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Longitudinal and Transverse Excitations in a Glass

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The dynamic structure factor and its generalization for transverse excitations for the normal modes of a Lennard-Jones glass are calculated. The results are compared with those for a polycrystal. The longitudinal dispersion curve shows a remarkably deep minimum at the wave vector where the structure factor has a peak.

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Elementary excitations such as phonons have been studied extensively in crystalline materials by both experimental and theoretical techniques. For amorphous solids, however, the situation has not been nearly as thoroughly investigated nor as well understood. In particular, because of kinematic factors it has been impossible to study phonons near zero momentum transfer by inelastic neutron scattering. Whereas in crystals these excitations can be measured in the second Brillouin zone, in a glass there is no equivalent concept to these zones. In a few metallic glasses, spin waves have been observed[1,2] at small wave vector with neutron scattering but it was impossible to follow these excitations continuously, out to larger frequency. It has also been very difficult to calculate a dispersion curve for phonons in a glass since only average quantities are known, such as the radial distribution function or the density, whereas in a crystal all the atomic positions are known. Thus, despite the enormous interest in the amorphous state, there has been no experimental determination of the phonon dispersion curve for a glass. Of particular interest, because wave vector is no longer a good "quantum number," one would like to know how far out the dispersion curve can be followed and how the peaks in $S(k,\omega)$ broaden with increasing frequency.

Although there is no experimental probe to investigate transverse excitations in the same way that neutrons measure the longitudinal ones, they can be studied theoretically. Indeed, these excitations are the more interesting ones for a disordered material since they will be considerably different from what is found in crystalline structures. For example, much of the progress that has occurred in understanding the liquid state has come about through the investigation, by simulation and theory, of transverse phonons.[3] Transverse sound waves in a glass, although harder to study experimentally, can be studied via simulations on equal footing as longitudinal moves.

In the present paper we will present our study of the normal modes in a model glass produced by molecular-dynamics techniques. The samples studied consisted of 500, 250, and 100 particles interacting via a Lennard-Jones interatomic potential $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}]$. Periodic boundary conditions were used and the number density was $\rho^* = 0.95$. These samples were prepared by quenching the system from a well equilibrated liquid state to a temperature 10^{-5} of the equilibrium melting temperature. We refer to these systems as glasses since $g(r)$ has a split second peak, the structure factor shows no signs of any Bragg singularities, and the diffusion, on the time scale of our calculation, is zero. For the largest glass, consisting of 500 particles, the normal-mode eigenfunctions were obtained both by quench echo techniques[4] and by partial diagonalization of the dynamical matrix. For the small systems, where the matrix could fit entirely within the memory of the computer, straightforward diagonalization techniques were used. We have obtained the dynamical structure factor $S(k,\omega)$ for each of the individual modes. From this datum we have derived the dispersion curve for the phonons in the Lennard-Jones glass and found how the width of the peaks in $S(k,\omega)$ and $C_\perp(k,\omega)$ vary with increasing wave vector. Several features in these curves were found that were new and unexpected.

Figure 1 shows the function $f_\parallel(k,\omega)$ as a function of k for eight normal modes for a 250-particle glass. $f_\parallel(k,\omega)$ is given for a mode of frequency ω by

$$f_\parallel(k,\omega)=\langle|\sum_i \hat{k}\cdot\vec{P}_i^{\,\omega}\exp(i\vec{k}\cdot\vec{R}_i)|^2\rangle, \tag{1}$$

where $\vec{P}_i^{\,\omega}$, the polarization vector, is the maximum displacement of the ith atom vibrating in that mode and $\vec{R}_i$ is the position of that atom. The brackets indicate that the quantity is averaged over all k of the same given magnitude. $f_\parallel(k,\omega)$ is related to the one-phonon part of the coherent structure factor obtained by neutron scattering,[5]

$$S_{\text{coh}}(k,\omega)=e^{-2W}(\hbar k^2/2m)\times(2\omega\sinh\beta\omega)^{-1}f_\parallel(k,\omega), \tag{2}$$

where $2W$ is the Debye-Waller exponent.

We see in Fig. 1 that there are well-defined peaks in $f_\parallel(k,\omega)$ for both very low and very high ω modes. For the modes with lowest nonzero frequency, $\omega\tau=1.3$ [where $\tau\equiv\sigma(m/\epsilon)^{1/2}$], there are two regions of interest in k. Because we are dealing with a sample of finite length, L, and are using periodic boundary conditions, there is a lowest allowed value of k ($k_{\min}=2\pi/L$). At the lowest allowed frequency a full wavelength of a longitudinal sound mode will not completely fit inside the box and only the high-k tail of that sound peak will be observed. Thus at small k, $f_\parallel(k,\omega)$ decreases monotonically with increasing k and the low-k part of the sound peak is not seen. However, for the same mode, $\omega\tau=1.3$, there is also a well-defined broad peak near $k\sigma=7$. This value of $k\sigma$ corresponds to the first peak in the static structure factor. In a crystal one would get a peak at small ω near the first reciprocal lattice vector. This peak at $k\sigma=7$ corresponds to that structure. At higher ω, near $\omega\tau\simeq 10$, the first (sound) peak fully appears and is quite sharp. As ω increases further, the sound peaks in $f_\parallel(k,\omega)$ become broader in k as one would expect since eigenvectors in a glass do not have a sharp k. This can be seen at $\omega\tau\sim 14$ where the two peaks are both small and ill defined. The surprising fact is that as ω increases still further the peaks, instead of becoming broader in k, become better defined and become quite clear for the highest-frequency modes, some of which are highly localized in space. We would have expected these peaks in the high-frequency region to be the broadest of all. It is very remarkable that there is so much structure to be seen in $S(k,\omega)$ for a glass even in the region away from $k=0$.

