Harmonic Vibrational Excitations in Disordered Solids and the "Boson Peak"

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We consider a system of coupled classical harmonic oscillators with spatially fluctuating nearest-neighbor force constants on a simple cubic lattice. The model is solved both by numerical diagonalization and by applying the single-bond coherent potential approximation. The results for the density of states $g(\omega)$ are in excellent agreement with each other. If the system is near the borderline of stability a low-frequency peak appears in the quantity $g(\omega)/\omega^2$ as a precursor of the instability. We argue that this peak is the analogon of the "boson peak," observed in structural glasses and other disordered solids. By means of the level distance statistics we show that the peak is not associated with localized states. [S0031-9007(98)06516-8]

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A ubiquitous and rather intriguing feature in the physics of glasses is the anomalous behavior of the low-frequency part of the vibration spectrum and the corresponding thermal properties [1]. While the origin of the linear low-temperature specific heat is commonly attributed to the existence of double-well potentials or two-level systems [1], there is still considerable debate about the so-called "boson peak" [2]. This peak shows up in the density of states (DOS) $g(\omega)$ as an excess contribution [3–10], compared to the usual Debye behavior [$g(\omega) \propto \omega^2$]. Similar phenomena also appear in disordered crystals [9,11]. Because of the development of new experimental techniques allowing one to perform Brillouin scattering measurements in the THz range [12–14], as well as pertinent molecular dynamics simulations [15–21], the question concerning the nature of the modes in the boson peak region has gained much additional interest recently. The boson peak also seems to persist at elevated temperatures, where its relation to the liquid-glass transition and the corresponding relaxation dynamics is a matter of discussion [22–26].

Several models have been formulated to explain the physical origin of the boson peak [10,27]. In the soft-potential model [28,29] the existence of anharmonic localized potential wells (and double wells) are considered as the reason for the excess DOS. In other approaches only harmonic degrees of freedom have been considered, i.e., systems of harmonic oscillators, which are coupled by fluctuating force constants. In the phonon-fracton model [30–33] the force constants fluctuate between a finite (constant) value and zero, constituting a bond percolation problem. In another series of studies continuous distributions of force constants were considered [34]. Both types of models exhibit a crossover from propagating to non-propagating waves at a characteristic frequency. The appropriate versions of the effective medium approximation [coherent-potential approximation (CPA) for lattices with disorder [35] and effective-medium approximation (EMA) for amorphous solids [34]] predict for both models an excess DOS near the crossover frequency [31,32,34]. Unfortunately a direct numerical diagonalization analysis of the phonon-fracton model did not show any excess DOS near the phonon-fracton crossover [33]. Therefore the possibility could no more be ruled out that in the case of a continuous force constant distribution the excess DOS might also be an artifact of the EMA.

In the present Letter we present for the first time compelling evidence that a strongly disordered three-dimensional system of coupled harmonic oscillators with a continuous force constant distribution exhibits an excess low-frequency DOS (boson peak) as a generic feature. This is achieved by comparing the results of a CPA calculation with those of a numerical diagonalization. We show that the effect is most pronounced if the system is almost unstable. The boson peak thus appears as a precursor of an instability.

Our model consists of a set of coupled scalar harmonic oscillators placed on a simple cubic lattice with lattice constant $a = 1$. The coupling among the oscillators is modeled by nearest-neighbor force constants K_{ij}, which are treated as independent (quenched) random variables, chosen according to a distribution with density $P(K_{ij})$. The corresponding Hamiltonian has off-diagonal elements $\mathcal{H}_{ij} = K_{ij}$ and diagonal elements $\mathcal{H}_{ii} = -\sum_{j\neq i} K_{ij}$. For a stable system all eigenvalues $\lambda_i = -\omega_i^2$ are negative (except one of them, which is always zero), ω_i denoting the vibrational eigenfrequencies. In all calculations we have chosen a truncated Gaussian distribution with $P(K) = P_0 \exp\{-(K - K_0)^2/2\sigma^2\}\theta(K - K_{\min})$.

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Here $\theta(x)$ denotes the step function, P_0 is a normalization constant, and K_0 and σ denote the maximum value and the width, respectively. In our calculations $\sqrt{K_0}$ serves as frequency scale (i.e., $K_0 = 1$ in our units). The lower cutoff of the force constant distribution is denoted by $K_{\min}$. This cutoff is introduced to allow for the study of strongly disordered systems with a restricted amount of negative force constants.

