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A model of elastically and anelastically produced temperature derivatives of acoustic wave velocities in inorganic oxide glasses

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The temperature dependence of 15 MHz ultrasonic bulk wave velocity in the range 4 to 600 K has been measured in the entire range of glasses that can be prepared by mixing MoO_3 with P_2O_5 in open crucibles. In all cases the temperature gradients are negative. However, when the contribution to the velocity variation caused by (anelastic) two-well relaxational effects is subtracted, the residual velocity variation is always positive with respect to temperature. It is suggested that this effect, which has been reported to be present in other glasses but not in crystals, is still caused by two-well systems, but is elastic in nature. It is argued that under certain conditions the expansion of a glass due to increases in temperature softens the vibrations of particles in transverse two-well systems. In the simple case of wave propagation along a chain this leads to a positive temperature gradient of the shear modulus, and in an isotropic system positive gradients will similarly be caused in all elastic moduli. A detailed model is presented to justify the proposal quantitatively by identifying the conditions under which such behaviour could take place. One cause would be the presence of an appreciable number of two-well systems of barrier height $\ll kT$ at room temperature. For the MoO_3–P_2O_5 system it is estimated that 25% of cation–cation spacings contracted by between 0 to 1% from equilibrium (crystalline) values, to produce barrier heights $\leqslant 0.005$ eV, would explain the observations. On the other hand an appreciable fourth-power term in the transverse force potentials (i.e. high third-order bending force constants) would cause a similar effect even if a much smaller number of barriers were present, but of height $> kT$ indeed, such a mode softening term has exactly the opposite effect on the temperature gradients of velocity to what it has in single-well systems.

1. Introduction

The MoO_3–P_2O_5 glass system has proved to be a most interesting, perhaps unique one. In a number of papers [1–4] the present authors have shown it to exhibit changes in sign (and perhaps discontinuities) in the composition gradient of a number of physical properties. These include the elastic moduli at room temperature, the melting temperature and a number of parameters associated with ultrasonic relaxation absorption. Of particular note is the fact that sometimes there is one change in sign whilst with other properties there are two. Much work still needs to be done before a coherent structural model explaining all the observations can be assembled. The present reported observations on the behaviour of ultrasonic longitudinal wave velocity, on increasing the temperature from 4 to 600 K, are no less striking than the previous data. No experimental details of the preparation and chemical characterization of the glasses are given here as full documentation exists elsewhere [1, 4].

2. Experimental procedure

Measurements were performed on 1.6 mm diameter × 5 mm thickness rods with 15 MHz X-cut quartz transducers. The rods had optically polished faces flat to within 1 to 2 seconds of arc after preparation with Metals Research (Metals Research Ltd, Melbourn, Royston, UK) equipment (Multipol T1 polishing machine and a Mk III polishing jig adjusted by means of an autocollimator). The specimens were coated with vacuum-evaporated aluminium to provide an earth electrode and permit the use of uncoated transducers. The procedures for sweeping the sample temperature from 4 to 300 K, using a commercial cryostat (Oxford Instruments) were exactly as described in a previous paper on relaxation absorption experiments [4]. The method of changing the ambient temperature between 300 and 600 K using a purpose-built furnace and sample holder have been described elsewhere [5]. For coupling the specimens to the transducer, Nonaq stopcock grease was found satisfactory for 4 to 300 K, whilst for 300 to 600 K the best of many materials tried was OV-25 (a silicon-based grease chemically described as a gas chromatographic stationary phase) supplied by J.J's Chromatography Ltd., Hardwick Industrial Estate, King's Lynn.

The pulse echo apparatus described by Higazy and Bridge [6] was employed. Here fairly long pulses of fast rise time are first propagated so that corresponding

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cycles in successive echoes are readily identified. Time delays between them are measured to ± 0.2 nsec absolutely and relatively to ± 100 psec with a digital delay generator based on a 100 MHz clock. The time delay so obtained is next used to identify corresponding cycles in successive echoes of long echoes of slow rise time. From the measured time delay between these cycles the true phase velocity is obtained. Once corresponding cycles have been labelled in this way by the digital delay pulse, it is a simple matter to keep track of each cycle as the ambient temperature is gradually changed and the evaluation of the time delay with temperature thus obtained. Whilst this measurement technique is much simpler to set up than others based on a frequency counter and requiring cyclic matching technique (pulse–echo overlap, pulse superposition etc.) there is no evidence that it is any less sensitive for most kinds of sample. A distinct advantage is that it is automatable, i.e. the programmable delay generator can be interfaced to an on-line computer, although this has not been done by the authors. Corrections for sample expansion were carried out using expansion data for the temperature range from 300 K to the transformation temperature only [7], assuming that it could be extrapolated to the lower temperatures. Fortunately, as the correction was small, errors due to anomalous expansion behaviour are likely to be quite small.

3. Comparison of results with previous work on other glasses

It is well known that whereas in pure dielectric crystals the temperature coefficients of ultrasonic wave velocities are small and negative, much larger gradients, both positive and negative, are found in glasses [8–10].

The fractional change in the velocity $(c_T - c_{he})/c_{he}$, where c_T is the velocity at temperature T and c_{he} the velocity at 4.2 K, is plotted in Figs 1 and 2 for all the Mo–P–O glasses. The velocity decreases steadily with increasing temperature. Although the mean coordination number of these glasses ranged from 3 to 5, there is no true evidence of a minimum occurring, unlike that which has been observed in other tetrahedral coordinated glasses such as SiO_2, GeO_2, $Zn(PO_3)_2$ and BeF_2 (see Fig. 1). However, a slight inflexion is observable for all the glasses at around room temperature. The velocity at constant temperature decreases with increasing amount of MoO_3 content in the range 0 to 53 mol % MoO_3 and then increases in the range 53 to 86 mol % MoO_3 (see Fig. 3).

Superficially, it would appear that all glasses studied so far can be divided into two classes in respect of the velocity variation when the temperature is increased from about 4 K. Firstly, there are those glasses which start with a negative temperature gradient, changing to a positive gradient at high temperatures. Secondly, there are the glasses in which the temperature gradient always remains negative. The present glass system with the inflexion instead of a sign change at an intermediate temperature is something of a borderline case. However, the distinction, in our opinion, is an artificial one based on a lack of analysis in previous literature of the different possible contributions to the velocity change. It is generally accepted that all glasses exhibit an ultrasonic relaxation absorption with a broad distribution of Arrhenius relaxation times, and it is readily shown (Section 4) that the association velocity dispersion leads essentially to negative temperature gradients of velocity. Plausibly, if this effect is strong enough, the residual velocity variation obtained on subtracting the relaxational contribution might be positive with respect to temperature in all glasses, and the dual classification of glasses disappears. In effect, the positive temperature gradient of non-relaxational origin becomes a property quite generally characteristic of the vitreous state (rather like two-well relaxation absorption), since for crystals the gradient is always negative. In Section 5 we propose a model which indeed allows positive and negative temperature gradients of velocity in glass whilst permitting only negative gradients in crystals.

