

Normal-Mode Analysis by Quench-Echo Techniques: Localization in an Amorphous Solid

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(Received 13 October 1981)

A new technique is presented for investigating the normal modes of an amorphous solid with use of molecular-dynamics simulations. This method, based on the quench echo, can be used even in cases where the dynamical matrix is too large to be diagonalized. This technique has been applied to study the onset of localization in a Lennard-Jones frozen fluid.

PACS numbers: 63.20.Pw, 63.50.+x

In a recent paper¹ we have described a new physical phenomenon, the quench echo, which was observed in molecular-dynamics simulations of solids. This echo occurs in the kinetic energy of a solid which has been prepared by two successive quenches of the velocity; when the quenches are separated by an interval t_1 , the echo appears in the form of a deep minimum in the kinetic energy at a time t_1 after the last quench.

In the present paper we show that this phenomenon can be developed into a new and powerful tool for studying the eigenvectors and eigenfrequencies of normal modes in large complex solids, even in cases where the dynamical matrix is too large to be diagonalized on present-day computers.² The behavior of the eigenvectors in an amorphous solid has enabled us to examine the onset of phonon localization. We find that at high frequencies the phonons are all very well localized. As the frequency is lowered they become more spread out and extend over the entire sample.

The sample we have studied is a 500-particle amorphous solid obtained by rapid cooling from the liquid state.³ Periodic boundary conditions were used and the particles interacted via a Lennard-Jones potential: $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ with a cutoff at $r = 2.5\sigma$. This glass was well equilibrated for $200\,000\Delta t$ [Δt is the time step for each iteration: $\Delta t = 0.01\tau = 0.01\sigma(M/\epsilon)^{1/2}$, M being the mass of the particles] at a reduced temperature $T^* \equiv k_B T/\epsilon = 0.11$ and at a fixed number density $\rho^* = 0.95$.

For a harmonic solid we have derived¹ an expression for the kinetic energy (or instantaneous temperature) as a function of time after an arbitrary number of quenches. Each quench instantaneously sets every velocity to zero so that the kinetic energy, and therefore T^* , is also instantaneously zero. Subsequent to the quench, some of the potential energy of the system is converted to kinetic energy as time passes. After several quenches separated by the intervals t_1, t_2, \dots, t_N , the kinetic energy can be expressed as

$$T = \int_0^\infty D(\omega) A^2(\omega) \cos^2 \omega t_1 \cos^2 \omega t_2 \cdots \cos^2 \omega t_N \sin^2 \omega t d\omega,$$

where $D(\omega)$ is the density of normal modes at frequency ω and $A(\omega)$ is proportional to the average amplitude of the modes at that frequency. The time t is measured from the instant of the last quench. If the intervals are all equal to t_1 then

$$T = \int_0^\infty D(\omega) A^2(\omega) \cos^{2N} \omega t_1 \sin^2 \omega t d\omega,$$

which for large N can be approximated by

$$T = \left(\frac{\pi}{N}\right)^{1/2} \frac{1}{2t_1} A^2 \sum_n D\left(\frac{n\pi}{t_1}\right) \sin^2\left(\frac{n\pi}{t_1} t\right),$$

where we have replaced the random coefficients $A^2(\omega)$ by their average value, $\frac{1}{2}A^2$. If $\pi/\omega_D < t_1 < 2\pi/\omega_D$, where ω_D is the highest frequency of a mode in the solid, then $D(n\pi/t_1)$ is nonzero only for $n=1$ and only one mode exists (except for accidental degeneracies which would not be expected in a glass). Therefore after many quenches separated by the same interval t_1 (or multiples of it, mt_1) all the modes in the solid are completely drained of energy except the one with $\omega = \pi/t_1$.

