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Computation of collective modes and acoustic investigations at different temperatures of vitrous silica

R V GOPALA RAO and R VENKATESH
Division of Physical Chemistry, Jadavpur University, Calcutta 700 032, India

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Abstract. This paper is mainly concerned with elastic and acoustic properties of vitrous silica besides the computation of phonon frequencies. Thus the phonon frequencies of vitrous silica have been calculated assuming the electronic bulk modulus, K_e, as equal to zero. New equations have been derived to relate the pressure derivatives of second order elastic constants to the acoustic Gruneisen's parameters using both Bhatia–Singh's parameters and Schofield's equations. The calculated longitudinal and transverse Gruneisen's parameters and the predicted absorption band spectra from Nagendranath's equation and Bhatia Singh's parameters are in good agreement with experiment. The calculated mean acoustic mode Gruneisen's parameter evaluated from the pressure derivative of Nagendranath's equation is also in good agreement with experiment.

Keywords. Phonon frequencies; pressure derivatives of elastic constants; longitudinal and transverse Gruneisen's constants; absorption band.

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1. Introduction

Recently, various aspects of vitrous silica have been investigated [1–5]. Some of the important properties that have been investigated are the acoustic properties [1], neutron diffraction studies [2–4], velocity measurements [5] of densified a-SiO_2 etc. Vitrous silica is of great technical importance. It is a pure, single-phase glass and its non-linear acoustic properties are singularly anomalous. The temperature dependence of elastic stiffness constants, as measured by Wang *et al* [6] are negative up to 70 K and then become positive. Recently the pressure dependence of longitudinal sound wave velocity in vitrous silica has been measured [7] through Brillouin spectroscopy between 50 K and room temperature. It is found that there is a reduction in velocity by the application of pressure. Negative pressure derivatives of second order elastic stiffness tensor components and positive third order elastic constants (TOEC) reveal anamolous effects in the vibrational anharmonicity while the mode Gruneisen's parameter's are negative [6]. Hence a knowledge of acoustic mode Gruneisen constant is important in understanding low temperature thermal expansion. Hence we felt a theoretical investigation of phonons, acoustic and elastic properties of vitrous silica is important. As pointed out earlier SiO_2 is remarkable in the sense that the pressure derivatives of second order elastic constants (SOEC) and also that of bulk modulus is negative unlike in normal substances like TeO_2 glass [8], amorphous As [9] and As_2S_3 [10]. Even though the SOEC pressure derivatives are negative it is remarkably isotropic over a wide temperature range. Vitrous silica has been shown to possess tetrahedral structure [11, 12] and the average number of nearest neighbours has been estimated [11] to be 4.3. Extensive elastic and acoustic work has been done on vitrous silica. We give only the reference to the recent studies of Wang *et al* [6] in which other references can be found. Wang *et al* made a detailed experimental study of the SOECs, their pressure derivatives as well as the acoustic Gruneisen's constants as a function of temperature. We also derive the phonon frequencies through Bhatia–Singh's (BS) method [13].

2. Theory

A. *Computation of phonon frequencies*

Bhatia and Singh [13] derived the following expressions for the longitudinal and transverse phonon frequencies

$$\rho\omega_{\mathrm{L}}^2(k) = \frac{2n_c}{a^2}(\beta I_0 + \delta I_2) + \frac{K_e K_{\mathrm{TF}}^2 k^2 [G(kr_s)]^2}{k^2 + K_{\mathrm{TF}}^2 \tilde{g}(k)}. \tag{1}$$

$$\rho\omega_{\mathrm{T}}^2(k) = \frac{2n_c}{a^2}\left[\beta I_0 + \frac{\delta}{2}(I_0 - I_2)\right]. \tag{2}$$

Here n_c stands for the number of nearest neighbours, a is the nearest neighbour distance, K_{TF} is the Thomas–Fermi inverse screening length, K_e is the electronic bulk modulus. r_s the Wigner–Seitz radius, $G(kr_s)$ is the shape factor and $\tilde{g}(k)$ is the Linhard–Langer–Vasko expression for the k dependent dielectric constant. Since these expressions have been discussed earlier [14, 15] we do not give any more details here. Since vitrous silica is not a semiconductor and is a dielectric we take K_e the electronic bulk modulus to be equal to zero and calculate $\omega_L(k)$ and $\omega_T(k)$ from (1) and (2). To evaluate β and δ we use the experimental values of C_{11} and C_{44} as given by Wang *et al* [6].

