

## Phonon Localization and Anharmonicity in Model Glasses

Sidney R. Nagel

*The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637*

and

Gary S. Grest

*Corporate Research Science Laboratory, Exxon Research and Engineering Company, Annandale, New Jersey 08801*

and

A. Rahman

*Argonne National Laboratory, Argonne, Illinois 60439*

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We have studied the localization of normal modes in a model glass as a function of several parameters and found that the fraction of modes which are localized remains small even when the disorder is very large. We have also studied how anharmonic effects, such as the Grüneisen parameter, are influenced by whether or not a mode is localized or extended.

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One of the most dramatic consequences of disorder in a three-dimensional solid is the localization of some of its elementary excitations.<sup>1</sup> Electron localization occurs first in the high- and low-energy band tails and, as disorder is increased, proceeds towards the center of the band. In the case of phonons the low-frequency acoustic modes remain extended while only the high-frequency band tail becomes localized upon disordering the solid.<sup>2-5</sup> Whereas electron localization has profound effects on the properties of the solid, phonon localization has a much smaller impact on the behavior of the solid. The fundamental reason for this is that the electronic transport properties of a solid are dominated by those electrons within  $kT$  of the Fermi level. These electrons may be either localized or extended. For phonons, on the other hand, there is no equivalent concept to a Fermi level and even when  $T$  is high enough to excite some localized

phonons, the lower-frequency, extended phonons already dominate most of the thermal properties.

In this paper we will investigate the localization of phonons in samples with varying amounts of disorder using computer-simulation techniques. We will show that there are some unique properties of localized modes in glasses which do distinguish them from extended states. In the study of phonons it is possible to simulate the interacting many-body system; for electrons, however, this is not possible. At low amplitudes of vibration, the motion is harmonic and the normal modes do not interact with one another. At higher amplitudes of vibration, the anharmonicities in the interparticle potential become important. Thus simply by increasing the oscillation amplitude of a mode, one can make it interact with all the other modes in the sample.

The samples studied consisted of 500, 1000, or 4096 particles interacting via the potential<sup>6</sup>

$$V(r) = \begin{cases} 4\epsilon h [(\sigma/r)^{12} - (\sigma/r)^6] + (h-1)\epsilon, & r < 2^{1/6}\sigma, \\ 4\epsilon [(\sigma/r)^{12} - (\sigma/r)^6], & 2^{1/6}\sigma \leq r, \end{cases}$$

For  $h = 1.0$  this reduces to the usual Lennard-Jones potential. By reducing  $h$  we can soften the repulsive core of the potential. The interaction was usually truncated at  $r = 2.5\sigma$ . We used periodic boundary conditions. The samples were prepared by quenching the systems from a well-equilibrated liquid state to  $T < 10^{-5}$  of the equilibrium melting temperature where no diffusion could be observed. The normal modes were then calculated by a recursive technique. A number of glasses were studied.

Two samples consisted of 500 particles all of the same size with a number density  $\rho^* = 0.95$  and  $h = 1.0$  and  $0.8$ . A third sample, was made up of 500 particles with two different sizes, with  $h = 1.0$  and  $\rho^* = 1.8$ . Half of the particles had diameter  $\sigma$  and the other half had diameter  $0.5\sigma$ ; the masses of both particles were the same and the depth of the interatomic potential between all pairs of particles was  $\epsilon$ . We have also investigated how the range of

interaction affects localization. In a 500, 1000, and 4096 particle glass with  $h = 1.0$  and  $\rho^* = 0.95$  the range was reduced from  $r = 2.5\sigma$  to  $r = 2^{1/6}\sigma$ , that is, to a pure repulsive potential.