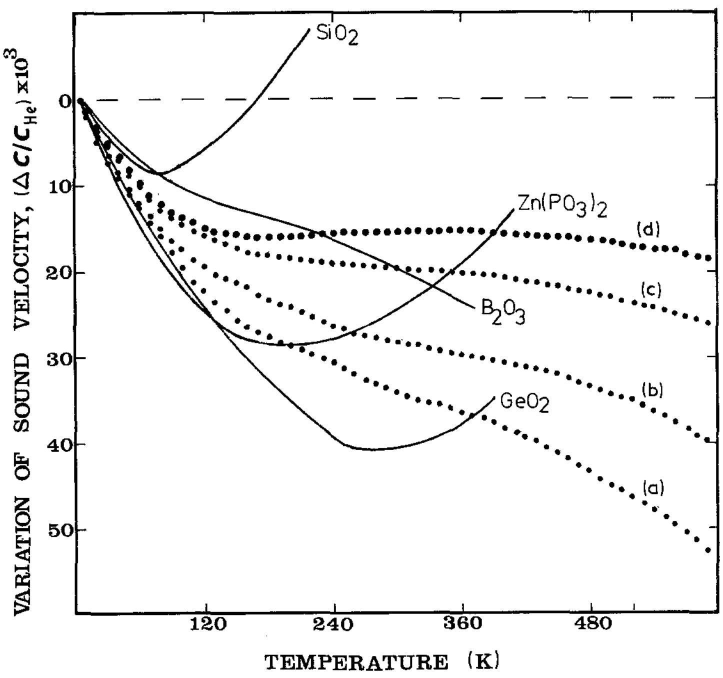

Figure 1 Fractional variation of the longitudinal sound wave velocity $(c_T - c_{he})/c_{he}$ with temperature in Mo–P–O glasses at 15 MHz: (a) 29.2, (b) 37.5, (c) 44.2, (d) 47.4 mol % MoO_3. For SiO_2, GeO_2, $Zn(PO_3)_2$ and B_2O_3 glasses, the data have been taken at 20 MHz from Krause and Kurkjian [9]. Full circles represent the experimental values for Mo–P–O glasses. (c_{he} = velocity at 4.2 K).

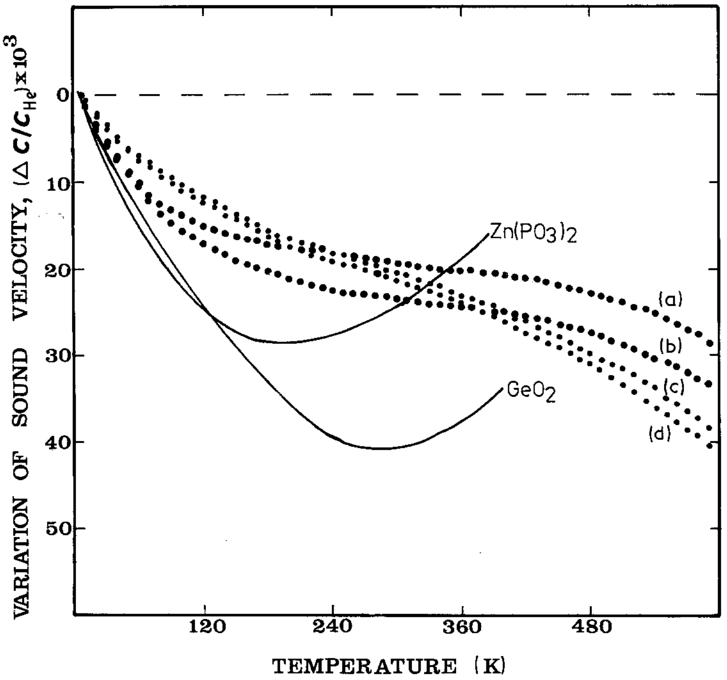

Figure 2 Fractional variation of the longitudinal sound wave velocity $(c_T - c_{he})/c_{he}$ with temperature in Mo–P–O glasses at 15 MHz: (a) 55.0, (b) 61.6, (c) 69.5, (d) 80.8 mol % MoO_3. For GeO_2 and $Zn(PO_3)_2$ glasses, the data have been taken at 20 MHz from Krause and Kurkjian [9]. Full circles represent the experimental values for Mo–P–O glasses. (c_{he} = velocity at 4.2 K).

4. Residual velocity variation in Mo–P–O glasses after subtraction of anelastic contribution

We shall make the usual assumption that a glass behaves like a standard linear solid [11, 12] with low dispersion and a broad distribution of relaxation times, τ. The internal friction Q^{-1} and phase velocity c for wave propagation can thus be written [11–13]

$$Q^{-1} = \frac{2\alpha c}{\omega} = \int_0^\infty \frac{C(\tau)\,\omega\tau\,\mathrm{d}\tau}{1+\omega^2\tau^2} \approx \sum_i \frac{C_i\omega\tau_i}{1+\omega^2\tau_i^2} \tag{1}$$

$$c = c_\infty\left(1 - \frac{1}{2}\int_0^\infty \frac{C(\tau)\,\mathrm{d}\tau}{1+\omega^2\tau^2}\right) \approx c_\infty\left(1 - \frac{1}{2}\sum_i \frac{C_i}{1+\omega^2\tau_i^2}\right) \tag{2}$$

where α is the wave absorption coefficient in nepers per unit length, ω is the angular frequency, c_∞ is the phase velocity for $\omega \to \infty$, and $C(\tau)\,\mathrm{d}\tau \equiv C_i$, is the relaxation strength for absorption processes with relaxation times in the range τ to $(\tau + \mathrm{d}\tau)$. One can express $C(\tau)$ in the form $\Delta M/M$ where M is the appropriate unrelaxed modulus obtaining at $\omega \to \infty$, and ΔM is the contribution to the difference between the unrelaxed modulus (i.e. the change in elastic modulus) caused by all relaxation processes with relaxation times in the range τ to $(\tau + \mathrm{d}\tau)$. The summations on the right-hand side are approximations to the integrals on their left and are suitable for numerical manipulations by computer. Here $C_i(\delta V)/\delta V = C(V)$ where $\delta V = V_i - V_{i-1}$, the interval between the energies in consecutive terms in the sum, so that $\Sigma C_i = \int_0^\infty C(V)\mathrm{d}V$.

