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Physica B 219&220 (1996) 270-272

PHYSICA B

Interstitial resonance modes as a source of the boson peak in glasses and liquids

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Abstract

Although it is recognized that the boson peak is a universal and fundamental feature of glass and liquid dynamics arising from low-frequency vibrational modes which are absent in crystals, the source of these modes is still under investigation. The effects are detected as a "bump" in low temperature specific heat measurements, an excess vibrational density of states in inelastic neutron scattering and the "boson" peak in Raman scattering. It is shown that the magnitude, location, and softening of the Boson peak as it persists into the supercooled liquid state are well accounted for by the interstitialcy model of condensed matter states as the resonance modes of self-interstitials.

1. Introduction

Besides the characteristic and familiar signatures of a quasi-linear excess specific heat and quasi-quadratic thermal conductivity temperature dependence of glasses below about 1 K [1], as well as a reduction of shear modulus and saturation of ultrasonic attenuation [2], there are characteristic effects in the 5–10 K range arising from low-frequency vibrational modes which are absent in crystals [1, 3]. These latter effects are also found to be universal [4, 5] and are thought to be fundamental features of glass dynamics. They are detected as a "bump" in low-temperature specific heat measurements [6, 7], an excess vibrational density of states in inelastic neutron scattering [5, 6] and the "Boson peak" in Raman scattering [4, 8]. The thermal properties below 1 K have been rationalized in terms of a phenomenological two-level system (TLS) tunneling model [9, 10] arising from a double well potential whose source is unspecified, and it is sometimes said that the TLS model cannot account for the shear modulus softening or the excess low frequency vibrational states found.

However, the interstitialcy model for condensed matter states [11] leads to a physical realization of a double (or multiple) well potential with TLS behavior for the low temperature thermal properties. The reference level of the potential depends on the defect concentration in such a way as to account also for the shear softening, and vibrational levels higher than the tunnel-split ground state account for the specific heat 'bump' [12]. We elaborate on this here to show that the magnitude, location, and softening of the Boson peak as it persists into the supercooled liquid state can be accounted for in a simple, natural and quantitative way by the resonance modes of self-interstitials.

2. The boson peak

Fig. 1 [13] shows that the spectrum of excess low energy (E) density of vibrations $g(E)$ found by inelastic neutron scattering in glasses of different types has a universal form when normalized by E^2 for a scale E/E_m. The curves for ceramic, metallic and superionic materials are

SSDI 0921-4526(95)00716-4

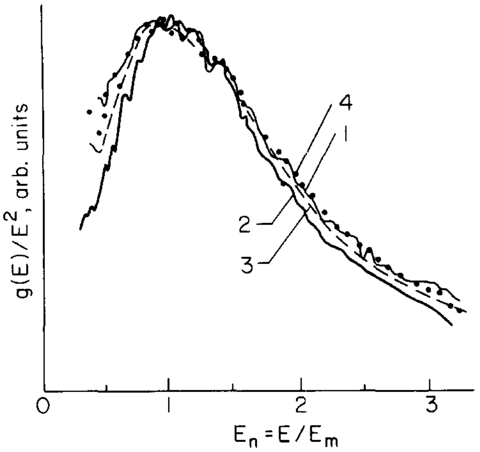

Fig. 1. Density of vibrational states of some glasses, normalized by E^2 in a scale $E_n = E/E_m$: (1) As_2S_3 ($E_m = 2.65$ meV); (2) SiO_2 (5.1 meV); (3) $Mg_{70}Zn_{30}$ (5.5 meV) [4]; (4) $(AgI)_{0.65}$ $(Ag_2O + B_2O_3)_{0.35}$ (1.75 meV) (After Malinovsky et al. [13]).

similar. The peaks are higher than the Debye background $g_D(E) \sim E^2$ curves by factors of 2–6 for different glasses. Similar results are found for the frequency spectrum of glasses of differing chemical composition for Raman scattering. The temperature dependence of the spectra in the peak region is determined by a Bose distribution function $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$, giving rise to the term "boson peak", which is also applied to the related inelastic neutron scattering and excess specific heat results. The height and position of the peak are correlated inversely. For temperatures T below the glass temperature T_g, there is little change of either. For $T > T_g$, the peak height increases and position decreases. Defining a characteristic length L by $f \sim v/2L$, where f is the frequency and v is the sound velocity, both f and v decrease with increasing temperature, but L remains approximately constant. On annealing near T_g, the peak height decreases.

