

Quantitative Evaluation of Anharmonic and Disorder Effects on Glassy Dynamics

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Measurements of the pressure dependence at $T = 80$ K of the vibrational spectrum of a polymorphic material in its amorphous (G), orientationally disordered crystal (ODC), and ordered crystal (C) phases has permitted the separation of orientational and site disorder effects on Grüneisen parameters used here, *pars pro toto*, as a measure of anharmonicity. The greater anharmonicity found for G compared to ODC is consistent with their differences in specific heat, while the very similar and strong vibrational attenuation in the two glassy phases indicates that phonon scattering for T above the thermal conductivity plateau arises mainly from orientational disorder of the molecules. [S0031-9007(98)08355-0]

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Since the discovery of universality in the low-temperature thermal properties of amorphous solids [1], the term “glassy” has come to describe any material exhibiting some dynamic behavior [2–4] usually associated with glasses. As glassy behavior has also been found in a variety of disordered crystals, the relative roles played by structural disorder and, e.g., anharmonic or nonlinear interactions [5] need to be resolved experimentally.

Although glassy behavior below 1 K is well described by tunneling phenomena, the higher-temperature thermal activation regime is complicated [6] by the combined effects of larger amplitude vibrations more susceptible to anharmonicity and stronger disorder-induced phonon scattering. Anharmonicity in disordered systems can suppress Anderson localization of excitations [7] and thereby influence the high-temperature thermal conductivity [8] that is found to be universally lowest in the amorphous phase [9] of materials.

In order to help clarify the nature of “glassiness” at higher temperature, we provide here a model-free assessment of the relative importance of anharmonicity and structural disorder for a glassy material in the high temperature ($T \sim 80$ K) thermal activation regime. The experimental separation of these two effects should establish whether different ranges of vibrational frequency feel the effects of disorder and anharmonicity in different ways, helping to motivate an adequate microscopic model for glasses.

Our approach is to study the anharmonicity in three different phases of the same material under the same thermodynamic (T and P) conditions. Ethanol is one of the few materials which can exist at a given temperature as a fully ordered crystal C (monoclinic), as an orientationally disordered crystal ODC (bcc with random orientations of the molecules), and as a glass G [10]. The ODC phase retains positional (site) order, whereas the G phase has neither positional nor orientational order (i.e., complete long-range structural disorder). All three phases can be

produced *in situ* through mild thermal treatments, and we have already carried out studies of their structural [11] and dynamic [12] properties.

Our estimates of the anharmonicity of these three phases were deduced from the T and P dependences of their molar volumes and low-frequency vibrational spectra. Measurement of the pressure dependence of the vibrational spectra of the ordered crystal not only gave a “baseline” for separating the anharmonic effects intrinsic to the interparticle potential from those which are a consequence of glassiness, but also served to provide an absolute scale of frequencies to which the dynamics of the disordered phases can be referred. In addition, an independent confirmation of our results was provided by light-scattering spectroscopy measurements of the Brillouin frequency shift as a function of temperature for both G and ODC.

The measurements of the P and T dependences of the vibrational spectra $Z(\omega)$ and molar volumes V_m were carried out using the IN6 and IN5 time-of-flight neutron spectrometers and the D1B neutron diffractometer, respectively, at the Institut Laue-Langevin (Grenoble, France). The sample of fully deuterated ethanol was contained in a gas-pressurized (He) cell to which hydrostatic pressures up to 3 kbar were applied *in situ* at 80 K. The three phases were produced and confirmed as described elsewhere [11,12]. The diffraction measurements provided not only dV_m/dP but also the volume thermal expansion coefficient $\beta = d \ln V_m / dT$ down to ~ 50 K, for which no reliable data were available. For both C and ODC these quantities were easily derived from the P and T dependences of the lattice constants, which in turn were determined from a Rietveld analysis of the (powder) diffraction patterns. For the G phase, two different methods were followed and provided consistent results. The first relied on the interpretation of the parameters defining the first diffraction peak in both ODC and G as discussed in Refs. [11] and [13], wherein the

