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Excess modes in the vibrational spectrum of disordered systems and the boson peak

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We study a disordered vibrational model system, where the spring constants k are chosen from a distribution $P(k)\propto 1/k$ above a cut-off value $k_{\text{min}}>0$. We can motivate this distribution by the presence of free volume in glassy materials. We show that the model system reproduces several important features of the boson peak in real glasses: (i) a low-frequency excess contribution to the Debye density of states, (ii) the hump of the specific heat $c_V(T)$ including the power-law relation between height and position of the hump, and (iii) the transition to localized modes well above the boson peak frequency.

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The vibrational spectrum and the corresponding thermal properties of a large number of disordered materials exhibit two characteristic anomalies.[1,2] While the anomalous linear low-temperature specific heat can be described well by the model of two-level systems,[3] the origin of the second important anomaly, the boson peak, is still under discussion. It is not clear, if both anomalies are related.[4] The boson peak refers to an excess contribution to the usual Debye density of states (DOS) at low frequencies.[5–10] In silicate and germanate glasses, for example, the boson peak frequency ω_{peak} was reported between 4.5 and 13.5 THz, about $16-40$ times below the upper band edge ω_{E}.[8,9] In silicate glasses[4,5,10] and polybutadiene and polysterene glasses,[10] the peaks occur at frequencies about $4-9$ times smaller than the corresponding Debye frequency ω_{D}.

The boson peak also shows up as a small hump in the scaled specific heat $c_V(T)/T^3$ in the temperature range $2-30$ K.[1,2,4–6,11] The humps for different materials have a common shape. Position and height follow a power-law dependence,

$$c_V(T_{\text{hump}})/T_{\text{hump}}^3 \sim T_{\text{hump}}^{-x}, \tag{1}$$

with x close to 2 (Ref. 11) [see Fig. 3(b)]. The hump in the specific heat is more pronounced for strong and intermediate than for fragile glasses.[4] Apart from molecular dynamics simulations on relatively small systems that do not yet give a clear picture of the origin of the boson peak,[12] relaxational and vibrational models have been proposed. Many experiments indicate that the relaxation-type soft potential model[13] is appropriate for fragile glasses, while vibrational models are more appropriate for strong and intermediate glasses[14,15] (see also Ref. 16).

In this paper, we do not wish to enter the controversial discussion of the microscopic origin of the boson peak. Instead, we concentrate on an idealized disordered vibrational model system that can be solved by standard numerical procedures. We show that the model system is able to reproduce several important features of the boson peak in glassy materials.

Our starting point is the same as the one of Schirmacher *et al.*,[17] who considered a simple cubic lattice of coupled harmonic oscillators with random scalar spring constants between nearest-neighbor masses. The spring constants were chosen from a truncated Gaussian distribution with a lower cut-off value k_{min}. As a result of the disorder, a hump in the scaled DOS $Z(\omega)/\omega^2$ occurs at relatively high frequencies. When shifting k_{min} towards negative values (which imposes some unrealistic instability to all infinite lattices) the hump is shifted towards frequencies about $2-3$ times smaller than ω_{D}, which is still far from the frequency range where the boson peak occurs. Model systems with homogeneous distributions of positive spring constants (see below) yield maxima in the same frequency range as the Gaussian model system.

In this work we also consider a disordered vibrational model system. The scalar spring constants k are chosen from a power-law distribution $P(k)\propto 1/k$ above a positive cut-off value k_{min}. We can motivate $P(k)$ by assuming a distribution of the free volume. We find that a low-frequency peak occurs in the DOS at ω_{peak}, in a frequency range comparable to the one of the boson peak of real glasses. We expect that in our model system external pressure will shift the peak towards larger frequencies, an effect which has also been observed experimentally. Investigating the localization properties of our model system we find that the modes around the peak are extended. Localized modes occur above a crossover frequency $\omega_c\approx 3\omega_{\text{peak}}$. This interesting property seems to be in line with experiments in real glasses. The peak at ω_{peak} is also visible in $c_V(T)$ as a small hump, which shows similar features as the boson peak in real systems, among them the power-law dependence (1).