After making a large number of quenches the system is allowed to develop without any extraneous manipulation. If the moment of the last quench is taken as $t=0$, the quantities $R^2(t) = \sum_i [r_i(t) - r_i(0)]^2$ and $T(t) = \sum_i v_i^2$ show a perfect sinusoidal behavior with periods $2\pi/\omega$ and π/ω , respectively. Any departure from such behavior is an indication of the "impurity" of the mode being isolated. In practice, we have found three sources of difficulties that make the isolation of a single normal mode by this method a nontrivial task.

(i) Nearly degenerate modes of frequency $\omega = \omega_1 \pm \Delta$ can be difficult to separate from the desired mode. One can detect the presence of such nearby modes by observing that the kinetic energy shows a characteristic beating as a function of time. To get rid of the unwanted mode one must simply let the system run undisturbed until the two modes are a quarter period out of phase and quench the system again at this time. The desired mode will be unaffected while the unwanted mode will have all its energy drained from it.

(ii) Another difficulty in isolating a high-frequency mode is that low-frequency modes may still be present after many quenches. Fortunately $R^2(t)$ is very sensitive to low-frequency modes since if two modes have the same kinetic energy, their displacements will vary as ω^{-2} . Again these low-frequency modes can be removed by quenching the solid at a time when the low-frequency mode has a maximum kinetic energy and the high-frequency mode has zero kinetic energy. All these judgments can be made by the time behavior of R^2 and T .

(iii) The third difficulty is relatively minor. The frequency corresponding to the time interval t_1 between successive quenches may not be the frequency of any mode in the solid. To remedy this situation one can simply shift the time t_1 by an appropriate small amount so as to correspond to the period of the oscillations appearing in the kinetic energy after several quenches have been performed.

There are many possible variations on the method we have described above to isolate normal modes. In particular one can alternately heat and quench the system at quarter-period intervals instead of just quenching at half-period intervals as described above.

We have isolated a large number of normal modes in the Lennard-Jones frozen fluid described above. We were interested in studying the localization of the modes in this system and so we concentrated our attention on the high-frequency

region of the density of states. With use of the method explained above, a mode was considered "pure" when finally T and R^2 showed no degradation in their perfect sinusoidal behavior for at least 150 complete cycles (~ 900 steps of molecular-dynamics integration).⁴ The final temperature of the solid after a single mode was purified was low, $T^* < 10^{-4}$, so that anharmonic effects were negligible. Anharmonicity could be important in real solids with light atoms where even the quantum zero-point energy could be sufficient to produce observable anharmonic effects. In this paper we are studying only the harmonic system which is well described by classical mechanics.

For each mode we have calculated two quantities with which to characterize the degree of localization. The first is $P^{-1} = N \sum v_i^4 / (\sum v_i^2)^2$, or the inverse of the so-called "participation ratio," used by Bell and Dean² for the same purpose. For modes extending over the whole system this quantity will be of order unity (for a thermal system it is $\frac{5}{3}$); for localized modes its value will be large. We have also calculated the kinetic energy-kinetic energy correlation function.

$$h(r) = \frac{\sum_{i,j} v_i^2 v_j^2 \delta(r - r_{ij})}{\sum_{i,j} \delta(r - r_{ij})},$$

where r_{ij} is the distance between the particles i and j . The denominator is the radial distribution function at distance r .

In Fig. 1 we show $h(r)$ for two modes, one highly localized and one extended. Notice that the localized mode has a large slope on this logarithm scale and decays by 3 orders of magnitude in a distance of four interatomic spacings. In this mode 98% of the kinetic energy is contained in twelve atoms. The extended mode does not show any tendency to decay. This dramatic change in behavior has occurred in a narrow range of frequency. The slope, L^{-1} , of $\ln h(r)$ vs r for the various modes is shown as a function of frequency in Fig. 2(a). Below $\omega_T = 24.5$ the modes are clearly extended over the size of the system while above that frequency the modes get progressively more localized with increasing frequency. The same trend can be seen in Fig. 2(b), where the quantity P^{-1} is plotted versus frequency. At high frequencies the inverse participation ratio is large while at lower frequencies it is small. A normal mode with a frequency as low as $\omega_T = 8$ has been isolated showing the same trend, i.e., very small values of L^{-1} and P^{-1} .