variation of the centroid Q_p of the main amorphous peak with P and T is taken as an indication of the change in density, in much the same way as is done for cubic crystals. The second method was to derive the number densities ρ_i from the Fourier transforms of the difference functions $\Delta S_i(Q) = S_i(Q) - S_0(Q)$, where i denotes a particular T or P value, and $S_0(Q)$ is the measured static structure factor at ambient T or P . Most systematic errors (e.g., strong scattering from the pressure cell) are thereby removed and the transform gives directly $-4\pi[\rho_i - \rho_0]$, providing a good estimate of ρ_i (and hence V_m).

The pressure dependence of the volume per molecule was then fitted to a straight line (see middle inset of Fig. 1), giving slopes of -0.977 (40), -0.827 (33), and -0.445 (80) $\text{\AA}^3 \text{kbar}^{-1}$ for C, ODC, and G. The low value for the glass was obtained self-consistently using the two analysis methods and is therefore not an artifact. The measured $d \ln V_m / dT$ at $T = 80$ K for the three solids are 3.01 , 3.76 , and $2.20 \times 10^{-4} \text{ K}^{-1}$ for C, ODC, and G. The uncommonly large value for the crystal seems to come from the onset at intermediate temperatures of fast internal (methyl group and

torsional) motions as manifested by an upturn in the specific heat [13].

The $Z(\omega)$ frequency distributions were derived following procedures described elsewhere [10], and their physical soundness was assessed through comparison of their calculated low-temperature specific heats with our measurements of C_p for the three phases. Figure 1 shows that the $Z(\omega)$ for the glass and ODC phases are remarkably close, whereas that for the C phase shows a distinctive shape having a well-defined shoulder at about 6.5 meV (see the inset in the lower frame), which on the basis of lattice-dynamics calculations [10] is known to signal the limit between frequencies corresponding to zone boundary transverse-acoustic phonons and the lowest optic branches. The availability of data covering a large range of energy transfers enabled the normalization of $Z(\omega)$ to an absolute scale of nine modes, comprising six rigid-body molecular rotations plus translations and the three lowest-lying intramolecular degrees of freedom. As a result, a limit to the maximum frequencies corresponding to motions of "acoustic" nature can be set, which could enable one to explore heuristically whether the effects of increasing density are felt differently by "modes" of mostly acoustic or "optical" polarizations.

Figure 1 shows that the $Z(\omega)$ stiffen considerably under moderate pressures. To put this quantitatively, we would describe the volumic dependence of some characteristic frequency $\langle \omega \rangle$ in terms of a Grüneisen constant $\gamma = -\partial \ln \langle \omega \rangle / \partial \ln V_m|_T$ [14]. However, the absence of a lattice (G phase) and our relatively high measurement temperatures impede a true microscopic description in terms of individual-mode Grüneisen parameters. Instead, we use the reduced frequency moments $\omega_n = [\frac{n+3}{3} \int_0^{\omega_{\max}} d\omega \omega^n Z(\omega)]^{1/n}$ of the measured $Z(\omega)$ integrated up to an ω_{\max} which can correspond to either the Debye frequency or to the measurement temperature ($\hbar \omega_{\max} = k_B T_{\text{meas}}$) [14]. A sampling of these frequency moments (at 80 K and near-ambient pressure) is given in Fig. 2. The similarity in shape of the ω_n curves for ODC and G (which differ significantly from that of the crystal) indicates that the spectra for these disordered solids cover the same frequency range and differ only by a small frequency shift. The overall phonon scattering/attenuation in ODC and G are likewise very similar, as attested by the near-equal widths of their spectra $S(\omega) \propto Z(\omega) / \{\omega [1 - \exp(-\hbar \omega / k_B T)]\}$.