If we make the usual assumption that the relaxing mechanisms are particles in double-well potentials of barrier height V, and asymmetry (separation of two-well minima) Δ, then [4, 13, 14]

$$\tau = \tau_0 \exp(V/kT)\,[1 + \exp(\Delta/kT)]^{-1} \tag{3}$$

$$C(\tau)\mathrm{d}\tau = \frac{D^2}{\varrho c^2}\left(\frac{\mathrm{d}[1+\exp(\Delta/kT)]^{-1}}{\mathrm{d}\Delta}\right) n(\Delta)n(V)\mathrm{d}\Delta\,\mathrm{d}V \tag{4}$$

where k is Boltzmann's constant, T is absolute temperature, τ_0^{-1} is the classical vibration frequency (attempt frequency) for the particles in either well, D is the energy shift of the two-well states in a strain field of unit strength, averaged over all possible well orientations, ϱ is the density, $n(V)\mathrm{d}V$ is the number of two-well systems with barrier height in the range V to $(V + \mathrm{d}V)$, and $n(\Delta)\mathrm{d}\Delta$ is the number of two-well systems with barrier height in the range V to $(V + \mathrm{d}V)$, having assymetries in the range Δ to $(\Delta + \mathrm{d}\Delta)$. In performing the integrations in Equations 1 and 2 it will usually be satisfactory to neglect variations in D and τ_0 compared with the more drastic effect of

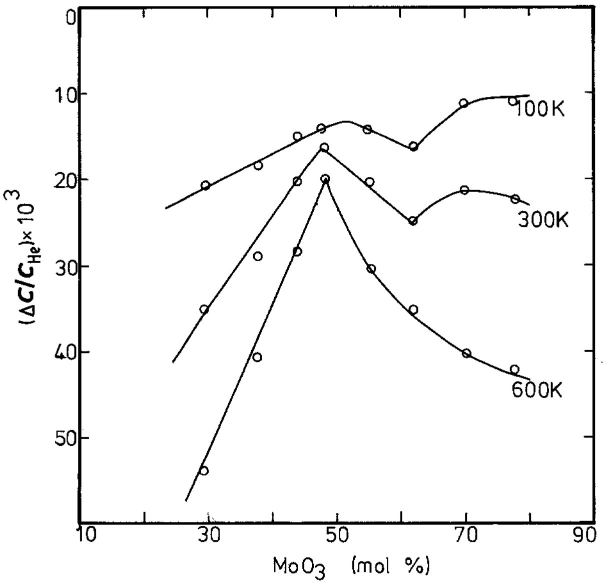

Figure 3 Fractional variation of the longitudinal sound wave velocity $(c_T - c_{he})/c_{he}$ with composition at constant temperature T in Mo–P–O glasses at 15 MHz.

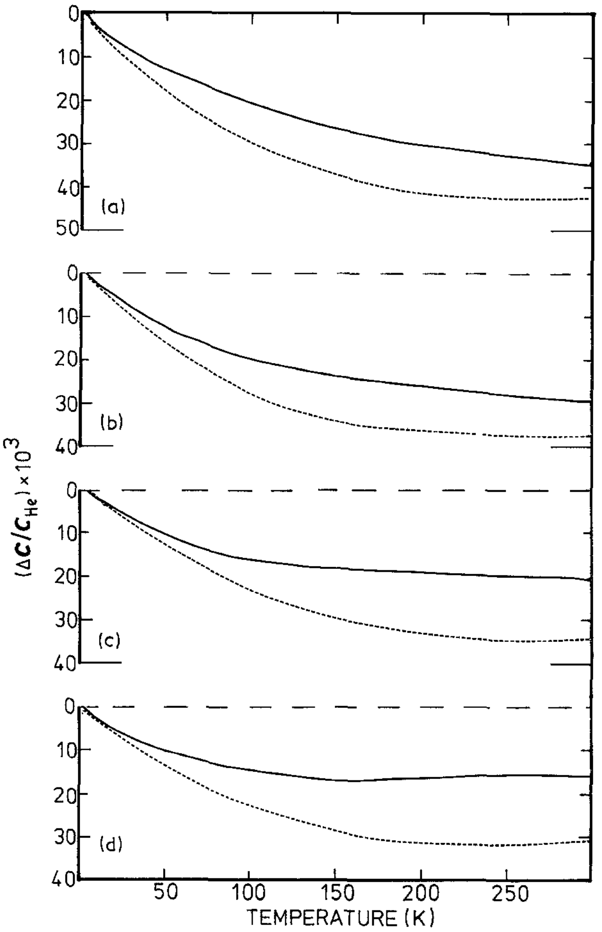

Figure 4 Fractional variation of the longitudinal sound wave velocity $(c_T - c_{he})/c_{he}$ with temperature in Mo–P–O glasses at 15 MHz: (a) 29.2, (b) 37.5, (c) 44.2, (d) 47.4 mol % MoO_3. Solid line represents the experimental values and dashed line shows the theoretical fit as explained in the text.

variations in V and Δ inside the exponential functions. Clearly an infinite number of $C(\tau)$ functions can be fitted to experimental Q^{-1} and c data, depending upon the choice of $n(\Delta)$ and $n(V)$ which we treat as unknowns. One extreme simplifying assumption is to write $n(\Delta) = n_0$, a constant independent of Δ and V. If a sharp cut-off in the integrations is adopted at $\Delta = 2kT$ (the contributions to the integrals being small for $\Delta \geqslant 2kT$), one finds [4, 15] that in the integrals of Equations 1 and 2

$$C(\tau)\,d\tau = C(V)\,dV = (2n_0D^2/\varrho c^2)n(V)\,dV \quad (5)$$

and

$$\tau = \tau_0 \exp(V/kT) \quad (6)$$

i.e. the relaxation strengths are independent of temperature. An assumption of the opposite extreme is to assume $n(\Delta) = 0$ for $\Delta \neq 0$ (symmetric wells) which results in $\tau = 2\tau_0 \exp(V/kT)$ and $C(\tau)\,d\tau = (D^2/4\varrho c^2 kT)n(V)\,dV$, i.e. relaxation strengths proportional to reciprocal temperature. We shall pursue further only the first model which in our opinion is the most plausible, at least for the present glasses. It is entirely reasonable that Δ can be comparable with V, given that the mean energy kT_m available at the melt preparation temperatures [2] ($T_m \sim 855$ to 1475 K) for producing frozen-in assymetries is $\sim$0.065 to 0.113 eV, comparable with the range of mean activation energies V_p of 0.07 to 0.123 eV [4], obtained by assuming that the temperature dependence of the loss peaks follow the Arrhenius law

$$\omega\tau_0 \exp(V_p/kT) = 1 \quad (7)$$

We anticipate that this relationship will hold approximately irrespective of the precise form of the $C(V)$ function in Equation 1, although it becomes almost exact [15] if one assumes $n(V) = (1/V_p)\exp(-V/V_p)$.

Substituting $C(V)\,dV = C(\tau)\,d\tau$ in Equation 1 we have previously obtained [4] an experimental value of $C(V)$ for each glass by fitting to the measured data on the temperature and frequency dependence of Q^{-1}. An excellent fit was obtained in all cases, suggesting that other attenuation mechanisms were negligible compared with the relaxation loss. Further, by assuming $n(\Delta) = n_0$ for $\Delta < V_p$ and zero for $\Delta > V_p$, n_0 becomes V_p^{-1} so that the total number of two-well systems per unit volume, n, could be calculated from the equation

$$n = \int_0^\infty n(V)\,dV = (\varrho c^2 V_p/2D^2)\int C(V)\,dV \quad (8)$$

after adopting a value of D given by our theoretical model of the deformation potential [4].

