Frustration and Sound Attenuation in Structural Glasses

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Three classes of harmonic disorder systems (Lennard-Jones-like glasses, percolators above threshold, and spring disordered lattices) have been numerically investigated in order to clarify the effect of different types of disorder on the mechanism of high frequency sound attenuation. We introduce the concept of frustration in structural glasses as a measure of the internal stress, and find a strong correlation between the degree of frustration and the exponent α that characterizes the momentum dependence of the sound attenuation $\Gamma(Q) \simeq Q^\alpha$. In particular, α decreases from $\approx d + 1$ in low-frustration systems (where d is the spectral dimension) to ≈ 2 for high-frustration systems such as the realistic glasses examined.

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The nature of collective excitations in disordered solids has been one of the major problems of condensed matter physics during the past decades; the recent development of a high-resolution inelastic x-ray scattering facility [1] made Brillouin-like experiments possible in the region of mesoscopic exchanged momenta $Q = 1-10\ \text{nm}^{-1}$, which led to the realization that propagating soundlike excitations exist in glasses up to the terahertz frequency region. The quantity that characterizes the collective excitations, and which has been determined experimentally in many glasses [2] and liquids [3], is the dynamic structure factor $S(Q,\omega)$. Although specific *quantitative* differences exist among systems, the following qualitative characteristics are common to all of the investigated materials: (i) There exist propagating acousticlike excitations for Q values up to Q_m, with $Q_m/Q_o \approx 0.1-0.5$ (where Q_o is the position of the maximum in the static structure factor), which show up as, more or less, well-defined Brillouin peaks at $\Omega(Q)$ in $S(Q,\omega)$; the specific value of Q_m/Q_o is correlated with the fragility of the glass. (ii) The slope of the (almost) linear $\Omega(Q)$ vs Q dispersion relation in the $Q \to 0$ limit extrapolates to the macroscopic sound velocity. (iii) The width of the Brillouin peaks, $\Gamma(Q)$, follows a power law, $\Gamma(Q) = DQ^\alpha$, with $\alpha \approx 2$ within the statistical uncertainties. (iv) The value of D does not depend significantly on temperature, indicating that the broadening (i.e., the sound attenuation) in the high frequency region does not have a dynamic origin, but is due to disorder [4]. These general features of $S(Q,\omega)$ have been confirmed by numerical calculations on simulated glasses [5], obtained within the framework of the mode coupling theory [6], and, more recently, ascribed to a relaxation process associated with the topological disorder [7]. However, except for the simple one-dimensional case [8], the widespread finding $\Gamma(Q) = DQ^2$ has not yet been explained on a microscopic basis.

To this end, in this Letter we investigate, in the harmonic approximation, systems showing disorder of different characteristics and the role played by the latter in determining the value of the exponent α. The analyzed systems show either substitutional (bond percolators and spring disordered systems on a lattice) or topological disorder [model glasses obtained by molecular dynamics (MD) simulations]. We also introduce the concept of "frustration" both for structural glasses and, under appropriate conditions, for lattice-based systems; we give a measure of it, and find a correlation between the value of α and the degree of frustration. In particular, for all types of disorder we find that, when frustration is absent, $\alpha \approx 4$, while increasing the frustration lowers the value of α towards and even below the value 2.

Our samples fall into three major classes: bond percolators above threshold with identical springs connecting nearest-neighbor (NN) occupied sites, topologically ordered systems with spring disorder, and model glasses obtained by MD. The first two classes are based on a cubic lattice, while the third represents topological disorder. In the first class the disorder is due to the presence of unconnected or void sites of the lattice [9]; in the second class [10] all sites are occupied and NN atoms interact through springs whose elastic constants are randomly chosen from a Gaussian distribution which may or may not include a negative tail. In both classes the elasticity is scalar and each atom has only one degree of freedom. The atoms of the topologically disordered class interact through variants of the 12-6 Lennard-Jones (LJ) pair potential $V_{\rm LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, i.e.: (a) standard LJ, $V^{(a)}(r) = V_{\rm LJ}(r)$; (b) LJ with interaction cut at the inflection radius, $r_o = (26/7)^{1/6}\sigma$, $V^{(b)}(r) = V_{\rm LJ}(r)$ for $r < r_o$ and $V^{(b)}(r) = 0$ for $r > r_o$, so that practically only NN interact; (c) LJ modified to always have a positive curvature, $V^{(c)}(r) = V_{\rm LJ}$ for $r < r_o$ and $V^{(c)}(r) = 2V_{\rm LJ}(r_o) - V_{\rm LJ}(r)$ for $r > r_o$; (d) LJ without the attractive part (soft sphere), $V^{(d)}(r) = 4\epsilon(\sigma/r)^{12}$; (e) binary LJ mixture of 80% atoms of type A, 20% of type B, having the same mass but different LJ potential parameters for AA, AB, and BB interactions [11].