For each of the high-frequency modes in these glasses we computed the inverse participation ratio<sup>7</sup>:  $P^{-1} = N \sum_i v_i^4 / (\sum_i v_i^2)^2$ , where  $\bar{v}_i$  is the polarization of the mode on particle  $i$  and  $N$  is the total number of particles.  $P^{-1}$  should be of order unity if the mode is extended and will be large if it is localized. In Fig. 1, we plot  $P^{-1}$  versus reduced frequency  $\omega\tau$  [ $\tau = \sigma(m/\epsilon)^{1/2}$ ] for several of the glasses. In Fig. 1(a), we show the results for our largest glass, the 4096-particle system. The localization threshold is well defined by a sharp break in the data at  $\omega\tau = 25.5$ . We can calculate the fraction of the total number of modes which are localized using the criterion that a mode is localized if  $P^{-1} > N^{1/2}$ , as has been done in numerical studies of electron localization. We find that only 1% have frequencies above the threshold. In Fig. 1(b) we plot  $P^{-1}$  for our most disordered sample, the 500-particle 50-50 alloy glass. This is for a smaller system than that shown in Fig. 1(a), so that the threshold is not as well defined, but we again find that 3% of the modes are localized. We find this result surprising since we would have naively expected that the fraction of localized states would markedly increase when we decrease the amount of short-range order. The static structure factor reaches a height of 6 at its first peak for the glass in Fig. 1(a) but is less than 2 for the glass in Fig. 1(b), indicating that the amount of short-range order has indeed been significantly reduced. Finally, in Fig. 1(c), we plot  $P^{-1}$

for three 500-particle, monatomic glasses, with (i)  $h = 1.0$  and range  $2.5\sigma$ , (ii)  $h = 1.0$  and range  $2^{1/6}\sigma$ , and (iii)  $h = 0.80$  and range  $2.5\sigma$ . We find that 1%, 1%, and 1.6% of the modes are localized, respectively, for these three cases. Note that the curves have been displaced for clarity. Indeed, for all the glasses we studied we have found a similar fraction of localized modes; only the position of the threshold changes. Our studies of two 500-atom glasses with  $h = 1.0$  and range  $2.5\sigma$ , as well as three glasses with  $N = 500, 1000,$  and  $4096$  for  $h = 1.0$  and range  $2^{1/6}\sigma$  show that there is little statistical fluctuation in the number of modes with  $P^{-1} > N^{1/2}$ . The use of some other criterion<sup>7</sup> to determine whether a mode is localized will change the precise fraction of localized modes but will not change the overall result that these glasses have very few localized modes. The range of the potential, the softness of the repulsive core, and alloying with spheres of differing sizes do not appreciably affect the fraction of localized modes. One way that this fraction can be increased significantly is by varying the masses.<sup>2</sup> Our concern here, however, has been solely on the effect of topological disorder with symmetric potentials on the localization of phonons and for this reason we have chosen all of the masses to be equal.

We have also studied the anharmonic properties of localized modes by computing the Grüneisen parameter of each mode;  $\gamma_i = d \ln \omega_i / d \ln V$ , where  $V$  is the volume. We found that  $\gamma_i$  was near 3.2 for all modes, including the lowest-frequency acoustic modes of our sample. It showed no change near the localization threshold. The average value of  $\gamma_i$