It is clear by inspection of Equations 2, 5 and 6 that, irrespective of the precise form of $C(V)$, the relaxation always causes c to decrease with increasing temperature. As $T \to 0$, $C \to c_\infty$; thus we can assume that the velocity at the lowest temperature (4 K), $c_{he} \approx c_\infty$, so that

$$(c_T - c_{he})/c_{he} = -\frac{1}{2}\int_0^\infty \frac{C(V)\,dV}{1 + \omega^2\tau_0^2\exp(2V/kT)}$$
$$= -\frac{1}{2}\sum_i \frac{C_i}{1 + \omega^2\tau_0^2\exp(2V_i/kT)} \quad (9)$$

The $C(V)$ functions, so precisely fitted to the Q^{-1} data, were used in this equation to obtain the temperature dependence of c caused by two-well relaxing systems in the glasses. The results are displayed as dotted lines in Figs 4 and 5. It is clear that in all cases the temperature gradient of c, due to relaxation, is substantially more negative than the observed gradient at all temperatures. Thus there is a residual velocity variation due to other causes, which is always positive with respect to temperature changes at all temperatures investigated.

5. Interpretation of results

We present a linear chain model which predicts the possibility of both positive and negative temperature gradients of velocity in glasses and negative gradients only for crystals. The gradients are purely elastic in origin, arising from anharmonicities in the interatomic force potentials, and follow from a simple analysis of longitudinal and transverse vibrational modes. Gruneissen constants are not calculated; however, the presentation has the advantage of giving a clear physical picture of the anharmonic effects in acoustic wave propagation.

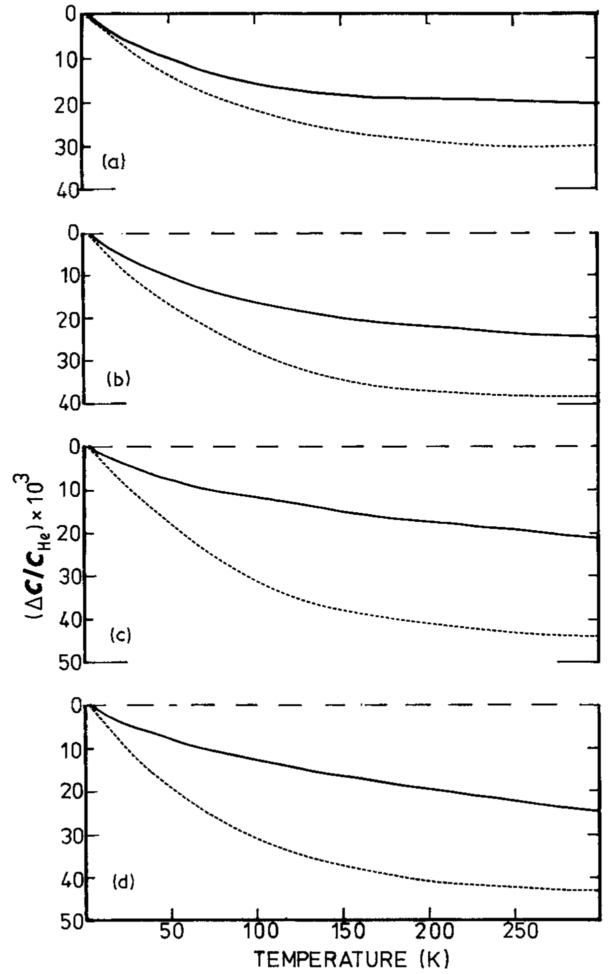

Figure 5 Fractional variation of the longitudinal sound wave velocity $(c_T - c_{he})/c_{he}$ with temperature in Mo–P–O glasses at 15 MHz: (a) 55.0, (b) 61.6, (c) 69.5, (d) 80.8 mol % MoO_3. Solid line represents the experimental data and dashed line shows the theoretical fit as explained in the text.

5.1. Longitudinal vibrations

The potential energy of a pair of atoms displaced by an amount X from their equilibrium separation at 0 K can be written

$$U(X) = AX^2 - BX^3 - CX^4 \qquad (10)$$

where A, B, and C are all positive. So the restoring force tending to return the atoms to their equilibrium separation is

$$F = -\frac{\partial U}{\partial X} = -aX + bX^2 + cX^3 \qquad (11)$$

where $a = 2A$, $b = 3B$ and $c = 4C$ and the negative sign indicates that F acts in the opposite direction to X. The first term in Equation 11 represents the harmonic (Hooke's law) approximation. The second (anharmonic) term produces an asymmetry in F, depressing the level of $|F|$ below the Hooke's law value for positive X, whilst increasing $|F|$ above the Hooke's law value for negative X. The third term, symmetric with respect to F, causes $|F|$ to increase less rapidly with $|X|$ at large vibrational amplitudes – an effect known as the softening of the vibration [16] – which has pronounced influence during phonon mode softening in materials which show incipient acoustic mode instabilities.

For a small extra displacement (i.e. additional to that caused by thermal vibration) ΔX, caused by an external applied stress acting along the chain axis (as in a longitudinal acoustic wave), the effective elastic modulus is

$$M_L = nr_0\left|\frac{\partial F}{\partial X}\right| = nr_0\,|a - 2bX - 3cX^2| \qquad (12)$$

where r_0 is the equilibrium atomic spacing in the chain (bond length) and n is the number of bonds per unit cross-sectional area perpendicular to the chain. For $X \to 0$, $M_L \to (M_L)_0 = nr_0a$, so defining $\Delta M_L = (M_L)_0 - M_L$,

$$\frac{\Delta M_L}{(M_L)_0} = -\frac{2bX + 3cX^2}{a} \qquad (13)$$

ΔM oscillates with X during a thermal vibration. Defining a mean value we have

$$\frac{\Delta \bar{M}_L}{(M_L)_0} \approx -\frac{2b\bar{X} + 3c\bar{X}^2}{a} \qquad (14)$$

Assuming, for simplicity, classical Boltzman statistics (even though the approximation is a poor one at the temperatures considered here), i.e. a weighting factor of $\exp(-U/kT)$ on all values of X and X^2,

$$\bar{X} = (b/a^2)kT \qquad (15)$$

$$\overline{X^2} = kT/a \qquad (16)$$

so that

$$\frac{\Delta \bar{M}_L}{(M_L)_0} \approx -\left[\left(\frac{2b^2}{a^3}\right)kT + \left(\frac{3c}{a^2}\right)kT\right] \qquad (17)$$

and

$$\frac{1}{(M_L)_0}\left(\frac{\partial \bar{M}_L}{\partial T}\right) \approx -\left[\left(\frac{2b^2}{a^3}\right)k + \left(\frac{3c}{a^2}\right)k\right] \qquad (18)$$

On the right-hand side the first term might be described as the thermal expansion term, whilst the second one is the mode softening term. Although a, the "first-order stretching force constant", is often well known from independent sources, b and c are generally not. It would be worthwhile to rewrite Equation 18 in terms of directly measurable quantities, if possible, and in fact this can be done using the expansion coefficient. At the same time the preceding model can be improved by writing

$$\bar{X} = \alpha r_0 T \qquad (19)$$

instead of Equation 15 and allowing for the effect of transverse vibrations on the expansion $\bar{X}$ as follows. From classical Boltzmann statistics the expansion coefficient caused by longitudinal vibrations is [17]

$$\alpha_L = bk/a^2 r_0 \qquad (20)$$

Assuming that during a transverse vibration of an atom in a chain there is a tendency for the equilibrium atomic separation r_0 to be maintained, a vibration of mean displacement $\overline{Y^2}$ produces a longitudinal contraction of

$$\Delta X_T = (r_0^2 - \overline{Y^2})^{1/2} - r_0$$

and since from Boltzmann statistics

$$\overline{Y^2} \approx kT/a' \tag{21}$$

where a' is the first-order bending force constant, the expansion coefficient due to transverse vibrations is

$$\alpha_T = \frac{\Delta\bar{X}_T}{r_0}\left(\frac{1}{T}\right) \approx \frac{-k}{2a^1 r_0^2} \tag{22}$$