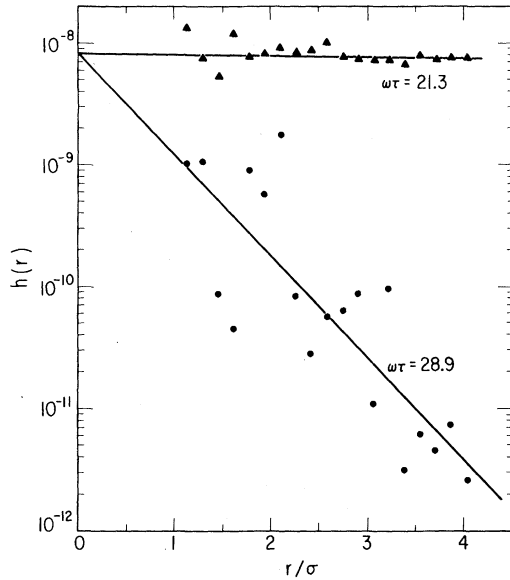


FIG. 1. The function $h(r)$ vs r/σ for an extended mode with $\omega\tau=21.3$ (triangles) and for a localized mode with $\omega\tau=28.9$ (circles).

The structure of the individual normal modes was analyzed to determine the mutual coordination of the atoms participating in highly localized modes. This analysis was undertaken because of a recent theory by Cohen, Singh, and Yonezawa⁵ which predicted that the most localized modes in a solid would be in regions with even-numbered coordination rings. We found that all the localized modes are made up of threefold rings of participating atoms indicating that the theory is not applicable to our close-packed amorphous solid.

We have checked that our modes are indeed the true normal modes of the system. Although the 1500×1500 matrix exceeded the available storage it was possible to diagonalize the dynamical matrix for a subset of the particles (up to 300) inside a spherical region if all the atoms outside the sphere were kept stationary. We have done this in regions where we found highly localized normal modes by the quench method. The eigenfunctions of the dynamical matrix were found to correspond to the localized modes we found from our quench analysis but only for the highly localized modes; the more extended ones are not completely contained within the sphere of particles allowed to move. In only one case we found that a localized mode which we had isolated by quenching was actually a combination of two nearly degenerate modes.

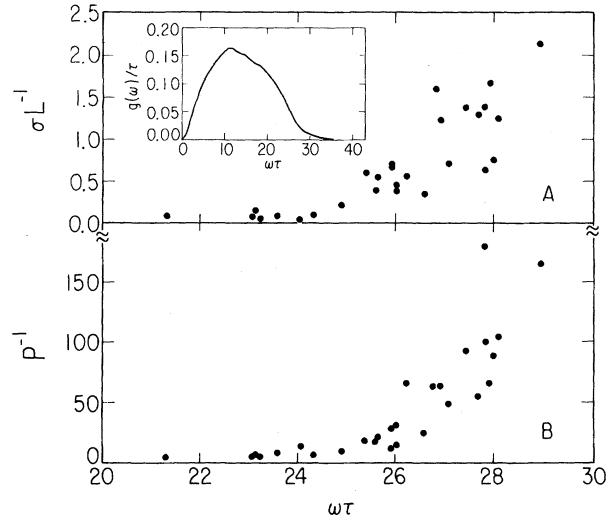


FIG. 2. (a) L^{-1} , the slope of $\ln h(r)$, vs frequency. (b) P^{-1} vs frequency. The inset in (a) shows the density of states for this system (taken from Ref. 3).