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The LJ glasses were produced by a fast quench (down to typically $T_m/10$, where T_m is the melting temperature) of the liquid configurations starting from temperatures just above T_m. The liquid configurations were obtained by standard MD equilibration runs. The frozen configurations at $T_m/10$ were then further equilibrated in order to check against crystallization. Finally, a steepest descent was applied to find the (glassy) minimum configuration $[\{\bar{x}^o(i)\}_{i=1,\ldots,N}]$ at $T = 0$. For each LJ-like potential, two sets of glasses were prepared: one had $N = 2000$ atoms and its dynamical matrix was diagonalized, while the other, 10 000 atoms, was used for the calculation of $S(Q,\omega)$ and the density of states by the method of moments [12]. In both cases we obtained positive eigenvalues, indicating stable configurations. The bond percolators had dimension 80^3 and two bond concentrations, 0.45 and 0.65, respectively; the spring disordered lattices had dimension 80^3. For both, $S(Q,\omega)$ was calculated by the method of moments. In the latter systems, the spring constants k were extracted by a Gaussian distribution with unitary mean and variance; the distribution was cut on the low-k side at $k_o = 0.3$, 0, -0.6, and -1. Runs on elongated systems ($20 \times 20 \times 3000$) were also performed, reproducing the results of the cubic samples in the common Q region. In all cases, the width of the Brillouin peaks in $S(Q,\omega)$ was estimated both by a Lorentzian fit and by evaluating the width of the spectrum at half-height; even when—at high Q—$S(Q,\omega)$ does not resemble a Lorentzian too closely, the two procedures gave results in excellent agreement.

All of the LJ-like systems have the characteristic that, although the system is in a minimum of the total potential energy and is stable, not all pairs of interacting atoms are at equilibrium distance, which produces internal stress in the system [13]. It is also possible that some of the particles are—at equilibrium—in a *maximum* of the potential energy; these situations also contribute to the presence of stresses in the glass [14]. Let $V(i)$ be the potential energy of the ith particle at $T = 0$, and let a single particle be displaced from its equilibrium position by an external agent; then all surrounding particles are no longer at equilibrium and, if the system can relax, they will move towards the new equilibrium position, where each particle in general has a different value of potential energy, $V'(i)$. This can be either smaller or larger than $V(i)$. We define as "frustrated" those particles which have $V'(i) < V(i)$, i.e., those particles that, under a small external perturbation, can relax towards a more energetically comfortable situation. The "external perturbation" can be a normal mode. Under the effect of a single normal mode, all particles are displaced from their equilibrium positions along the direction indicated by the eigenvector and change their potential energy; as we will see, this change can be negative. More precisely, when the pth normal mode—with eigenfrequency ω_p and eigenvector $\bar{e}_p(i)$—is switched on in the system, and therefore the particle positions become $\bar{x}^o(i) + a\bar{e}_p(i)$, the ith particle changes its potential energy by $\mathcal{E}_p(i)$, which is easily written in terms of the system eigenvectors as

$$\mathcal{E}_p(i) = -Ma^2/4\Sigma_{\alpha\beta}\Sigma_j D_{ij}^{\alpha\beta}[e_p(\alpha,i) - e_p(\alpha,j)] \times [e_p(\beta,i) - e_p(\beta,j)], \tag{1}$$