Our Grüneisen constants can then be calculated from discrete differentiation of the V_m and ω_n with respect to pressure, resulting in $\gamma_n = -d \ln \omega_n / d \ln V_m$, where higher n correspond roughly to higher frequencies. The γ_n are quite insensitive to the ω_{\max} cutoff value, in analogy to what we found in Ref. [15] for calculations from $Z(\omega)$ of the $\langle u^2 \rangle$ mean square amplitudes of vibration. Namely, the main effect of extending the integration range above 6.5 meV was to systematically increase the value of $\langle u^2 \rangle$ while leaving the trends and differences between the

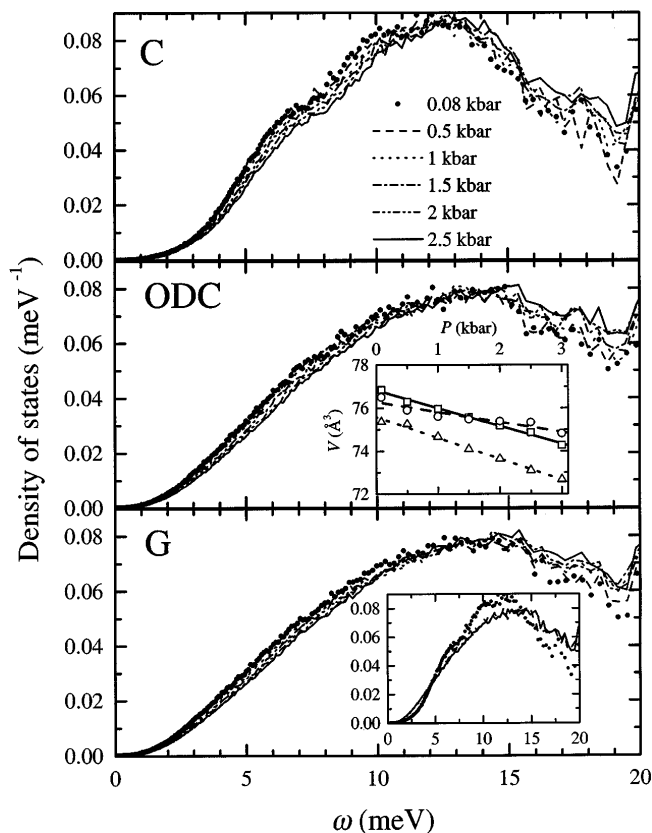


FIG. 1. The spectra of each ethanol phase at 80 K. The middle frame inset shows the pressure dependence of the volumes per molecule of the three solids (G: circles, ODC: squares, C: triangles). The lower frame inset shows a comparison of the spectra of the G and ODC phases (solid and dash dots, indistinguishable at this scale) and the C phase (circles).

pressure-dependent $\langle u^2 \rangle(P)$ curves of the three ethanol phases basically unaffected, showing that their shapes are governed mainly by acoustic modes.

The results for γ_n shown in Fig. 2 give a clear characterization of the anharmonic behavior of the glass and ODC phases with respect to the crystal, up to first order (i.e., contributions involving higher-order derivatives could be non-negligible). The marked dependence of γ_n on n indicates strong frequency dependencies of anharmonicity (similar for G and ODC as contrasted with C). In the latter case, additional evidence of anharmonic behavior is given by an upturn in the specific heat for $T \gtrsim 100$ K [13]. The values of our Grüneisen constants indicate that the C phase is moderately anharmonic compared to rare gas solids at equivalent temperatures, whereas the G phase data are comparable to those for fcc Ar at $T \geq T_m/2$ [16] and pertain to a regime where nonlinearity is so strong that it cannot be treated as a small perturbation to harmonic dynamics.

The higher-order γ_n show smaller differences between the three phases than do their low- n counterparts. What seems remarkable is the strong proximity between the γ_n 's of C and ODC for $n = 2, 3$, indicating that the large nonlinear effects experienced by atomic motions in the ODC and even for the ordered crystal above ≈ 16 meV are a consequence of the anharmonic components of the intermolecular potential and that orientational disorder is not relevant at those energies. The differences in the high-order γ_n of G and ODC set different bounds to the frequency ranges where the nonlinear effects are felt by these two glassy phases.