In Fig. 3 we show the dynamic structure factor⁶ divided by $|k|^2$ for two modes on either side of the localization threshold to see if inelastic neutron scattering can distinguish between a localized and an extended mode. The same behavior is seen for all the high-frequency ($\omega\tau > 21$) modes we have isolated. We see that there is no qualitative difference between the structure factor for these two modes. The value of $S(k, \omega)$ is peaked near $k\sigma = 4.5$ which is approximately one half the distance to the first peak in $S(k)$. These modes are thus made up primarily of neighboring atoms

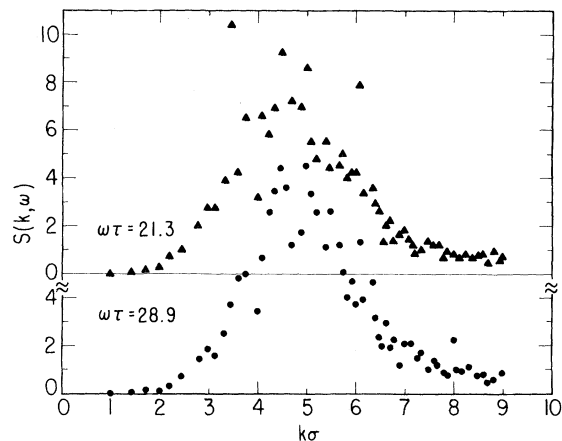


FIG. 3. $|k|^{-2}S(k, \omega)$ vs k for the two modes with frequencies $\omega\tau=21.3$ (triangles) and $\omega\tau=28.9$ (circles).

moving out of phase with respect to one another.

We have presented here a new technique for investigating the normal-mode structure of an amorphous solid using molecular-dynamics studies. This technique can be used where all conventional techniques of diagonalizing the dynamical matrix no longer work since the matrix is too large and not sparse enough to diagonalize even on modern-day computers. The technique should also be applicable to finding other kinds of eigenfunctions of second-order equations, such as the wave functions of electrons. We have applied the technique to the localization of modes in a Lennard-Jones frozen fluid and found that there is a threshold frequency above which localization occurs. The study of localization by molecular-dynamics techniques is of particular interest since it is a true interacting many-body system. As the amplitude of a mode is increased it interacts more strongly with other modes. The way in which localization affects the interaction of modes has not been previously studied. Simulations of electron localization⁷ do not offer the possibility of studying this kind of phenomena. We are currently pursuing the studies of our localized modes as a function of amplitude in order to understand how mode-mode interactions affect their properties.

This work was supported in part by National Science Foundation Grants No. DMR 80-21256 and No. DMR 80-17756 and by the U. S. Department of Energy. S. R. N. benefited from an Alfred P. Sloan Foundation Fellowship.

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²For a review of this work, see R. J. Bell, in *Methods in Computational Physics*, edited by G. Gilat (Academic, New York, 1976), Vol. 15, p. 216.

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⁴To obtain a mode of high purity we typically quenched the system periodically approximately fifty times and then let the system run unperturbed to detect the presence of low-frequency modes and modes nearly degenerate in frequency with the desired mode. Twenty additional quenches, with longer intervals between them, were usually sufficient to purify the mode.

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⁶In fact what is shown in Fig. 3 is the "one-phonon part" of $S(\mathbf{k}, \omega)$ divided by k^2 .

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Ultrafast Configurational Relaxation of Optically Excited Color Centers

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(Received 29 October 1981)

The configurational relaxation time for the $F_A(\text{II})$ center in KCl:Li has been measured with use of picosecond laser techniques. The saddle-point configuration of the electronically excited state is stabilized by means of multiphonon emission, and has a zero-temperature lifetime of 13 psec.

PACS numbers: 61.70.Dx, 63.20.Mt, 78.45.+h

In this Letter, we report the first direct measurement of the configurational relaxation time for color centers. In particular, we have measured the rise of optical gain from the relaxed excited state (RES) of $F_A(\text{II})$ centers following excitation with a subpicosecond optical pulse. For the $F_A(\text{II})$ center in KCl:Li, we find that the configurational

relaxation has a lifetime of 13 psec for temperatures below 10 K and shows a temperature dependence characteristic of a multiphonon process.

The F_A center is an F center in which one of the host cations adjacent to the vacancy is replaced by a dopant cation.¹ Type-II F_A centers are distinguished from F centers and type-I F_A centers