprisingly fair quantitative agreement with experiment and computer simulation.

As regards the future outlook, we first mention that our work does not take into account the possibility of damping of phonons. This is important particularly for high q phonons and, indeed, necessary for the calculation of $S(q,\omega)$. We should note that when the damping is high, a dispersion relation obtained from $S(q,\omega)$ has not necessarily the same physical significance as that derived from an approach such as ours—the distinction arises from the fact that the dispersion is different for the temporally and spatially absorbed waves.[40] A second problem is the calculation of vibrational spectrum from the dispersion relations obtained here. Unlike a crystalline material, in an amorphous material there is no periodicity in q space and hence no natural restriction on q values for longitudinal or transverse excitations to occur. Since the nearest-neighbor distance varies from the mean a in a glass from region to region, one possible way is to take for the number of q values between q and $q + dq$ an expression of the type

$$\mathcal{N}(q)dq = \frac{\Omega}{2\pi^2} q^2 e^{-q^2/q_c^2} dq \ , \tag{35}$$

where q_c is a parameter. The factor in front of the exponential ensures that for $q \ll q_c$, $\mathcal{N}(q)$ reduces to the standard expression as it should. Because $\int \mathcal{N}(q)dq = \Omega n_i$, one has

$$q_c = (8\pi^{3/2} n_i)^{1/3} \ ,$$

which may be compared with the Debye cutoff $q_D = (6\pi^2 n_i)^{1/3}$. We hope to pursue these problems in a later work.

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