For the numerical treatment we considered a cubic box of size L and imposed periodic boundary conditions. The resulting $L^3 \times L^3$ Hamiltonian matrix was diagonalized using the NAG-LAPACK routine DSYEV. The distribution of eigenvalues exhibits gaps due to finite-size effects. In order to eliminate these effects we calculated the integrated density of levels $F_L(\lambda) = \sum_i \theta(\lambda - \lambda_i)$ for a given size L, smoothed this function and averaged it over different sizes, ranging from $L = 10$ to $L = 14$. This procedure yielded a function $\bar{F}(\lambda)$, the derivative of which gives the density of levels $n(\lambda) = d\bar{F}(\lambda)/d\lambda$. From this the vibrational DOS follows as $g(\omega) = 2\omega n(-\omega^2)$.

For an approximate solution of our model we have used the single-bond CPA [35]. This theory is formulated in terms of a frequency-dependent force constant ("self energy") $\Gamma(\omega)$, which can be visualized as the inverse of an acoustic dielectric function. The frequency-dependent complex sound velocity $v(\omega)$ is given by $\Gamma(\omega) = v(\omega)^2$. In CPA the quantity Γ is determined self-consistently in terms of the local Green's function $G_0(z) = \sum_{k_x k_y k_z} [z + 6 - 2(\cos k_x + \cos k_y + \cos k_z)]^{-1}$ of the ordered cubic lattice (the sum runs over the Brillouin zone and $z = -\omega^2 + i\epsilon$) as follows:

$$\left\langle \frac{\Gamma(z) - K_{ij}}{1 - [\Gamma(z) - K_{ij}][1 - z\tilde{G}_0(z)]/3\Gamma(z)} \right\rangle = 0 , \quad (1)$$

with $\tilde{G}_0(z) = G_0[z/\Gamma(z)]/\Gamma(z)$ and $\langle A \rangle = \int dK_{ij} \times P(K_{ij}) A(K_{ij})$. The DOS is obtained from a numerical solution of Eq. (1) and use of the relation $g(\omega) = -(2/\pi)\omega \, \mathrm{Im}\{\tilde{G}(z)\}$.

From our calculations we find that if the amount of negative force constants becomes too large the system becomes unstable. Without lower cutoff (i.e., $K_{\min} = -\infty$) this happens for $\sigma > 0.6$. In CPA the instability occurs at a slightly higher value. In order to be able to study a strongly disordered system with $\sigma = 1$ we introduced the lower cutoff $K_{\min}$ which controls the amount of small and negative force constants. Here the system becomes unstable near $K_{\min} = -0.6$ (numerical diagonalization), whereas in CPA the instability occurs at $K_{\min} = -0.85$.

In Fig. 1 we present the results for $g(\omega)/\omega^2$ obtained in CPA (lines) and by numerical diagonalization (symbols) for various values of σ and $K_{\min}$. For comparison the spectrum of the ordered lattice ($\sigma = 0$) is also shown. The excellent agreement of the CPA calculations with the numerical analysis [36] (except for the immediate vicinity of the instability) indicates both the reliability of the CPA and the correctness of the procedure utilized

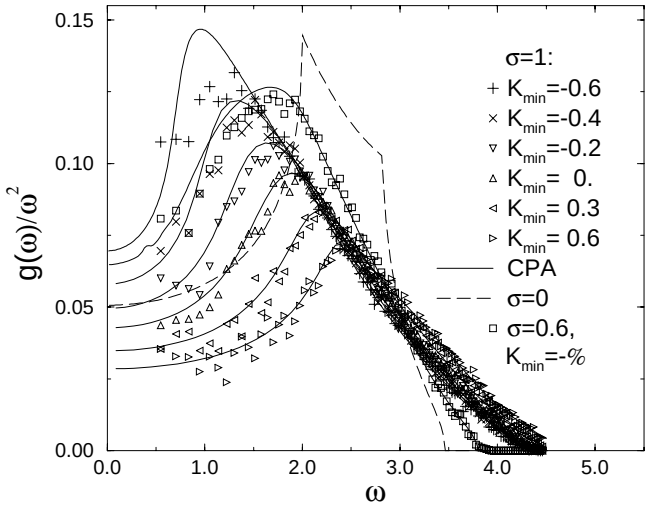

FIG. 1. Reduced DOS $g(\omega)/\omega^2$ versus frequency for force constant distributions with (i) $\sigma = 0$ (no disorder, dashed line), (ii) $\sigma = 0.6$ and $K_{\min} = -\infty$, as well as (iii) $\sigma = 1$ and different lower cutoffs $K_{\min}$. The symbols represent the numerical diagonalization, the full lines the CPA results. The agreement is achieved without any adjustable parameters.