Assuming that the experimental expansion coefficient is

$$\alpha = \alpha_L + \alpha_T \tag{23}$$

Equations 19, 22, 23 and 18 can be combined to eliminate b, yielding

$$\frac{1}{(c_L)_0}\left(\frac{\partial c_L}{\partial T}\right) = \frac{1}{2(M_L)_0}\left(\frac{\partial M_L}{\partial T}\right)$$
$$= -\frac{1}{2}\left(\frac{2r_0^2 a(\alpha + k/2a'r_0^2)\alpha}{k} + \frac{3ck}{a^2}\right) \tag{24}$$

where c_L is the speed of longitudinal wave propagation along the chain. Further one can write, identifying the speed at liquid helium temperature $(c_L)_{he}$ with $(c_L)_0$,

$$\frac{(c_L)_T - (c_L)_{he}}{(c_L)_{he}}$$
$$\approx -\frac{1}{2}\left[\frac{2r_0^2 a(\alpha + k/2a'r_0^2)\alpha}{k} + \frac{3ck}{a^2}\right](T - T_{he}) \tag{25}$$

In the above two equations all quantities in the first term on the right-hand side are either known (independently of the left-hand side) or reasonable guesses can be made (ordinarily a' is one order of magnitude less than a), and the second term will be relatively small. One can use Equations 24 or 25 to check if sensible orders of magnitude for temperature gradients of modulus or velocity are given by our model. We shall try this for the MoO_3–P_2O_5 glass series. For pure P_2O_5 we have $\bar{r}_0 = 1.56 \times 10^{-10}$ m, $a = 450\,\mathrm{N\,m^{-1}}$, $a' \approx 45\,\mathrm{N\,m^{-1}}$ and $\alpha \approx 15 \times 10^{-6}$ (extrapolated from the glass of lowest MoO_3 content). For $T = 293$ K, substitution in Equation 25 yields

$$\frac{(c_L)_{293} - (c_L)_{he}}{(c_L)_{he}} \approx -73 \times 10^{-3}$$

For a glass of the highest MoO_3 content, $\alpha \approx 9.5 \times 10^{-6}$, $\bar{r}_0 \approx 1.9 \times 10^{-10}$ m, and from Table 2 of Bridge and Patel [4] (assuming that $a' \approx a/10$), $\bar{a} \approx 260\,\mathrm{N\,m^{-2}}$ and $a' \approx 26\,\mathrm{N\,m^{-2}}$, implying that

$$\frac{(c_L)_{293} - (c_L)_{he}}{(c_L)_{he}} \approx -31 \times 10^{-3}$$

These values compare rather favourably with the range of experimental extremal values of $\approx -40 \times 10^{-3}$. However, as stated earlier, if we accept the correctness of the relaxation contribution to negative temperature gradients of velocity, we are looking for an alternative mechanism which produces positive gradients.

More rigorously, for the vibrations of an atom in a chain, we ought to be considering a symmetric potential in which each atom moves between two others, rather than the asymmetrical potential of Equation 10. Superficially, the symmetric potential appears to give zero expansion coefficient. To resolve this anomaly one needs to remember that the symmetric potential is obtained by overlapping two asymmetrical potentials like Equation 10, and the mean overall width of the symmetrical resultant (i.e. the separation of the two outside atoms) is increased, by thermal vibrations, i.e. by the asymmetrical component of Equation 10. To see this we need only write Equation 10 in the form (neglecting the small fourth-order term) $U(\bar{X}) = A\overline{X^2} - B\overline{X^3} \approx (A - B\alpha T)\overline{X^2}$, i.e. formally equivalent to a symmetrical potential with a temperature-dependent Hooke's law force constant.

The only important factor missed by considering a two-atom rather than a three-atom potential is the existence of a central barrier caused by gross elongations of the outside atoms from equilibrium positions (longitudinal two-well potentials). Classically, for a given particle energy E relative to the well bottoms ($E >$ barrier height V) the velocity v of the particle in the vicinity of the barrier is $[2(E - U)/m]^{1/2}$, where m is the particle mass, so that the vibrations soften, i.e. M_L decreases, with increasing V. As thermal expansion can only increase V (albeit a tiny effect), the effect of the barrier is simply to contribute further to a negative $\mathrm{d}M_L/\mathrm{d}T$ (this conclusion is confirmed by a detailed calculation in the later section on transverse vibrations). Finally, a more exact, fuller calculation of $\Delta M_L/(M_L)_0$ (for comparison with Equation 17, i.e. neglecting the effect of transverse vibrations on α) is given by

$$\bar{M}_L = \frac{\left\{nr_0 \int_{-\infty}^{+\infty}\left[\left(\frac{\partial F}{\partial X}\right)\exp\left(\frac{-U}{kT}\right)\right]\mathrm{d}X\right\}}{\left[\int_{-\infty}^{+\infty}\exp\left(\frac{-U}{kT}\right)\mathrm{d}X\right]}$$

and writing

$$\exp\left(\frac{-U}{kT}\right) = \exp\left(\frac{-aX^2}{2kT}\right)$$
$$\times\left[1 + \left(\frac{b}{3}\right)X^3 + \left(\frac{c}{4}\right)X^4\right]$$

yields an almost identical result in the same order of approximation (dropping terms of higher than fourth power):

$$\frac{\Delta M_L}{(M_L)_0} = \left|\left(\frac{2b}{a^3}\right)k + \left(\frac{3c}{a^2}\right)k - \frac{3}{16}\left(\frac{c}{a^2}\right)k\right|$$

As r_0, a, a' and c are positive, for α positive Equation 24 suggests that $\partial M/\partial T$ (and correspondingly $\partial c/\partial T$) is always negative, which is indeed the case for all crystalline solids and for many glasses (including ours) over most of their temperature range. However, the anomalous positive $\partial c/\partial T$ gradients which exist for tetrahedrally coordinated glasses like silica [9, 10, 18, 19] and BeF_2 over large temperature ranges (at high temperatures) cannot be explained by our simple model, nor can the residual positive $\partial c/\partial T$ gradients occurring after subtracting the contribution due to two-well relaxation in our own glass series and probably in many others. Actually if we considered just the case of vitreous silica, taking account of its anomolously low expansion coefficient, Equation 17 remains fairly credible; for it predicts $\partial M/\partial T \to 0$ for $\alpha \to 0$, i.e. the equation predicts a swing from large negative gradients for large α and rather small negative gradients for $\alpha \to 0$, and we could argue that the reason why the gradient does not actually become positive in the latter case is because of the crudity of the model. However, this whole argument fails when one considers that the other tetrahedrally coordinated glasses all have α values as high as those in normal glasses, i.e. those with negative $\partial c/\partial T$. The above facts suggest that the behaviour of transverse vibrational modes must be examined to explain the positive gradients. However, it is worth noting that longitudinal vibrations alone (Equation 24) do give a positive $\partial c/\partial T$ when α is negative – an extremely rare but not unknown occurrence.