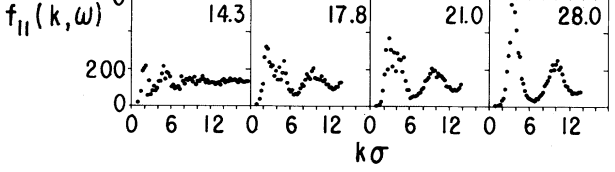

FIG. 1. $f_\parallel(k,\omega)$ vs $k\sigma$ for eight normal modes in the 250-particle glass, which was prepared by rapidly quenching the system from a liquid state to a temperature 10^{-5} of the equilibrium melting temperature.

In Fig. 2 we show the function analogous to $f(k,\omega)$ for transverse excitations,

$$f_\perp(k,\omega)=\langle|\sum_i \hat{k}\times\vec{P}_i^{\,\omega}\exp(i\vec{k}\cdot\vec{R}_i)|^2\rangle. \tag{3}$$

We see that for small values of $\omega\tau$, $f_\perp(k,\omega)$ has a more pronounced structure than does $f_\parallel(k,\omega)$ at small values of $k\sigma$. This is simply because the transverse sound velocity is smaller than the longitudinal velocity so that, for the same value of $\omega\tau$, the transverse wavelength more nearly fits within the size of the box than does the longitudinal one. As the frequency is raised, the peaks get broader and for values of $\omega\tau\sim 17$, the peak has almost completely disappeared. However, as seen in Fig. 2, at higher frequencies the peak in $f_\perp(k,\omega)$ again begins to emerge more clearly even though these are highly localized states. There is one very clear difference between the behavior of $f_\perp(k,\omega)$ and $f_\parallel(k,\omega)$. In $f_\parallel(k,\omega)$ there were always multiple peaks for each normal mode (although they became indistinct for $\omega\tau\sim 12$). In $f_\perp(k,\omega)$ there is only one clear peak for most of the excitations. Only for $\omega\tau>23$ does a second, very broad, peak begin to

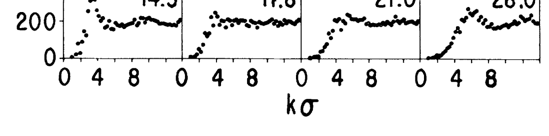

FIG. 2. $f_\perp(k,\omega)$ vs $k\sigma$ for the same eight normal modes shown in Fig. 1.

emerge above the background at higher wave vector.

From the data for all the $3Nf_{\parallel}(k,\omega)$'s and $f_{\perp}(k,\omega)$'s, it is possible to construct a dispersion curve for the normal modes. This is shown in Fig. 3, where $\omega\tau$ is plotted against the value of $k\sigma$ where the function has its maximum value. In Fig. 3(a), we have shown the positions of the first two peaks observed in $f_{\parallel}(k,\omega)$ and in Fig. 3(b) the position of the single peak seen in $f_{\perp}(k,\omega)$. The width of k of individual peaks has not been included, since one can get a good idea from Figs. 1 and 2 how well defined the peaks are in each frequency range. The scatter in the data points shows how the position of the peaks varies from one mode to another and gives another idea of the width of the excitations. From Fig. 1 we can see that the widths are narrow at low frequency, and become broader at intermediate frequencies and sharper again in the highest-frequency regime. The widths of the various peaks do not depend on the size of the system. We have compared the curves for systems of 100 and 500 particles. The curves in all cases had the same dispersion of the peak with frequency and similar values of the width.

The results that we have presented here for the excitations in a glass bear a striking resemblance to what is found in a polycrystalline sample.[6] In particular the dispersion curve for longitudinal excitations shows the same overall structure, with a minimum occurring near the peak in the static structure factor for a glass or the region of the first reciprocal lattice vector for a polycrystal. The shapes of the curves for $f_{\parallel}(k,\omega)$ also show similarities. The longitudinal sound peak gets broader with increasing ω in both the glass and polycrystal. In the region near $\omega\tau \simeq 12$ the valley between the peaks has begun to fill up in the polycrystalline sample,[6] similar to the lack of structure seen in the glass in the same frequency range. In the transverse modes, similarities still exist between the glass and the polycrystal[7] but they are less dramatic. In the polycrystal the dispersion curve for the transverse modes is not as nearly linear as it is in the glass. Also the velocity of transverse sound in the glass is approximately 20% smaller than in the crystal. Most unexpected is that in the polycrystal the transverse dispersion curve does show signs of a zone boundary and of a repeated zone scheme. In the glass there is no sign of the transverse modes having a second peak with intensity significantly above the background near $k\sigma = 7$.