The specific heat bump relative to the Debye specific heat is shown in Fig. 2 for four different glasses [14]. Measurements are becoming available for many more materials.

3. The interstitialcy model

According to the interstitialcy model, liquids are crystals containing a few percent of interstitials in thermal equilibrium, and glasses are frozen liquids. In a recent comparison [15] of the predictions of the model with available evidence, it was found that the structure, dynamics and thermodynamic properties in the crystalline,

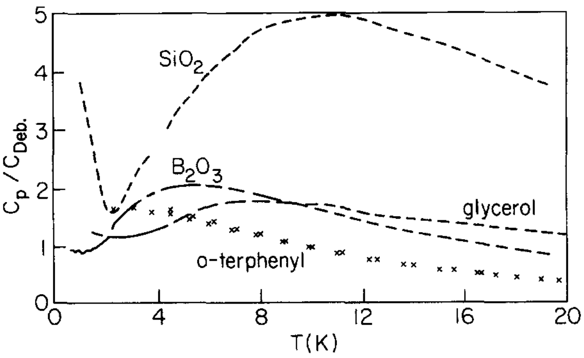

Fig. 2. Low-temperature heat capacity of different glasses normalized to the Debye values (After Sokolov et al. [14]).

liquid and glassy states are accounted for easily, simply and naturally in a quantitative, comprehensive and unified way by the model.

The interstitial resonance modes have been calculated for copper by Dederichs et al. [16]. The results depend somewhat on the interatomic potential chosen. There are five resonance modes per interstitial, expected to lie near $\omega_D/7$, were ω_D is the Debye frequency. In addition, there are six local modes lying above the maximum perfect lattice frequency. There are no measurements available for copper, but local modes for $Ni_{33.3}Zr_{66.7}$ have been detected by Suck [17] from inelastic neutron scattering data. These have been used [15] to obtain an estimate of the interstitial concentration of $c^I = 0.03$ in the glassy state.

4. The specific heat bump

For the simplest approximation, we take all the resonance modes ω_R to be the same, with the interstitial contribution to the specific heat C_I given by the Einstein function

$$C_I = c^I f\, Nk\, [x^2 \exp x/(\exp x - 1)^2], \tag{1}$$

where $x = \hbar\omega_R/kT \equiv \theta_R/T$, c^I the interstitial concentration, and f the number of resonance modes per interstitial. Then with $C_D = 234\, Nk\,(T/\theta)^3$, and $\delta C = C^I - C_D$, we have

$$\frac{\delta C}{C_D} = \frac{c^I f}{234}\left(\frac{\omega_D}{\omega_R}\right)^3 \frac{x^5 \exp(x)}{(\exp x - 1)^2}. \tag{2}$$

Eq. (2) has a maximum height $H = (\delta C/C_D)_m$ of

$$H = 4.6\frac{c^I}{(0.03)}\frac{f}{5}\left(\frac{\omega_D}{7\omega_R}\right)^3 \tag{3}$$

at the temperature T_B of

$$T_B = \frac{\theta}{35}\left(\frac{7\omega_R}{\omega_D}\right). \tag{4}$$

For $f = 5$, $7\omega_R/\omega_D = 1$, and $c^I = 0.03$, these are $H = 4.6$ and $T_B = \theta/35$. For a distribution of resonant mode frequencies, H is reduced.

The predictions of $T_B \sim \theta/35$ and $H \leqslant 4.6$ are in reasonable agreement with available data. An experimental relation of $T_B \approx \theta/40$ was found recently by Carini et al. [18] for a range of five glasses of various types. Also, the dependence of T_B and H on c^I is in reasonable accord with the qualitative properties of the boson peak listed earlier in Section 2 since the temperature dependence of θ is approximately that of the sound velocity v, which decreases strongly for $T > T_g$, and c^I is constant (frozen) for $T \ll T_g$, increases for $T > T_g$, and decreases with annealing (relaxation) near T_g.

A unified description of both the tunneling and the low-frequency vibrational states, but not of the softening of θ and the shear modulus G, can also be given with the soft potential (SP) model of Karpov et al. [19, 20]. A difference between the two approaches is that different parameters of the phenomenological SP model are used for the tunneling and vibrational states, while the interstitialcy model obtains both effects from the same potential, as well as the softening of θ and G.

5. Conclusion

The boson peak magnitude, position and softening as the liquid state is entered arises naturally from the interstitialcy model for condensed matter states as the self-interstitial resonance modes.

Acknowledgement

This work is supported by the National Science Foundation under Grant DMR93-19773.

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