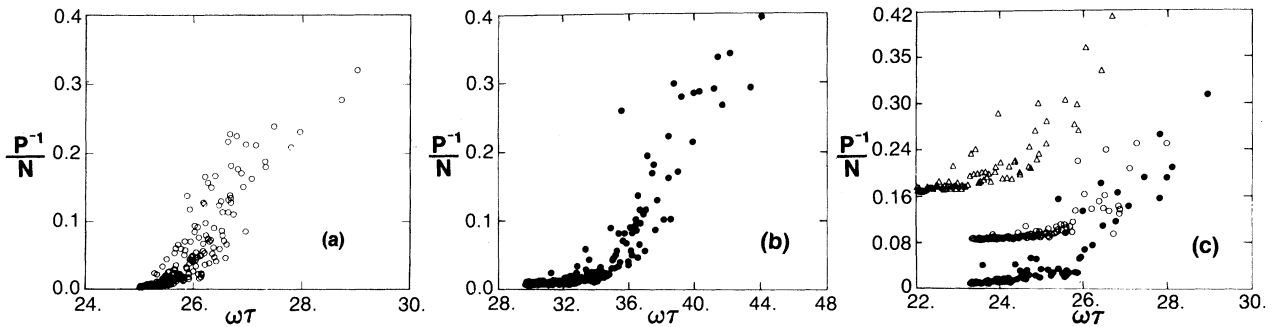


FIG. 1. The inverse participation ratio  $P^{-1}/N$  vs  $\omega\tau$  for a number of glasses. The 200 highest-frequency modes are shown in (a) for a 4096-atom glass with  $h = 1.0$  and range of interaction  $2^{1/6}\sigma$ . In (b), the 200 highest-frequency modes are shown for the 50-50 glass with 500 atoms. In (c), the 100 highest-frequency modes are plotted for three glasses,  $h = 1.0$  and range  $2.5\sigma$  (closed circle),  $h = 1.0$  and range  $2^{1/6}\sigma$  (open circle), and  $h = 0.80$  and range  $2.5\sigma$  (open triangle) for 500-atom glasses. For clarity, the results in (c) have been displaced along the vertical axis. We consider the modes to be localized if  $P^{-1}/N > N^{-1/2}$ , which is 0.0156 for the 4096-atom glass in (a) and 0.045 for the 500-atom glasses in (b) and (c).

for all the modes in the glass ( $\bar{\gamma} = 3.2$ ) is actually smaller than the value ( $\bar{\gamma} = 3.5$ ) in the corresponding fcc crystal at the same density. The spread in  $\gamma_i$  was larger for the crystal than for the glass.

Another probe of the anharmonicity of a mode is to measure its frequency shift as the amplitude of oscillation is changed. To do this we have performed molecular-dynamics simulations when only one normal mode of the sample is excited. For this situation the temperature  $T^*$ , which is just proportional to the kinetic energy of the system, oscillates sinusoidally between 0 and  $T_{\max}^*$ .  $T_{\max}^*$  is proportional to the square of the amplitude of the mode. If all velocities are multiplied by some large factor,  $T_{\max}^*$  will increase and  $T^*$  will not oscillate in a sinusoidal manner because, as a result of anharmonic interactions, many other normal modes will be excited. These extraneous modes can be eliminated with quench-echo techniques.<sup>3</sup> After this procedure has been followed, the temperature will again oscillate between 0 and a new value of  $T_{\max}^*$ . We can therefore determine the frequency shift of a mode by comparing the frequency of oscillation of the temperature as a function of  $T_{\max}^*$ . We note, however, that this is not the same result that would be found if all modes in the solid are equally excited. Our method allows us to determine the shift in frequency when only a single mode is allowed to vibrate. The results are shown in Fig. 2. We see that all frequencies shift to lower values. Below the localization threshold the value of  $-d\omega\tau/dT^*$  is very small and increases above the threshold. Thus, even though  $\gamma_i$  does not show any difference between the anharmonicity of localized and extended modes,  $-d\omega\tau/dT^*$  does show a large difference.

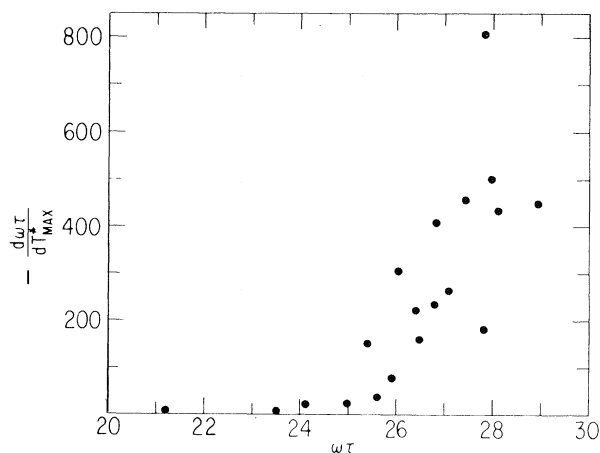


FIG. 2. The shift in frequency with respect to the amplitude of the vibration,  $-d\omega\tau/dT^*$ , vs  $\omega\tau$ .