where D is the dynamical matrix. Obviously $\mathcal{E}_p(i)$ depends trivially on the amplitude of the normal mode, a, and on other system-dependent quantities such as the mass, M, and the interaction strength, represented by the largest eigenfrequency ω_o. The relevant quantity is therefore the adimensional quantity $\hat{\mathcal{E}}_p(i) = \mathcal{E}_p(i)/Ma^2\omega_o^2$. In an ordered structure, the eigenvectors are plane waves and $\hat{\mathcal{E}}_p(i)$ is independent on the particle i. In the disordered structure, however, for each mode there is a distribution of $\hat{\mathcal{E}}_p(i)$. This distribution (an example is shown in the inset of Fig. 2 below for a mode of full LJ with $\omega/\omega_o = 0.03$), characterized by its mean value μ_p $(= \omega^2/2\omega_o^2)$ and variance σ_p^2, can be so broad that many atoms decrease their energy under the action of a mode and, therefore, they are frustrated. To be quantitative, we can define the "index of frustration," F_p, as the standard deviation of the distribution of $\hat{\mathcal{E}}_p(i)$. To characterize the disordered structure itself with its degree of frustration, we can use the low frequency limit of F_p; indeed a normal mode induces in the sample a stress that, by itself, produces an "uncomfortable" situation for the atoms. Only in the long wavelength (low frequency) limit does the stress induced by the normal modes become negligible and the frustration truly associated with the disordered structure shows up. To evaluate F_p we need to diagonalize the dynamical matrix, and this puts an upper limit to the dimension of the investigated systems. On the other hand, $S(Q,\omega)$ is calculated by the method of moments [12], which allows larger samples to be treated.

The normalized widths, $\Gamma(Q)/\omega_o$, of the Brillouin peaks in $S(Q,\omega)$ of the LJ-like systems are reported in Fig. 1 as a function of Q/Q_o. Data from 2000- and 10 000-atom systems are reported together in the figure, indicating that there are no noticeable size effects on $\Gamma(Q)$. From Fig. 1 we note that, (i) in the low-Q region, the law $\Gamma(Q) \propto Q^\alpha$ represents very well the data with α values as reported in the legend (see inset, where the different data are mutually shifted and the full lines represent the power laws); (ii) there is a progressive decrease of slope in passing from the modified LJ system ($\alpha = 3.5$) to the soft potential ($\alpha = 1.5$). The slopes seem to coalesce into two groups; for systems *a*, *d*, and *e*, $\alpha \approx 2$, while, in the case of *b* and *c*, $\alpha > 3$. We are now going to correlate this type of behavior with the presence and the degree of frustration in the samples.

The frustration index, F_p, of the five LJ-like samples is reported in Fig. 2 for some modes spanning the whole frequency spectrum as a function of the normalized mode frequency ω_p/ω_o [15]. If we consider the variation of F_p, the systems can again be arranged into two groups: the NN

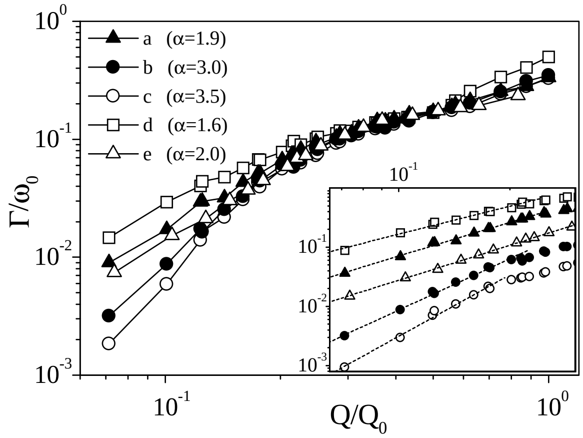

FIG. 1. Normalized width of the inelastic peaks of $S(Q,\omega)$, $\Gamma(Q)/\omega_o$, for the LJ-like systems as indicated in the legend, as a function of the normalized exchanged momentum, Q/Q_o. The inset shows in an expanded scale the low-Q portion; here the data were mutually shifted in order to show the best-fit straight lines with the slopes α reported in the legend.