To be specific, we chose the spring constants from a normalized distribution function

$$P(k)=\frac{1}{\ln(k_{\text{max}}/k_{\text{min}})}\,\frac{1}{k} \qquad k\in[k_{\text{min}},k_{\text{max}}], \tag{2}$$

where $k_{\text{max}}/k_{\text{min}}$, the only parameter in the distribution, controls the amount of small spring constants. The form of Eq. (2) can be motivated as follows: Consider a disordered system, where the neighbor distances a_{ij} between the particles are in the interval $[a_{\text{min}},a_{\text{max}}]$. The limits a_{min} and a_{max} are related to the size of the particles and the maximum diameter of holes in the system, respectively, and thus characterize to some extent the distribution of the free volume in the system. For simplicity, we assume that the distances are distributed homogeneously between $a_{\min}$ and $a_{\max}$. When the distances a_{ij} between two neighboring masses i and j fluctuate, the spring constants k_{ij} between them also fluctuate. We assume that the k_{ij} decay roughly exponentially with a_{ij}, $k_{ij} \approx k_{\min} \exp[(a_{\max} - a_{ij})/a^*]$ with a characteristic decay length a^*, which might be a reasonable assumption in a strong or intermediate glass with covalent binding[15] and negligible charge separations. Combining both assumptions, we arrive at Eq. (2), with the control parameter

$$k_{\max}/k_{\min} = \exp[(a_{\max} - a_{\min})/a^*]. \tag{3}$$

Note that the distribution (2) is equivalent to an homogeneous distribution of the logarithm of spring constants, $P(\log k) = \text{const}$.

We have calculated numerically the DOS of this model system, where in a simple cubic lattice unit masses m at nearest-neighbor sites i and j are connected by springs k_{ij} chosen from $P(k)$. Assuming scalar coupling constants k_{ij}, the different components of the displacements decouple and we obtain the same equations of motion

$$m \frac{d^2 u_j(t)}{dt^2} = \sum_i k_{ij} [u_i(t) - u_j(t)], \tag{4}$$

for all spatial components of u_j. The sum runs over the nearest-neighbor sites i of site j. The ansatz $u_j(t) = \psi_j^\alpha \exp(-i\omega_\alpha t)$ leads to an homogeneous system of equations for the N unknown ψ_j^α, from which the N real eigenvalues $\omega_\alpha^2 \geqslant 0$ and the corresponding eigenvectors $(\psi_1^\alpha, \ldots, \psi_N^\alpha)$, $\alpha = 1, \ldots, N$ can be determined.

To calculate the vibrational properties and the related specific heat c_V of the model system, we have employed the method of Williams and Maris[18] and the Lanczos algorithm.[19] In Fig. 1 we show the DOS $Z(\omega/\omega_0)$, with $\omega_0 \equiv \sqrt{k_{\max}/m}$, and the rescaled DOS $Z(\omega/\omega_0)/(\omega/\omega_0)^2$ for several values of $k_{\min}/k_{\max}$ between 10^{-2} and 10^{-5} (Ref. 20) and system sizes of up to 65^3 masses. For all values of $k_{\min}/k_{\max}$, both quantities show a broad maximum at frequencies ω_{peak}, which become smaller, if $k_{\min}/k_{\max}$ is decreased. Well below ω_{peak}, we observe the conventional Debye behavior, $Z(\omega) \propto \omega^2$. For comparison we also calculated the DOS of a vibrational model system with an homogeneous distribution of spring constants $k \in [0, k_{\max}]$ where the maximum in the DOS simply results from a broadening of the van Hove singularity. The systems with power-law distributed k_{ij} have their maxima in the low-frequency regime, where also the boson peak in glasses is observed. Estimating the Debye frequency ω_D from the plateaux in the scaled DOS [Fig. 1(b)], we find for the maxima in $Z(\omega)/\omega^2$ the values $\omega_D/\omega_{\text{peak}} \approx 3$ for $k_{\min} = 10^{-2}$, $\omega_D/\omega_{\text{peak}} \approx 4.5$ for $k_{\min} = 10^{-3}$, and $\omega_D/\omega_{\text{peak}} \approx 7$ for $k_{\min} = 10^{-4}$ and still larger values for smaller $k_{\min}$. In contrast, the peak for the homogeneous distribution, shows up at frequencies ω_{peak} only a factor of 2 below ω_{D}.