The $\gamma_{n=-1,-2,-3}$ constants characterize the low-frequency (and low-temperature) dynamics. In general, one expects $\gamma_{-3} \approx \gamma_\theta$, which measures the volumic dependence of the low-temperature limiting value of the Debye temperature, and therefore can be taken as the low-temperature limit of the macroscopic γ . Conversely, a bound for high temperatures is given by $\gamma_0 \approx \gamma_\infty$. The steep increase in γ_n for G and ODC with respect to C for $n \leq 1$ (Fig. 2) simply reflects the presence in the $Z(\omega)$ of the two glassy phases of excess modes (i.e., the "boson peak") compared to the crystal's Debye-like $Z(\omega) \propto \omega^2$ (see lower inset of Fig. 1). These excess modes, known to be localized to some extent, are more subject to anharmonicity than propagating modes of equal energy (i.e., those of the crystal) [17].

The measured γ_n 's provide some means to evaluate the low-temperature anharmonic frequency shifts. The purely volumic contributions are to first order [14] given by $\frac{\Delta\omega}{\omega}|_T = -\gamma_0 \Delta V/V_0$, where V_0 is the crystal volume at $T = 0$ K as estimated from linear extrapolations, resulting in values of 0.030, 0.026, and 0.042 for C, ODC, and G. The shift arising from a change in temperature is, again to first order, given by $-\left[\frac{\partial(\ln \omega_g)}{\partial(\ln T)}\right]_V = \Delta\omega_g/\omega_g$, with $\omega_g = \omega_0 e^{-1/3}$. Data for the temperature variation of the geometric mean frequency ω_g are from previous mea-

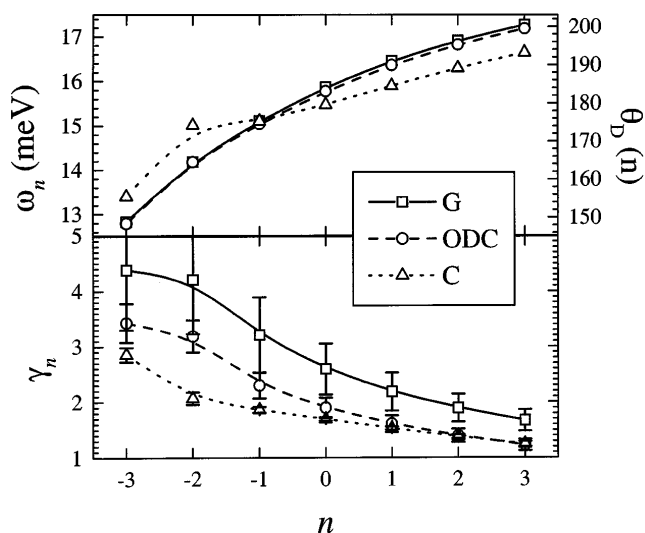


FIG. 2. The reduced frequency moments ω_n at 80 bar (upper frame) and the Grüneisen constants γ_n (lower frame) for the three ethanol phases at 80 K.

surements which have been reported in part [10]. Since these concern temperatures up to ≈ 20 K, the results of 0.032, 0.015, and 0.015 (C, ODC, and G) should be taken as lower bounds. As a result, total shifts $\Delta\omega/\omega$ of about 0.057 (C), 0.041 (ODC), and 0.062 (G) are obtained. The differences in the volumic anharmonicities of G compared to ODC contrast with the closeness of their widths in $S(\omega)$ (i.e., phonon attenuation), and serve to establish that the small difference seen in the locations of the maximum in $Z(\omega)$ of both solids, which translate into a shift of the peak in $C_p(T)/T^3$, should be ascribed to the difference in the strength of anharmonicity, rather than to the site disorder present only in G. Our values for the volumic dependence of the C phase can also be compared with Raman measurements at higher temperatures and pressures [18] that yielded frequency shifts of individual (mostly intramolecular) Raman lines that were an order of magnitude smaller than those measured at lower frequencies. The γ_{-3} also have a macroscopic correlate given in terms of the volume expansion coefficient β , the isothermal compressibility $\kappa_0 = -\partial \ln V / \partial P|_{T=80 \text{ K}}$ (also derived from our diffraction data) and the specific heat [10,13]. These macroscopic γ_{-3} values for C, ODC, and G at 80 K turn out to be 2.923, 4.001, and 4.382, which are close to the γ_{-3} derived from the $Z(\omega)$ (see Fig. 2).