(*b*) and the modified LJ (*c*) in the first group, and the other three systems (*a*, *d*, and *e*) in the second one. The behavior of F_p is qualitatively the same for all systems down to $\omega_p/\omega_o \approx 0.15$, but below this value the two groups diverge: F_p of systems of the first group, which show exponents $\alpha \geq 3$, decreases steadily, while for the other three systems (which have $\alpha \approx 2$) it tends towards a constant value, F_o, for $\omega \to 0$. The presence of such nonvanishing low frequency (and low-Q) frustration seems therefore to be strongly correlated to the mechanism that, in these systems, produces $\alpha \approx 2$. The previous conjecture is supported by the results obtained on the lattice-based systems with elastic constant disorder. In this case, since the equilibrium positions of the atoms are fixed at the lattice sites and the springs are all at rest, the systems are intrinsically nonfrustrated. There may exist frustration only if there are some negative elastic constants: the elastic disorder on its own does not produce internal stress and frustration. Therefore, in the spring disorder on a lattice, we would expect $\alpha = 4$ if $k_o \geq 0$, $\alpha < 4$ for $k_o < 0$, and α to decrease as k_o is decreased to produce higher frustration index. This is precisely what is observed in Fig. 3 for the four studied cases $k_o = 0.3$, 0, -0.6, and -1. As mentioned, we also evaluated $\Gamma(Q)$ for elongated samples of size $20 \times 20 \times 3000$ in order to reach smaller Q values; in no case did we observe a crossover to a Q^4 dependence for $k_o < 0$ [10], although it cannot be excluded that it might actually be observed on larger samples. It is worth noting that our numerical results are in quantitative agreement with a recent evaluation of α, performed on similar spring disordered lattices (Ref. [16]) by using a perturbation expansion on the disorder degree, that gives $\alpha = 4$ and $\alpha \to 1$ in the absence and in the presence of unstable modes, respectively. Further interesting indications come from the study of percolating networks above threshold. Here, as in the previous case with $k_o \geq 0$, there is no frustration; moreover the elastic constants are all equal and disorder is produced only by the presence of unoccupied sites. The width $\Gamma(Q)/\omega_o$ is reported as a function of Q/Q_o in Fig. 4 for two different concentrations of bonds. We see that for both concentrations there are two well-defined slopes, $\alpha_1 \approx 4$ and $\alpha_2 \approx 2.3$, separated by a crossover; the crossover value Q_c becomes smaller at smaller concentration. This behavior is well understood by considering the fractal nature of percolators: for $Q < Q_c$ the vibrations experience an almost homogeneous system with spectral dimension $d = 3$, while for $Q > Q_c$ the system is fractal and the dynamics is described by the spectral dimension $d = 4/3$ [17,18]. Thus the data of Fig. 4 indicate that in the whole Q range $\Gamma(Q) \propto Q^{(d+1)}$, where d is the appropriate spectral dimension. This is exactly the same phenomenology observed for the elastic-constant disordered systems on lattice without frustration. Indeed, when $k_o \geq 0$, in both three and two dimensions (the latter not reported here) we obtain $\Gamma(Q) \propto Q^{(d+1)}$, irrespective

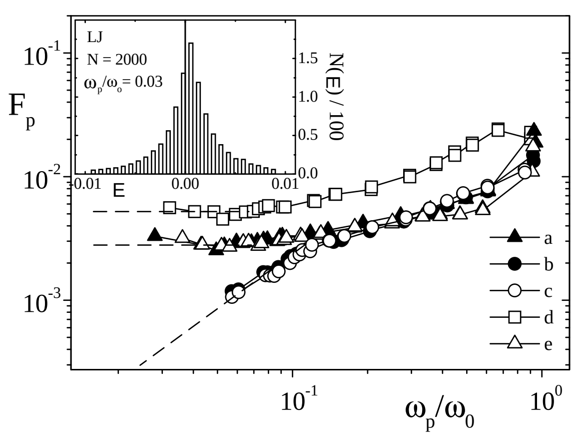

FIG. 2. Frustration index F_p for the LJ-like systems studied, as a function of normalized frequency, ω/ω_o. Inset: a typical distribution of $\hat{\mathcal{E}}_p(i)$ for a mode of full LJ with $\omega/\omega_o = 0.03$.