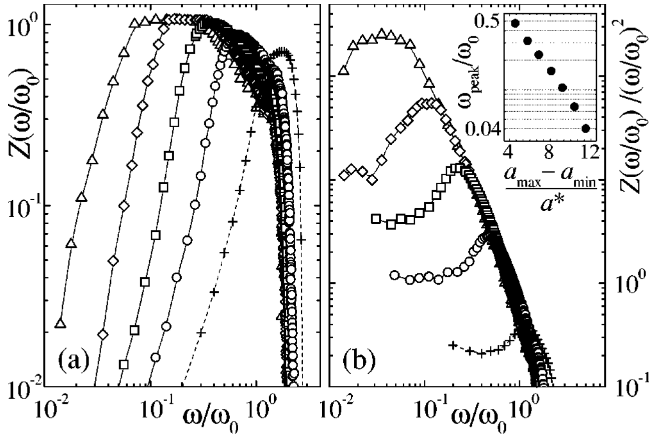

FIG. 1. (a) Density of states (DOS) $Z(\omega/\omega_0)$ and (b) rescaled DOS $Z(\omega/\omega_0)/(\omega/\omega_0)^2$ versus ω/ω_0 for our model system ($\omega_0^2 \equiv k_{\max}/m$). The symbols correspond to $k_{\min}/k_{\max} = 10^{-5}$ (△), 10^{-4} (◇), 10^{-3} (□), and 10^{-2} (○). The numerical results for an homogeneous distribution $k \in [0, k_{\max}]$ are also shown (dashed curves with + symbols). In the inset, the frequency positions $\omega_{\text{peak}}/\omega_0$ of the maxima of $Z(\omega/\omega_0)/(\omega/\omega_0)^2$ are shown versus the relative maximum size of holes $(a_{\max} - a_{\min})/a^* = \ln(k_{\max}/k_{\min})$.

When $k_{\min}/k_{\max}$ is enhanced, the maximum in $Z(\omega)$ tends to higher frequencies. Since in our model system $k_{\min}/k_{\max}$ is related to the free volume parameter $(a_{\max} - a_{\min})$ via Eq. (3), the peak is shifted towards higher frequencies, when $(a_{\max} - a_{\min})$ is reduced. We can imagine that $(a_{\max} - a_{\min})$ can be reduced by applying external pressure to the system. Indeed, experiments on glasses indicate that the boson peak is shifted to higher frequencies, when the glasses were permanently desified under pressure.[9] This is in line with the results of our model system.

Next we consider the specific heat $c_V(T)$, which is related to $Z(\omega)$ by:

$$c_V(T) = k_B \int_0^\infty d\omega \, Z(\omega) \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{\hbar \omega / k_B T}}{(e^{\hbar \omega / k_B T} - 1)^2}. \tag{5}$$

Figure 2(a) shows $c_V(T)/T^3$ versus temperature T for several values of $k_{\min}/k_{\max}$ as well as for the homogeneous distribution of spring constants. As expected from the behavior of $Z(\omega)$, a maximum in $c_V(T)/T^3$ occurs at T_{hump}, which is shifted towards lower temperatures and increases in height, when $k_{\min}/k_{\max}$ decreases. For testing for a common shape of the hump, we have plotted $[c_V(T)/T^3]/[c_V(T_{\text{hump}})/T_{\text{hump}}^3]$ in Fig. 2(b) as a function of T/T_{hump} and compared the results with the experimental curves for several vitreous silica.[11] It is interesting that the results for our model system at intermediate $k_{\min}/k_{\max}$ values agree reasonably well with the experimental data. No fitting parameter was involved. The figure shows also that major deviations from the common shape occur for the homogeneous model system in the low-temperature range.