5.2. Transverse vibrations

For an atom vibrating transversely between two others in a chain, the force potential is symmetric with respect to a displacement Y from and normal to the chain axis. Moreover, if the atomic spacings in the chain are contracted by a fraction e relative to the equilibrium value (e = actual spacing/the equilibrium spacing, so that e decreases with increasing contraction) a deformation from harmonic form occurs in the potential even for $Y \to 0$. We shall represent the deformed potential in the form

$$U(Y) \;=\; A'Y^2 - B'Y^4 + v\exp(-\mathrm{d}Y^2) \qquad (26)$$

where A', B', v and d are always positive, the Y^4 term represents the usual mode softening at high vibrational amplitudes, whilst the Gaussian term represents the distortion specifically caused by the contraction e. For the simple case of central forces the theoretical (quantitative) form of $U(Y)$ as a function of e has been calculated by Bridge and Patel (Fig. 5b and Equation 19 of [4]). The behaviour can be reproduced by Equation 26 by assuming that both v and vd increase with decreasing e. The result is that for a sufficiently large e such that $a/2vd < 1$ (where $a' = 2A'$) a double well appears in $U(Y)$ with central barrier height

$$V \;\approx\; v - \left(\frac{a'}{2d}\right)\left[1 - \ln\left(\frac{a'}{2vd}\right)\right] \qquad (27)$$

and half-width (half the separation of the two-well minimum)

$$W \;\approx\; \left[-\left(\frac{1}{d}\right)\ln\left(\frac{a'}{2vd}\right)\right]^{1/2} \qquad (28)$$

where the small fourth-power term has been neglected in making these calculations.

The force on the vibrating atom subject to the above potential is

$$F \;=\; -\partial U/\partial Y \;=\; -[a'Y^2 - b'Y^3 + 2vdY\exp(-dY^2)]$$

Let there be n bonds per unit cross-section, $n - n'$ of them associated with normal potential wells and n' of them associated with wells containing a deformation of the form of the Gaussian term in Equation 26. The shear modulus associated with a small change $\mathrm{d}Y$ in Y is

$$M_T \;=\; r_0\,|(n - n')(\partial F/\partial Y_1) + n'(\partial F/\partial Y_2)| \qquad (29)$$

where $(\partial F/\partial Y_1)$ is the derivative of the first two terms only on the right-hand side of Equation 28, $(\partial F/\partial Y_2)$ is the derivative of all three terms, and Y_1 and Y_2 denote the particle Y coordinates in the two kinds of well, which are not necessarily equal for averaging purposes. The result of this differentiation is

$$M_\mathrm{T} \;=\; nr_0\left\{a' - \left(1 - \frac{n'}{n}\right)3b'Y_1^2 - \left(\frac{n'}{n}\right)[3b'Y_2^2 + (2vd - 4vd^2Y_2^2)\exp(-Y_2^2)]\right\} \qquad (30)$$

Now a temperature increase will reduce the frozen-in contractions which occur in glasses, i.e. e increases with T. Correspondingly both v and vd will decrease with increasing temperature. Since the two terms containing these variables are of opposite signs the important point is that both positive and negative temperature gradients of M_T (the value of M_T averaged over all possible Y_1 and Y_2 values) are possible. Whilst $\overline{Y_1^2}$ can simply be taken as equal to kT/a', the ordinary "classical value" in the same degree of approximation as used for our analysis of longitudinal vibrations, the difficult step in justifying our proposition quantitatively is to calculate $\overline{Y_2^2}$. For arbitrary v and vd values, classical Boltzmann statistics yield products of exponentials which are not readily integrable, and in any case such a non-quantum treatment is probably not very realistic. For the present we shall consider only two extreme simplifying cases.

5.2.1. *High potential barriers* ($V \gg kT$)

For barrier heights $V \gg kT$ the atom vibrates in either of the two wells (with a mean energy that classically would be $\sim kT$) with occasional thermal excitation over or tunnelling through the barrier. Subsequent calculations will show that the barrier width W will be much greater than the classical vibrational amplitude (i.e. $\sim(kTd/a')^{1/2}$) in either well. In this case the square root of $\overline{Y_2^2}$ can be taken (Fig. 6) as approximately equal to half the barrier width, i.e.

$$\overline{Y_2^2} \;\approx\; -(1/d)\ln(a'/2vd) \;=\; W^2 \qquad (31)$$

Substituting this value and $Y_1^2 \approx kT/a'$ in Equation 30

$$\bar{M}_\mathrm{T} \;=\; nr_0\left[a' - \left(1 - \frac{n'}{n}\right)\left(\frac{3b'}{a'}\right)kT - \left(\frac{n'}{n}\right)\left\{3b'W^2 + \left[1 + 2\ln\left(\frac{a'}{2vd}\right)\right]a'\right\}\right] \qquad (32)$$

Now as T increases, thermal expansion causes e to increase and vd decreases. Since $a'/2vd < 1$, $\ln(a'/2vd) < 0$ and it becomes less negative with increasing T, leading to a negative contribution to $\mathrm{d}\bar{M}_\mathrm{T}/\mathrm{d}T$. However, as shown by subsequent calculations, W

simultaneously decreases with increasing e so that the positive expression $b'W$ decreases with increasing temperature, implying a positive contribution to $\mathrm{d}\bar{M}_T/\mathrm{d}T$. The latter result is most intriguing. In physical terms the presence of double wells forces the particles to vibrate at ordinary temperatures in a region where the fourth-power mode softening term is significant, whereas ordinarily in single wells this term would only become significant at very high temperatures (high vibrational amplitudes). The reduction of barrier widths with increasing temperature then removes the particles to regions of less mode softening, thus to increase $\bar{M}_T$ and give positive $\mathrm{d}\bar{M}_T/\mathrm{d}T$. Thus the mode-softening term gives exactly the opposite effect in a potential having a central barrier than it would in an ordinary single-well potential!