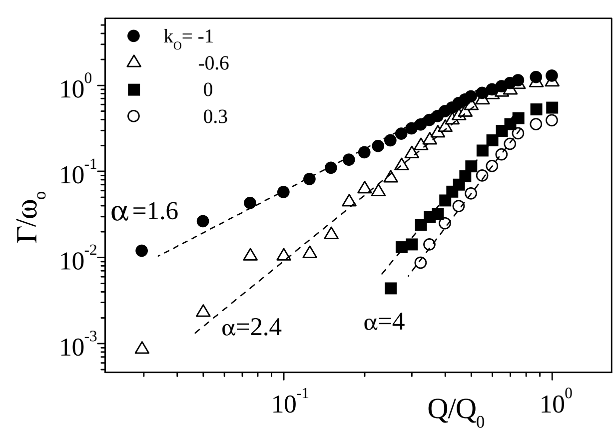

FIG. 3. Q dependence of the width of $S(Q,\omega)$ of the lattice-based systems with elastic-constant disorder, for different values of the minimum value (k_o) of the elastic-constant distribution.

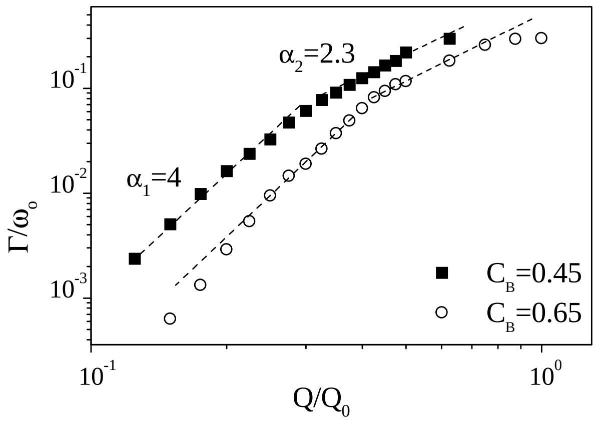

FIG. 4. Q dependence of the width of $S(Q, \omega)$ of bond percolators with two different bond concentrations above percolation threshold.

of the specific value of k_o. In these systems, as in the percolators, increasing the disorder without introducing frustration does *not* change the value of α, but merely shifts the $\Gamma(Q)$ curve to higher values. On the other hand, the behavior of the highly frustrated LJ-like systems appears to be different because if we try to extract spectral dimensions from the exponents of Fig. 1 we obtain unexpectedly low values resting in the range $d = 0.6-1$. Such small values are difficult to reconcile with those extracted from the ω dependence of the density of states, $\rho(\omega) \propto \omega^{(d-1)}$ [17,18] which, for the present binary mixture, full LJ and soft-sphere potential, yields $d \approx 2.4$. Thus, all of the previous results and discussion indicate that frustration may alter the Q dependence of $\Gamma(Q)$. For glasses, frustration means that, even if the system as a whole is in a minimum of the potential energy, single atoms may not be in an energetically comfortable situation, which implies that small rearrangements of the local structure (due, for instance, to a propagating density fluctuation) may induce rather large displacements of the atoms in question towards energetically more favorable configurations. We find a strong correlation between low α values and high frustration. This correlation suggests a possible microscopic explanation for the observed Q^2 behavior of $\Gamma(Q)$: in the presence of frustration, the propagation of density waves is accompanied by large and pseudorandom (i.e., not depending on the carrier sinusoidal displacement wave) displacements of the more frustrated atoms. This entails the presence, in the eigenvector, of large spatial Fourier components other than the one corresponding to the dominant-Q, i.e., broadening. Such broadening is more important at low Q because eigenvectors with low dominant-Q are less broadened by the "trivial" Q^4 effect found in nonfrustrated systems.

In conclusion, in this paper we have studied the role of different types of disorder in determining the exponent α, in order to get information on its microscopic origin. We have investigated the effects of positive vs negative elastic constants and of substitutional vs topological disorder. In this systematic study we have introduced a frustration index for the structural glasses under consideration. The results presented in this paper suggest that $\Gamma(Q)$ behaves like $Q^{(d+1)}$ in nonfrustrated disordered systems—such as, for example, all of the models on lattice without unstable modes—and that the exponent α decreases in the presence of appreciable frustration. Values $\alpha \approx 2$ are recovered for the realistic LJ variants examined.

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