for the elimination of finite-size effects in the numerical work. It is seen that the position and strength of the boson peak is controlled by the degree of disorder, especially by the amount of small and negative force constants. As expected, the Van Hove singularities disappear in the disordered system. As $K_{\min}$ decreases from positive to negative values for $\sigma = 1$, the peak in $g(\omega)/\omega^2$ shifts towards smaller frequencies. At the same time the peak intensity increases [37]. Obviously the low-frequency peak plays the role of a precursor of the instability introduced by the presence of small and negative force constants. We conclude from our calculations that a low-frequency peak in the reduced DOS is a generic feature of a disordered harmonic system and indicates the vicinity of an instability.

Another quantity of interest, in particular in the context of thermal conductivity data in structural glasses [1,38], is the mean free path of the phonons ℓ. Within the CPA treatment the mean free path can be identified with the decay length of the wave intensity $|\exp\{i\omega r/v(\omega)\}|^2$. It is therefore given by $\ell^{-1}(\omega) = 2\omega \, \mathrm{Im}\{v(\omega)\}/|v(\omega)|^2$ and behaves as $\ell^{-1} \propto \omega^4$ for $\omega \to 0$ (Rayleigh scattering). In Fig. 2 we have plotted $\ell(\omega)$ for the force constant distributions with $\sigma = 1$ of Fig. 1. It is seen that in all cases a crossover from the low-frequency weak Rayleigh scattering to an almost frequency-independent mean free path occurs (strong scattering regime). The boson peak (arrows) occurs near this crossover. This crossover is similar to that which appeared in the earlier coupled-harmonic-oscillator investigations [30–34]. We show also for comparison the (generalized) wavelength $\lambda(\omega) = 2\pi \, \mathrm{Re}\{v(\omega)\}/\omega$. It can be seen from Fig. 2 that ℓ and λ are of the same order of magnitude in the boson peak region. In this case the phonons may become

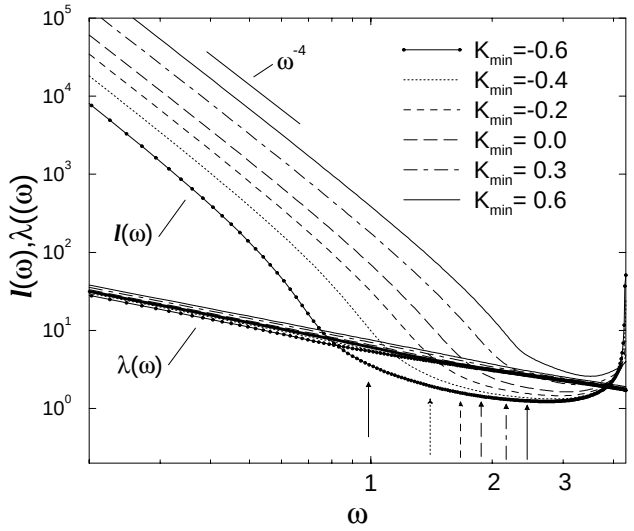

FIG. 2. Mean free path $\ell(\omega)$ with $\ell^{-1}(\omega) = 2\omega\,\mathrm{Im}\{v(\omega)\}/|v(\omega)|^2$ and wavelength $\lambda(\omega) = 2\pi\,\mathrm{Re}\{v(\omega)\}/\omega$, calculated in CPA for the distributions with $\sigma = 1$ of Fig. 1. The arrows indicate the position of the boson peak.