In conclusion, we have calculated, for the first time, the structure of the normal modes for a monatomic, close-packed glass. We have obtained the dispersion relation for the phonons which for longitudinal modes looks very similar to the results for polycrystalline materials. The dispersion ω vs k for transverse modes increases in an almost linear way from the lowest to the highest frequency. A most dramatic result was that the width of the peaks in $f_{\parallel}(k,\omega)$ and $f_{\perp}(k,\omega)$ do not behave in a monotonic manner. The largest widths occurred at intermediate frequencies. Because there is considerable structure in $f_{\parallel}(k,\omega)$ away from the acoustic region near $k = 0$ it may be possible to observe this interesting region of the dispersion curves with neutron-scattering techniques. In particular there is a clear presence of a pseudo zone boundary for the longitudinal excitations whereas no such thing exists for the transverse modes.

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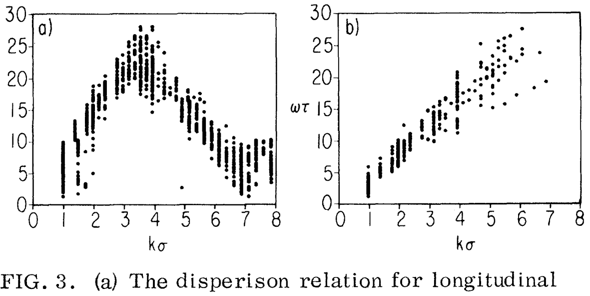

FIG. 3. (a) The disperison relation for longitudinal excitations, for the 250-particle glass of Fig. 1. (b) The dispersion relation for the transverse excitations.

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Anomalously Small Knight Shift and Relaxation Rate in the Nonalloying System: Isolated Yttrium Ions in Liquid Rubidium

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Time-differential and stroboscopic measurements of the perturbed angular γ-ray distribution for isolated ^{88}Y ions in liquid Sr and Rb are reported. A drastic drop in the Knight shift and the nuclear relaxation rate is observed as the Sr matrix is replaced by Rb. This implies an almost vanishing density of 5*s* states on the Y ion in Rb at the Fermi level. A volume expansion of the Y Wigner-Seitz cell is suggested as the mechanism causing this anomalous behavior in *Rb*Y.

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In the last few years some progress has been made in understanding the electronic structure of disordered systems, particularly of those liquid metals which show a metal-nonmetal transition.[1,2] The nature of such transitions is a main topic of current interest. Several models have been developed to investigate the central problem: What are the mechanisms for the changes of electronic structure which, in a few cases, could be directly observed by microscopic measurements?[1,3] It seems that there is a whole spectrum of different mechanisms leading to the general phenomenon of metal-nonmetal transitions.[1-4]

In this Letter we report the first observation of almost vanishing *s*-conduction-electron density at the Fermi level on a transition-metal ion in a metallic host. The phenomenon occurs for Y in a liquid Rb matrix whereas the *s* states reflect normal behavior for liquid *Sr*Y. The nonalloying systems *Rb*Y and *Sr*Y were made accessible by nuclear reactions which (i) lead to extremely dilute Y ions (concentration <1 ppm) in the liquid hosts and (ii) excite and orient the long-lived 8^+ nuclear isomer in ^{88}Y which serves as an ideal magnetic microscopic probe for the measurements of the static and dynamic response by perturbed angular γ-ray distribution (PAD) techniques. We were forced to improve the accuracy which had been hitherto obtained in γ-ray PAD experiments by an order of magnitude to measure the Knight shift, K, for *Rb*Y. The most surprising result is that both K and the magnetic relaxation rate τ_m^{-1} are extremely small for the system *Rb*Y. We suggest that this anomalous behavior is mainly caused by a drastic difference in volume between the Y and Rb ions.

Isolated ^{88}Y ions were produced by the reactions ^{87}Rb(α, 3n) and ^{88}Sr(d, 2n) in liquid (and solid) Rb, liquid Sr, and in a saturated solution of RbOH in H_2O with use of pulsed α and d beams provided by the cyclotron at the Kernforschungszentrum Karlsruhe. The Rb target was kept under high vacuum in Pyrex glass whereas Sr was kept in a tantalum crucible. The γ-ray anisotropy of the 8^+ isomer[5] ($T_{1/2} = 14$ ms, $g_N = 0.60$) in ^{88}Y was observed in an external field, B_{ext}, perpendicular to the beam-γ-detector [NaI(Tl)] plane.

Spin-lattice relaxation times τ_R were measured time differentially by the TDPAD method.[6] Examples are shown in Fig. 1. As a consequence of the very long half-life of the 8^+ isomer, one is forced to measure the TDPAD spectra at very small B_{ext} values ($\lesssim$10 G) which in turn limits the accuracy of the nuclear Larmor frequencies ω_L.

Therefore, the Knight shifts were investigated by the stroboscopic observation of the perturbed angular γ-ray distribution (SOPAD).[7] The reso-