5.2.2. Low potential barriers ($V \ll kT$, $W^2d \ll 1$)

For low barrier heights $\ll kT$ (or single flat-bottomed wells occurring when $a'/2vd > 1$, i.e. $\ln(a'/2vd)$ positive, the particle vibrates in a single well. To a first approximation the vibrational amplitude is clearly $\sim 2W$, and $\overline{Y_2^2} \sim W^2$. The calculation in the next section shows that even for very low barrier heights $W^2 \gg kTd/a'$. So $\overline{Y_2^2}$ cannot even approximately be represented by the classical expression kTd/a' applicable to a harmonic well, and we use W^2 instead (Fig. 6) as a first approximation. The subsequent calculation also shows that $W^2d \ll 1$ for small V, the inequality increasing as V decreases. Under these conditions $\exp(-d\overline{Y_2^2}) \rightarrow 1$, $4vd^2\overline{Y_2^2} \ll 2vd$, and Equation 30 approximates (writing $\overline{Y_1^2} = kT/a'$ as before) to

$$\bar{M}_T = nr_0\left[a' - \left(1 - \frac{n'}{n}\right)\left(\frac{3b'}{a'}\right)kT - \left(\frac{n'}{n}\right)(3b'W^2 + 2vd)\right] \tag{33}$$

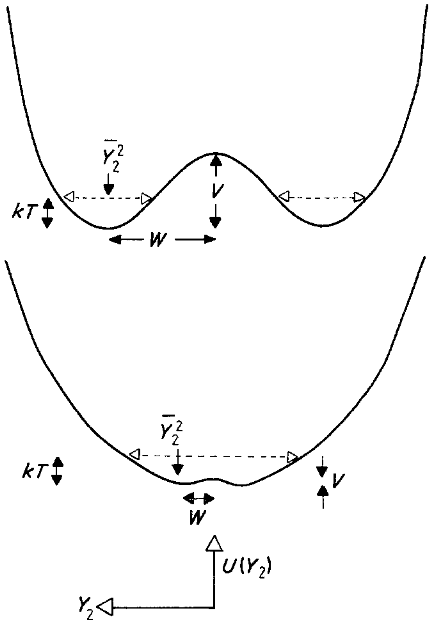

Figure 6 The mean square vibrational amplitude $\overline{Y_2^2}$ in a transverse two-well system is $\approx W^2$ both for $V \gg kT$ and $V \ll kT$.

Since both W and vd decrease with increasing e it is at once clear that W and vd will decrease as the temperature increases to reduce the frozen-in contractions in the glass. Thus the third (negative) term on the right-hand side decreases with increasing temperature. Thus M_T increases with temperature (i.e. $\partial M_T/\partial T$ is positive).

Noting that v, d and W are not independent variables with respect to temperature changes, we have

$$\begin{aligned}\frac{1}{(c_T)_0}\left(\frac{\partial c_T}{\partial T}\right) &= \frac{1}{2(M_T)_0}\left(\frac{\partial \bar{M}_T}{\partial T}\right)\\ &= -\left(\frac{n'}{a'n}\right)\left(\frac{3b'}{2}\frac{\delta(W^2)}{\delta T} + \frac{\delta(vd)}{\delta T}\right)\\ &\quad - \frac{1}{n}\left(1 - \frac{n'}{n}\right)\frac{3b'}{2(a')^2}\end{aligned} \tag{34}$$

where

$$\left(\frac{\delta(W^2)}{\delta T}\right) = \left(\frac{\delta(W^2)}{\delta e}\right)\alpha \tag{35}$$

$$\left(\frac{\delta(vd)}{\delta T}\right) = \left(\frac{\delta(vd)}{\delta e}\right)\alpha \tag{36}$$

and since the gradients in brackets on the right-hand side are negative, positive contributions to $\partial c_T/\partial T$ and $\partial M_T/\partial T$ arise from the first term on the right-hand side of Equation 3.4.

To summarize the cases of Sections 5.2.1 and 5.2.2, small thermal expansions will remove small barriers or well-flattening deformations to give a positive contribution to $\partial c_T/\partial T$. Further expansion to make $e > 1$ will increase the flattening of longitudinal wells and increase the negative contributions to $\partial c_T/\partial T$. The latter effect is probably negligible, however, because a much greater value of $|e - 1|$ is required to produce longitudinal two-well systems than transverse ones. The reduction of large tranverse barriers by thermal expansion can again produce both positive and negative contributions through the b' and vd terms in the force potential, respectively. A large number of low-lying transverse wells (i.e. wells of low e value), which are to be expected from the usual spread of the pair distribution functions obtaining in oxide glasses, will clearly favour positive gradients. Without many further assumptions it is possible to calculate how $\partial c_T/\partial T$ varies on balance in a particular glass — with the present state of the microscopic theory of two-well systems. However, as an example to check whether the above theory gives sensible orders of magnitude we shall try a calculation for the small barrier case (Equation 34), as the fewest assumptions on data to be used are involved here.

According to the central force model of Bridge and Patel [4] the potential of an oxygen atom moving transversely between two identical cations in an oxide glass (Fig. 7) is given by

$$U = \frac{-2\alpha}{r} + \frac{2\beta}{r^m}$$

where $\alpha = U_0r_0/(1 - 1/m)$, $\beta = U_0r_0^m/(m - 1)$ and $r^2 = e^2r_0^2\sin^2\theta_0 + r_0^2\cos^2\theta_0 + Y^2$. U_0 is the bond binding energy, m is a large positive integer, θ_0 is half

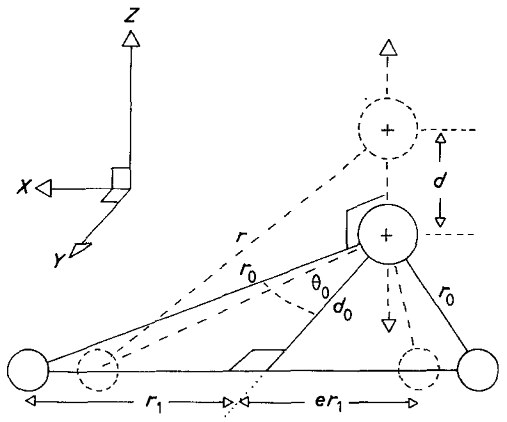

Figure 7 Coordinate system used to define a transverse two-well potential for an anion when the cation-anion-cation angle is less than 180°.

the cation–anion–cation angle, r_0 is the equilibrium atomic separation (bond length) and e (the elongation or contraction) is the ratio of the cation–cation separation to the equilibrium separation $r_0 \sin \theta_0$. The model is not a purely central force one. Since it assumes that transverse vibrations take place along the straight line d rather than in an orbit to circumvent the central barrier, a degree of bond directionality is implicit in the model. The above relationships yield

$$W = r_0(1 - e^2 \sin^2\theta_0 - \cos^2\theta_0)^{1/2} \qquad (37)$$

$$Y = \frac{2\alpha}{r_0}\left(1 - \frac{1}{(e^2 \sin^2\theta_0 + \cos^2\theta_0)^{1/2}}\right) + \frac{2b}{r_0^m}\left(\frac{1}{r_0^2 \sin^2\theta_0 + \cos^2\theta_0)^{m/2}} - 1\right) \qquad (38)$$

Taking $r_0 = 0.256\,\text{nm}$, $U_0 = 6.18\,\text{eV}$ and $\theta_0 = 70°$ (values appropriate for the P–O–P bond) and $m = 9$, $\alpha = 1.085\,\text{eV nm}$ and $\beta = 4.229 \times 10^{-8}\,\text{eV(nm)}^9$.

