

Comment on “High Frequency Dynamics of Glass Forming Liquids at the Glass Transition”

In a recent Letter, Masciovecchio *et al.* reported inelastic x-ray scattering spectra, $I(Q, \omega)$, of organic glass-forming liquids at temperatures T near their glass-transition temperatures T_g [1]. They conclude that soundlike modes are supported by these materials in their glass and liquid forms at spatiotemporal scales well within the microscopic realm. This conclusion challenges the present understanding of glasses and supercooled liquids, and, in particular, it conflicts with established views on their thermal properties. These portray thermal conduction at high T (or also high ω) as taking place in a strong phonon-scattering regime in which the “plane-wave picture” that heat is carried by long-wavelength phonons is neither necessary nor adequate.

To illustrate the difficulty in reconciling the position in [1] with standard teaching, one may consider, e.g., estimates of the phonon mean free path ℓ in glassy glycerol, a material studied in [1]. Using the dominant phonon approximation and experimental values of the thermal conductivity, specific heat, and ultrasound velocity at $T \approx 100$ K [2], one finds for both longitudinal and transverse phonons an estimate comparable to molecular dimensions, $\ell \leq 8$ Å. In fact, the universal strong phonon scattering in glasses reaches a Ioffe-Regel limit, $\ell \approx \lambda$, already at lower ω and corresponding lower T [3]. Beyond this limit, acousticlike excitations are nonpropagating, and their range is typically a few Å. On the opposite, data on glycerol at the same T taken from Fig. 3 of [1], when interpreted in terms of well-defined sound waves, lead to an estimate $\ell \approx 75$ Å, 1 order of magnitude above the one predicted from thermodynamics.

The difficulty with [1] results from the assignment of a soundlike character to intensities measured up to very high ω . To illustrate this, Fig. 1 displays *experimental* Raman spectra in the relevant ω range for glassy and crystalline *o*-terphenyl (OTP), another material studied in [1]. In the crystal, there are a large number of peaks at $\omega < 20$ meV. These are assigned to *at least* 45 Raman-active modes [4]. Their dispersion curves are drawn in Fig. 1 for a particular high-symmetry direction. The glass spectrum, superposed to the crystal one, covers a very similar range of ω . The dispersion curves of the crystal show that the three acoustic modes have an upper bound at $\omega \approx 2.5$ meV (see [4] for more details). It is unjustified to assign *all* the vibrational dynamics of the glass below 20 meV just to “sound modes” that would reach frequencies far larger than those of the crystal. When this is pursued, an *apparent* “dispersion relation” results from a plot of a frequency describing the center of gravity of the spectra versus Q . Such a plot is not the dispersion curve of a well-defined mode. It is only a device to describe averaged data, without any particular implication that one deals with anything

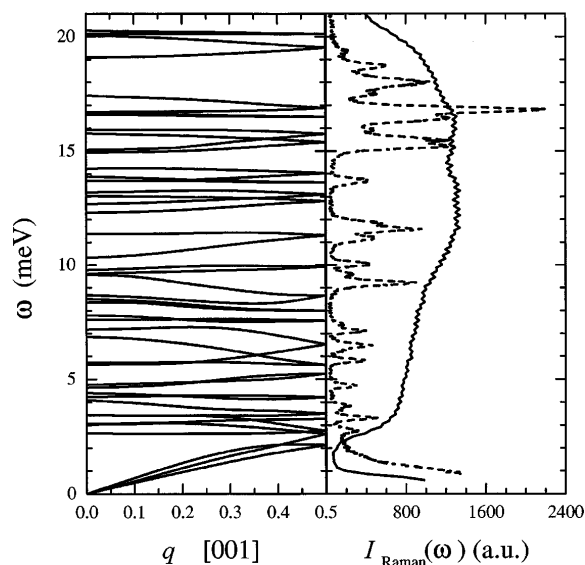


FIG. 1. (right) Raman spectra of glassy and crystalline OTP at 6 K. Calculated dispersion curves (left) [4].

like plane waves. The same observations apply to glycerol, for which data similar to Fig. 1 are also available [5].

An exercise that seems worth undertaking would be to perform a study similar to that in [1], at T values comparable and below those of the thermal conductivity “plateau.” At these low temperatures, phonon-scattering mechanisms are far less severe than those operative at temperatures explored in [1] and thus enable one to analyze sound propagation in terms of well-founded concepts.

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