To see, if the specific heat also satisfies the power-law relation (1) we have plotted $c_V(T_{\text{hump}})/T_{\text{hump}}^3$ as a function of T_{hump} in a double-logarithmic fashion. The result, shown in Fig. 3(a), agrees surprisingly well with the experimental data

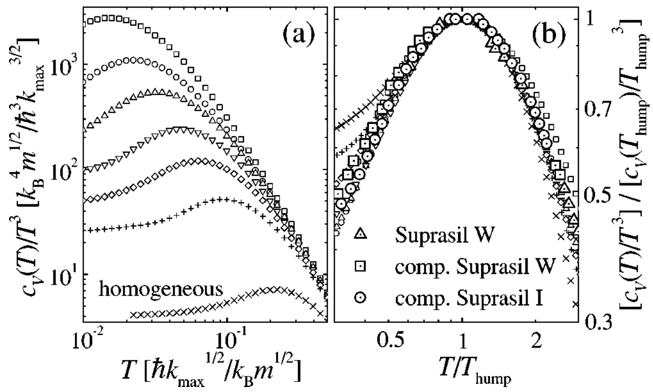

FIG. 2. (a) Rescaled specific heat $c_V(T)/T^3$ versus temperature T for $k_{\min}/k_{\max}=3\times10^{-5}$ (□), 10^{-4} (○), 3×10^{-4} (△), 10^{-3} (▽), 3×10^{-3} (◇), and 10^{-2} (+) and for an homogeneous distribution $k\in[0,k_{\max}]$ (×). In (b) the results from (a) are rescaled by dividing T by T_{hump} and $c_V(T)/T^3$ by $c_V(T_{\text{hump}})/T^3_{\text{hump}}$. Deviations from the common shape occur for the smallest and the largest parameter as well as for the homogeneous distribution of spring constants. The experimental values for several silica glasses (large symbols, redrawn from Fig. 1 of Ref. 11), are also shown.

for a large number of glassy and amorphous solids, shown in Fig. 3(b). The basic power-law (1) is reproduced with an exponent x that is, within the error bars, identical with the one of real glasses. Note that both, Figs. 3(a) and 3(b), show the same range for the x and y axes. Again, no fitting parameter was involved. It is interesting to note that also for crystalline systems the same power-law behavior has been found experimentally. An explanation of this is beyond the scope of this paper.

Finally we turn to the localization behavior of the vibrational modes in our model system. By general arguments, we can expect extended phonons for small frequencies $\omega<\omega_c$ and localized modes for high frequencies $\omega>\omega_c$. The localization mechanism for vibrations is quite similar to the Anderson localization of quantum particles in disordered solids (see also Refs. 21 and 22) and it is interesting to see, if the modes in the peak regime fall into the extended or into the localized range.

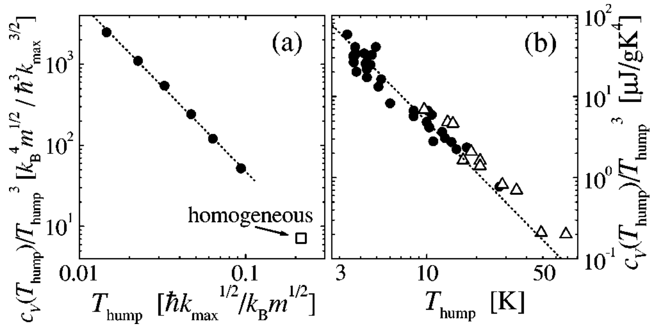

FIG. 3. (a) The values of the maxima of $c_V(T)/T^3$ from Fig. 2(a) versus the positions T_{hump} of the maxima. In the log-log plot the data fall onto a straight line described by a power law: $c_V(T_{\text{hump}})/T^3_{\text{hump}}\sim T^{-x}_{\text{hump}}$ with $x\approx2.1$ (dotted line). (b) Experimental results for several glasses and amorphous solids (●) as well as for some crystalline materials (△), redrawn after Fig. 2 of Ref. 11. The data for the glasses and the amorphous solids are consistent with our theoretical results $x\approx2.1$ (dotted line). If also crystalline systems are included, one obtains a smaller exponent. Note that the scales of both axes are only changed by constant factors in (a) and (b), so the range is exactly the same.