The above explicit form of potential is quite unsuitable for performing the exercise of the preceding section. We used the empirical form of Equation 27 because it was simpler to manipulate and demonstrate the physical principles behind the effect of two-well systems on $\partial c_T/\partial T$. It now remains, however, to compute values of v and d which specify Equation 26 in a manner consistent with Equations 37 and 38. For a selected value of e, values of W and V computed from these equations can be substituted into Equations 27 and 28 and the latter solved to yield v and d. As e decreases from one it turns out that V and W both increase, v increases and d decreases but at a slower rate so that vd increases. In MoO_3–P_2O_5 glasses a temperature change from 4 to 293 K causes an expansion of $\approx 0.5\%$ so it is reasonable to consider e values varying between 0.995 and 0.99. V changes from 0.014 to 0.005 eV during this change, corresponding closely to the case of Section 5.2.2 ($V \ll kT$) for variations up to room temperature, implying the validity of Equation 33. Corresponding values of other quantities are $W = 0.146 \times 10^{-10}\,\text{m}$, $v = 5.858 \times 10^{-20}\,\text{J}$, $d = 4.2 \times 10^{20}\,\text{m}^{-2}$ and $vd = 24.6$ for $e = 0.995$; whilst $W = 0.207 \times 10^{-10}\,\text{m}$, $v = 7.125 \times 10^{-20}$, $d = 3.7 \times 10^{20}$ and $vd = 26.3$ for $e = 0.99$. In computing these values we have assumed that $a \approx 450\,\text{N m}^{-1}$ (Table 1 of [4]) so that $a' \approx 45\,\text{N m}^{-1}$ in Equations 28 and 29, taking $a' \sim a/10$ as previously assumed in this paper. Thus we can define the following mean gradients for the range $e = 0.995$ to 0.99,

$$\frac{\delta(vd)}{\delta e} \approx -340\,\text{J m}^{-2} \qquad (39)$$

and

$$\frac{\delta(W^2)}{\delta e} \approx -4.3 \times 10^{-20}\,\text{m}^{-2} \qquad (40)$$

We shall assume that these figures will be approximately applicable to the MoO_3–P_2O_5 glass of the highest content that we have been able to obtain low temperature data on, i.e. the 29% mol MoO_3, 61 mol % P_2O_5 glass, the Mo–O and P–O bond strengths being almost the same [7]. For this glass $\alpha = 12 \times 10^{-6}$ so that

$$\frac{\delta(vd)}{\delta T} \approx -4.08 \times 10^{-3} \quad \text{J m}^{-2}\,\text{K}^{-1} \qquad (41)$$

$$\frac{\delta(W^2)}{\delta T} \approx -5.16 \times 10^{-13} \quad \text{m}^{-2}\,\text{K}^{-1} \qquad (42)$$

Since we have no independent means of estimating b' it will be useful to evaluate the contribution to $\partial c_T/\partial T$ arising simply from the $\delta(vd)/\delta T$ term in Equation 34 (i.e. $b' = 0$, implying no anharmonicity at large Y, in which case for a temperature change 4 to 293 K we can write

$$\frac{(c_T)_{293} - (c_T)_{\text{he}}}{(c_T)_{\text{he}}} = -293\left(\frac{n'}{a'n}\right)\left(\frac{\delta(vd)}{\delta e}\right)\alpha \qquad (43)$$

We now compare this result for shear wave velocity down a chain with our observations on compressional wave velocity in bulk glass. The reason why we consider such a comparison to be valid will be apparent from Section 5.3 below. For 29% MoO_3, 61% P_2O_5 glass, $a \approx 380\,\text{N m}^{-1}$ (Table I of [4]) so $a' \approx 38\,\text{N m}^{-1}$. Suppose that this and the value of $\delta(vd)/\delta e$ from Equation 39 are substituted into Equation 43. Then in order to reproduce the experimental value of fractional velocity change between helium and room temperature, which is 8×10^{-3} after subtracting the relaxation contribution, our model requires that $n'/n \approx 0.25$. So we require that 25% of P–O–P, Mo–O–P or Mo–O–Mo bonds have to have transverse barrier heights in the range 0 to 0.005 eV, corresponding to cation–cation fractional contractions in the range 0 to 1% ($e = 1$ to 0.99).

If one inspects the pair distribution function for the Si–O spacing in fused silica [20], the half-width about the equilibrium spacing is such as to render it entirely plausible that such an appreciable fraction of low-lying deformations exist. Pair distribution functions for phosphate glasses are not yet known, but they are unlikely to be narrower than in the silica case. For the MoO_3–P_2O_5 glass series, the number of two-well systems as a fraction of the number of oxygen atoms was computed by Bridge and Patel [4] from low-temperature acoustic relaxation data. They found that n'/n varied from 2 to 3% across the glass range. There is no inconsistency whatever between this figure and the above calculation and it is important not to confuse the two. Only barrier heights $\geqslant kT$ produce an appreciable contribution to acoustic relaxation, and in the relaxation measurements Bridge and Patel found an average barrier height of ≈ 0.07 to 0.123 eV across the range (i.e. V/kT varied from 3 to 5 at room temperature). The more copious lower-lying two-well systems, which we claim to be responsible for positive $\partial c/\partial T$ via an elastic mechanism, do not contribute to the relaxation mechanism because $V \ll kT$.

5.3. Isotropic materials and crystals

For both bulk- and shear-wave propagation in glass (respective wave velocities denoted by c_L and c_T), in general the acoustic stress will not be orientated normal or parallel to any given chain, and will cause combined bond stretching and bending effects. Thus one can define functions g and u by

$$\frac{\partial c_L}{\mathrm{d}T} = g\left(\frac{\partial M_L}{\mathrm{d}T}, \frac{\partial M_T}{\mathrm{d}T}\right)$$

$$\frac{\partial c_T}{\mathrm{d}T} = u\left(\frac{\partial M_L}{\mathrm{d}T}, \frac{\partial M_T}{\mathrm{d}T}\right)$$

making clear the possibility of positive and negative gradients in both cases. The positive gradients arise from an elastic interaction with transverse two-well systems. In a crystal there are no contracted interatomic spacings and thus no two-well systems, so that $v = 0$, $d = 0$ and only negative gradients exist.

6. Conclusions

Transverse double or flat-bottomed wells of low barrier height can account for positive temperature gradients of elastic moduli and acoustic wave velocities in glassy materials, by means of an elastic rather than relaxational interaction. In MoO_3–P_2O_5 glasses about 0.25 double wells or flat wells per oxygen atom of barrier heights $\leqslant 0.005$ eV (i.e. $\ll kT$ at 289 K) could explain the residual positive gradients after allowing for relaxational effects in the absence of the fourth-power "mode softening" term in the potential for transverse vibrations (Equation 27). On the other hand, a high mode softening term, i.e. a high value of b' in Equations 30, 32 and 33, could account for positive gradients even with smaller numbers of two-well systems. It is clear that a complete understanding of temperature gradients of elastic moduli in glasses generally requires the measurement of both acoustic wave velocities and wave absorption as a function of temperature, so that the relaxational contribution to the gradients can be computed and subtracted from the experimental gradients. When this procedure is carried out it is entirely plausible that all glasses will exhibit positive gradients in the "elastic" contribution to the observed gradients. In effect this feature will be a characteristic specific to vitreous structure because it arises from two-well systems.

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