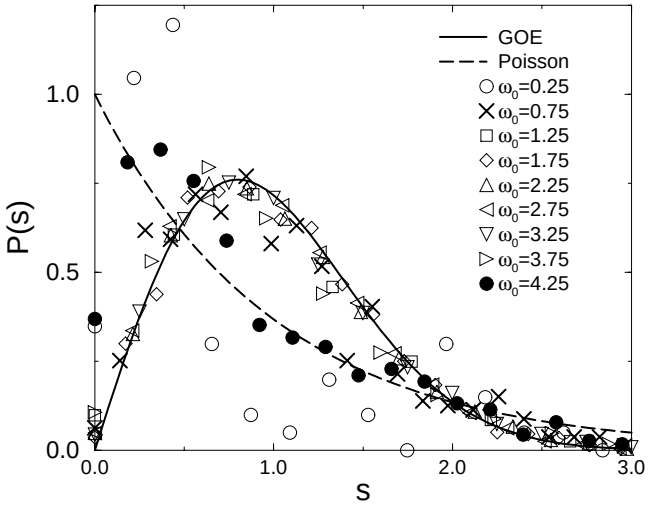

FIG. 3. Level distance statistics for the distribution with $\sigma = 1$ and $K_{\min} = -0.6$. The statistics has been taken from 11 samples with $L = 14$ in frequency intervals centered around ω_0 (see legend) with width $\Delta\omega = 1$. The GOE and Poisson distributions are depicted as well. The states around the boson peak $\omega \approx 1$ follow the GOE statistics and are therefore delocalized.

localized according to the Ioffe-Regel criterion [38]. This can be checked by an investigation of the level statistics [39]. If we define modified eigenvalues (with normalized mean level spacing) by $\epsilon_i = \bar{F}(\lambda_i)$, a histogram of the distances $s_i = |\epsilon_i - \epsilon_{i+1}|$ should yield a distribution according to the Gaussian orthogonal random matrix ensemble (GOE) $P(s) = \frac{1}{2}\pi s\,\exp\{-\pi s^2/4\}$ in the case of delocalized states, whereas one expects a Poissonian distribution $P(s) = \exp\{-s\}$ for localized states. This is due to the fact that the delocalized states show level repulsion, whereas the localized ones do not.

In Fig. 3 we show the level distance statistics corresponding to frequency intervals $\Delta\omega = 0.5$ for several interval midpoints ω_0, as evaluated from 11 samples with $L = 14$, $\sigma = 1$, and $K_{\min} = -0.6$. Except for the vicinity of the band edges ($\omega_0 = 0.25$, $\omega_0 = 4.25$) the statistics follows closely that of the GOE ensemble, which means that the corresponding states are delocalized. The data for $\omega_0 = 4.25$ are close to the Poisson distribution indicating a mobility edge near the band edge. In the low-frequency regime the finite-size effects are dominant. (The mode with a wavelength equal to the system size has $\omega = 0.45$.) In this regime one expects for the infinite system propagating modes [40]. The modes in the vicinity of the boson peak are obviously neither propagating nor localized, indicating a diffusive type of transport of vibrational energy. Such a diffusive motion of vibrational excitations has already been shown [15,17] to be typical for glasses and to be responsible for the temperature dependence of the thermal conductivity above the plateau region.

When comparing our results with real three-dimensional disordered systems like glasses [41] a few comments are in order. In materials which can be described in terms of interatomic potentials the force constant distribution $P(K)$ can be related in an obvious way to the atomic pair distribution and thus to structural disorder [34]. In "strong" glasses with covalent bonds $P(K)$ could be obtained from computer simulations. In both cases it seems worthwhile to study the interplay between $P(K)$ and the boson peak in detail [42].

We have treated a scalar model and thus ignored the vector character of the phonons completely. We believe, however, that our model already is able to mimic the behavior of transverse phonons in a glass. If the vector character is taken into account, one would expect an even stronger scattering due to the admixture of longitudinal degrees of freedom. This might enhance the strength of the boson peak and the localization tendency of the corresponding states. Therefore we still consider it as an open question, whether the modes associated with the boson peak are localized or delocalized. Our model shows, however, that is not necessary to postulate the existence of localized states or strongly anharmonic effects to obtain an excess contribution in the DOS.

As we have treated only harmonic interactions the effects associated with the glass-liquid transformation are outside the scope of the present model. However, the dynamics described by the mode-coupling theory in the idealized glass phase [25,43] appears to be similar to that described within the present model.

In conclusion, we have solved a simple model of coupled harmonic oscillators, both numerically and in coherent-potential approximation. Near the point of instability the model exhibits a low-frequency peak in the reduced density of states $g(\omega)/\omega^2$, which we view as the analog to the boson peak observed in structural glasses.

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