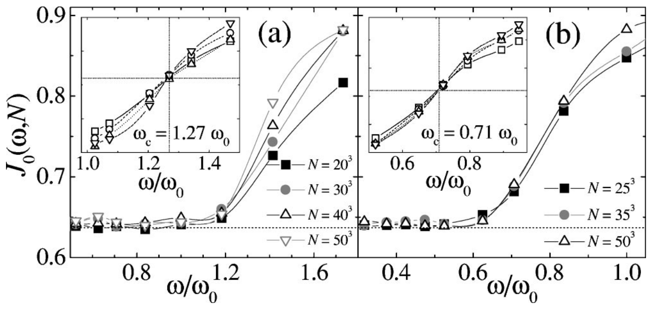

FIG. 4. Level statistics results for our model system with (a) $k_{\min}/k_{\max}=10^{-2}$ and (b) $k_{\min}/k_{\max}=10^{-3}$. $J_0(\omega,N)$ is shown versus ω/ω_0 for different system sizes N. Values of $J_0\approx J_0^{\text{Wigner}}=0.637$ indicate extended modes, while $J_0\approx J_0^{\text{Poisson}}=1$ indicates localized modes. In the insets, magnifications of the transition regions are shown, which allow to determine the transition frequencies ω_c from the intersection of the curves.

To estimate the ratio between ω_{peak} and ω_c, we have employed the method of level statistics.[23] Level statistics (with a fixed system size) have been applied earlier to the Gaussian model system,[17] indicating extended modes in the vicinity of ω_{peak}. In the method, one first calculates the eigenvalues ω_α^2 of the vibrational equation and then determines the eigenvalue spacings $s_\alpha=(\omega_\alpha^2-\omega_{\alpha-1}^2)/\Delta$, where Δ is the mean eigenvalue spacing in the frequency range considered. The dependence of the mean squared eigenvalue spacing $\langle s^2\rangle$ on the system size N indicates the localization behavior. With increasing system size, $J_0\equiv\frac{1}{2}\langle s^2\rangle$ tends to $J_0^{\text{Wigner}}\approx0.637$ for extended modes, while it approaches $J_0^{\text{Poisson}}=1$ for localized modes. Figure 4 shows the results of this analysis for $k_{\min}/k_{\max}=10^{-2}$ and 10^{-3}. From the figure we can deduce $\omega_c\approx1.3\,\omega_0$ for $k_{\min}/k_{\max}=10^{-2}$ and $\omega_c\approx0.7\,\omega_0$ for $k_{\min}/k_{\max}=10^{-3}$. For $k_{\min}/k_{\max}=10^{-4}$ we obtain $\omega_c\approx0.4\,\omega_0$ in an analogous way. A comparison with the position of the peak [taken from the inset of Fig. 1(b)] yields $\omega_c\approx2.7\,\omega_{\text{peak}}$, $\omega_c\approx3.1\,\omega_{\text{peak}}$, and $\omega_c\approx3.9\,\omega_{\text{peak}}$ for $k_{\min}/k_{\max}=10^{-2}$, 10^{-3}, and 10^{-4}, respectively.

Experimentally, it is not settled whether the frequency ω_{peak} of the boson peak is close to the localization delocalization frequency ω_c or well below. Scattering experiments on vitreous silica have been discussed controversially. One interpretation yields localized modes at the boson peak frequency $\omega_{\text{peak}}\approx6-9$ THz,[24] while others indicate the presence of propagating modes up to $\omega_c\approx20$ THz (Ref. 25) well above the boson peak. Very recent scattering experiments on glassy glycerol yield extended modes up to at least $\omega_c\approx2.5\,\omega_{\text{peak}}$.[26] The results from Refs. 25 and 26 are in line with the results of our model system.

In summary we have considered an idealized disordered vibrational model system, consisting of a simple cubic lattice of coupled harmonic oscillators with random scalar spring constants between neighbors. The spring constants were chosen from a power-law distribution $P(k)\propto1/k$ above a positive cut-off value $k_{\min}$. We have motivated the model by the presence of free volume in glassy materials. Since the model describes (surprisingly) well several nontrivial features of the boson peak in glassy systems, we believe that despite its simplicity it may capture essential parts of the physics of this odd phenomenon—in particular as no single fit parameter was involved.

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[20] These values may be in a realistic range for several glasses. For example, we can approximate $a_{\min}=1.5$ Å as a sensible Si-O closest distance and $a_{\max}\approx 5$ Å as a reasonable maximum neighbor distance, e.g., across a sixfold ring in SiO_2. When we further assume a decay length a^* around 0.5 Å, which does not seem unreasonable for the short-range potentials of SiO_2 we can arrive at values for $k_{\min}/k_{\max}=\exp[(a_{\min}-a_{\max})/a^*]$ around 10^{-3}.

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