The Brillouin light-scattering measurements were performed with a multipass Fabry-Pérot spectrometer in backscattering geometry from about 5 to 160 K (a full account of these measurements will be given elsewhere). The temperature variation of the fractional Brillouin frequency shift $\delta\omega_B/\omega_B$ for both G and ODC is shown in Fig. 3. The data reveal a clear crossover at about 40 K above which the magnitude of the change with temperature is larger. Similar findings have been reported for oxide glasses and polycrystalline materials [2,19]. The slope

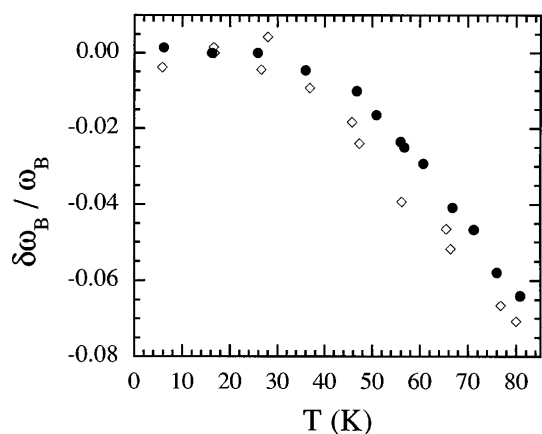


FIG. 3. Brillouin frequency shifts for the G (open symbols) and ODC (filled circles) phases as a function of temperature.

$\Delta(\delta\omega_B/\omega_B)/\Delta T$ is believed to be related to the internal friction (acoustic attenuation) [2], where an increase in slope indicates the onset of a large damping mechanism. The slopes (above 40 K) of the data in Fig. 3 are essentially the same for G and ODC, consistent with the near-equal widths in $S(\omega)$ from our neutron scattering data. In addition, the frequency shifts $\delta\omega_B/\omega_B$ at 80 K (not separable into constant volume and constant temperature contributions) show the same tendency as the total $\Delta\omega/\omega$ estimated above from the Grüneisen constants for ODC and G, a remarkable finding since only order-of-magnitude agreement could be expected between measurements carried out at optical frequencies and the averaged values from the spectral moment derivatives.

The proximity in the dynamics of the two glassy solids has recently been shown to extend to macroscopic scales in dielectric relaxation studies [20], where the characteristic frequencies and activation energies of the sub- T_g relaxations in G and ODC have been found to be remarkably close. Moreover, these studies identify large-amplitude molecular librations as the most plausible entities giving rise to such relaxations.

In summary, the strong similarity in the vibrational spectra and phonon attenuations of the two glassy phases suggests that the localization of vibrational excitations is due principally to orientational disorder. The anharmonic behavior of these two phases can, however, be quantitatively distinguished in terms of Grüneisen constants, with G showing greater anharmonicity than ODC, associated with a small frequency shift that is confirmed by specific heat and light-scattering data. The similar frequency dependences of anharmonicity of the two glassy phases differ strongly from that of the C phase which serves as an experimental baseline. Furthermore, our results iden-

tify the low-frequency “excess modes” part of the glass spectra as that most prone to the effects of anharmonicity, confirming earlier theoretical results for a Lennard-Jones glass [17]. We believe that these excess modes in ethanol involve fairly large-amplitude orientational excursions [20] which are reminiscent of the reorientations of CN dipoles in mixed halide crystals [21].

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