There is a simple explanation of this effect. If two modes at nearby frequencies, one localized and one extended, have the same total kinetic energy, then a particle in the localized mode will be moving with a higher velocity than one in the extended mode. This highly energetic atom will explore a larger portion of the anharmonic potential of its environment. The localized mode will therefore then start to "act more anharmonically" than the extended mode at a nearby frequency with the same total kinetic energy.

Because the sample is disordered there is no symmetry criterion which requires that, as a mode is excited more and more actively, the atoms should continue to oscillate about the same positions as they did at a lower amplitude of vibration. In Fig. 3 we show for the highest-frequency mode,  $\omega\tau = 28.9$ , and for an extended mode,  $\omega\tau = 21.2$ , how, as  $T_{\max}^*$  is increased, the centers of vibration of the particles change. Here

$$\langle \Delta r_e^2 \rangle = N^{-1} \sum_i [\bar{r}_{ie}(T_{\max}^*) - \bar{r}_{ie}(0)]^2,$$

where  $\bar{r}_{ie}(T_{\max}^*)$  is the position of atom  $i$  at the center point of its oscillation when the maximum temperature is  $T_{\max}^*$ . The data show that  $\langle \Delta r_e^2 \rangle = A(\omega) T_{\max}^{*2}$  over a very large range of temperatures. We have found that the coefficient  $A(\omega)$  is small below the localization threshold and grows smoothly, in a similar manner as does the data in Fig. 2, above the threshold. Since these cal-

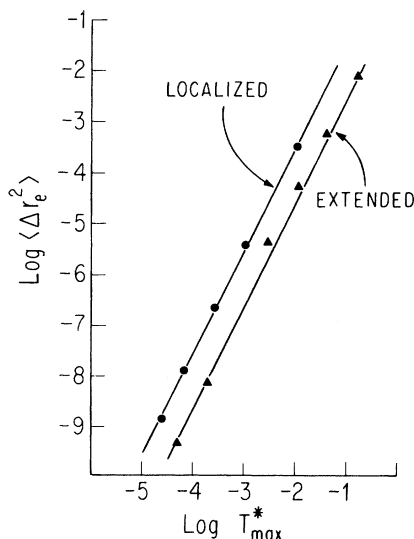


FIG. 3. Change of the center of vibration of the particles  $\langle \Delta r_e^2 \rangle$  vs the amplitude of the vibration  $T_{\max}^*$ .  $\omega\tau = 28.9$  (closed circles) and  $\omega\tau = 21.2$  (closed triangles).

culations were done at constant volume, we have not allowed any thermal expansion in the glass. This change in the center of vibrations corresponds in a sense to a *local* thermal expansion. However, care must be taken before this can be interpreted as thermal expansion in a real solid because our calculations are completely classical, and we know that in a real solid, quantum mechanics is important for explaining the thermal expansion at low temperatures.

In conclusion, we have shown that the fraction of localized modes in a glass is insensitive to a number of parameters such as the details of the potential, the range of interactions, and the amount of short-range order. The disorder was varied by making samples with particles of two sizes but the same mass. We have shown how localization of phonons influences some of the anharmonic properties of a solid. Indeed, although some measures of anharmonicity such as the Grüneisen parameter are not effected by localization, other parameters are. Measurements which probe the anharmonicity of a mode as a function of frequency (e.g., frequency shifts upon excitation) may therefore provide an

experimental probe of phonon localization in glasses.

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