

Origins of Terahertz Vibrations in Glassy and Crystalline Materials

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The dynamics of most solids and liquids include structure in the Terahertz range [1]. While the frequencies are low compared to nearest neighbour oscillations that populate infrared spectra, the amplitudes of Terahertz vibrations are often large. They incorporate many atoms moving in concert and can involve considerable collective kinetic energy. They are prolific in glasses, minerals, polymers and biomaterials [1-3]. Terahertz vibrations formally mark the beginning of the Vibrational Density of States (VDOS) and were first detected in glasses by low frequency Raman spectroscopy almost 45 years ago [4] and a few years later by inelastic neutron scattering (INS) [5] and later classified generically under the heading of the boson peak (BP).

The BP is prominent at low temperatures (~10 K) and was once believed to be unique to disordered systems. In particular, the intensity of the BP mirrors the excess specific heat ΔC_p discovered in glasses a few years earlier [6]. As its name implies the excess specific heat ΔC_p was observed to rise above the T^3 VDOS baseline predicted by the Debye model for the crystalline state as the temperature approaches 0 K. The Terahertz phenomenon was modelled for classical glasses like silica by librational modes of tetrahedra connected in the covalent network. These coupled librations equate with Two Level Systems (TLS) [3] which were shown to facilitate tunnelling as the temperature is lowered [5]. TLS may also prove useful in modelling catalytic activity and possibly the functionality of biological systems. Indeed there is view that in the denaturing of proteins, breaking the molecular conformation may be associated with a liquid-liquid order-disorder transformation [7]. This might involve a TLS switch which may in turn be driven by Terahertz modes, such as the under-damped delocalized Terahertz modes identified in lysozyme [2].

The Debye Model, however, only properly predicts the dynamics of the simplest cubic structures and not surprisingly Terahertz features are found in the crystalline equivalents of classical glass formers [8] and indeed in many other crystalline inorganic systems. Importantly the strength of the BP, and with it ΔC_p , increase with decreasing density. Accordingly, the size of the Terahertz band at the start of the VDOS for low density nano-structured systems like zeolites [9], MOFs and ZIFs [10,11] can be huge. The intensity of these terahertz features increases and average frequency ν decreases as the density decreases [12]. The size of the collective vibrations can be estimated from wavelength λ of acoustic vibrations V_s/ν , where V_s is the speed of sound. Consequently, as the Terahertz frequency ν falls the vibrations become larger in extent. Not surprisingly these Terahertz properties translate into solid state mechanics where the size of the BP has been shown to be coupled with Poisson's ratio (PR) [12]. Greater flexibility at the atomic level is associated with small values of the shear modulus G at the macroscopic level [12].

Finally, and somewhat non-intuitively, PR is empirically correlated with the Fracture Energy (FE). This is a sigmoidal relationship which differentiates brittleness (low PR values) from toughness (high PR values). The relationship extends over many decades of FE and covers numerous solid materials from glasses and dental cements, to metals, polymers and rubbers [13]. Specifically, brittle materials have constrained Terahertz collective modes and high values of G , while for tough materials these are far more floppy

and bulk moduli B are high. As PR is a function of (B/G) this naturally leads to small and large values respectively. The dramatic sigmoid that distinguishes macroscopic fragility (low FE) from ductility (high FE) remains puzzling, but differences in the Terahertz regime are likely to be key to its explanation.

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