The equations are [13]

$$C_{11} = n_c\left[\frac{1}{3}\beta + \frac{1}{5}\delta\right], \tag{3}$$

$$C_{44} = n_c\left[\frac{1}{3}\beta + \frac{1}{15}\delta\right], \tag{4}$$

where

$$\beta = \frac{\rho a^2}{2M}\left[\frac{1}{r}\frac{\mathrm{d}\phi}{\mathrm{d}r}\right]_{r=a}, \tag{5}$$

$$\delta = \frac{\rho a^3}{2M}\left[\frac{\mathrm{d}}{\mathrm{d}r}\left\{\frac{1}{r}\frac{\mathrm{d}\phi}{\mathrm{d}r}\right\}\right]_{r=a}. \tag{6}$$

Here ϕ is the pair potential. We calculate the phonon frequencies at four different temperatures.

B. *Derivation of the pressure derivatives of elastic constants from Bhatia–Singh's β and δ parameters*

$$\frac{\mathrm{d}C_{11}}{\mathrm{d}P}=n_c\left[\frac{1}{3}\frac{\mathrm{d}\beta}{\mathrm{d}P}+\frac{1}{5}\frac{\mathrm{d}\delta}{\mathrm{d}P}\right]. \tag{7}$$

$$\frac{\mathrm{d}C_{44}}{\mathrm{d}P}=n_c\left[\frac{1}{3}\frac{\mathrm{d}\beta}{\mathrm{d}P}+\frac{1}{15}\frac{\mathrm{d}\delta}{\mathrm{d}P}\right]. \tag{8}$$

From (6) it can be shown that

$$\frac{\mathrm{d}\delta}{\mathrm{d}P}=-\frac{\mathrm{d}\beta}{\mathrm{d}P}+\frac{\rho a^2}{2M}\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=a}+\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=a}\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{\rho a^2}{2M}\right). \tag{9}$$

$$\frac{\mathrm{d}}{\mathrm{d}P}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=a}=\left[\frac{\mathrm{d}}{\mathrm{d}V}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)\frac{\mathrm{d}V}{\mathrm{d}P}\right]_{r=a} \tag{10}$$

$$=\left[-\chi_T r\frac{\mathrm{d}^3\phi}{3\mathrm{d}r^3}\right]_{r=a}. \tag{11}$$

Here χ_T is the isothermal compressibility. Remembering that the Gruneisen's constant γ_g is given by [16, 17]

$$\gamma_g=\frac{-\frac{1}{6}a\left(\frac{\mathrm{d}^3\phi}{\mathrm{d}r^3}\right)_{r=a}}{\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=a}}, \tag{12}$$

one can show that

$$\left(\frac{\mathrm{d}\delta}{\mathrm{d}P}\right)_T=-\frac{\mathrm{d}\beta}{\mathrm{d}P}+2\chi_T(\delta+\beta)\left(\gamma_g+\frac{1}{6}\right). \tag{13}$$

Similarly it can be shown that

$$\left(\frac{\mathrm{d}\beta}{\mathrm{d}P}\right)_T=-\frac{\rho a^2\chi_T}{6M}\left(\frac{\mathrm{d}^2\phi}{\mathrm{d}r^2}\right)_{r=a}+\frac{\rho a\chi_T}{3M}\left(\frac{\mathrm{d}\phi}{\mathrm{d}r}\right)_{r=a}. \tag{14}$$

Thus finally we obtain

$$\frac{\mathrm{d}\delta}{\mathrm{d}P}=2\chi_T\left[\frac{\delta}{3}+(\beta+\delta)\gamma_g\right], \tag{15}$$

and

$$\frac{\mathrm{d}\beta}{\mathrm{d}P}=-\frac{\chi_T(\beta-\delta)}{3}. \tag{16}$$

Hence from (8) we get

$$\frac{\mathrm{d}C_{11}}{\mathrm{d}P}=n_c\chi_T\left[\frac{\delta+5\beta}{45}+\frac{2\gamma_g^L(\beta+\delta)}{5}\right]. \tag{17}$$

In an exactly similar way we obtain

$$\frac{dC_{44}}{dP} = n_c \chi_T \left[\frac{1}{9}(\beta - 0{\cdot}6\delta) + \frac{2}{15}\gamma_g^T(\beta + \delta) \right]. \tag{18}$$

Equations (17) and (18) are important and offer a method in the evaluation of the pressure derivatives of the SOECs. Vitrous silica is a highly isotropic substance and we can obtain dC_{12}/dP from the following equation

$$2\frac{dC_{44}}{dP} = \frac{dC_{11}}{dP} - \frac{dC_{12}}{dP}. \tag{19}$$

In this connection it is important to note that liquids in the high frequency region show rigidity which is a characteristic of solids [18, 19]. Hence it will be interesting and tempting to try the equations of Schofield [20] (Sch) to derive the pressure derivatives of SOECs. From Schofield's equations [20] we derive the following expressions for the pressure derivatives of SOECs as [21]

$$\frac{dC_{11}}{dP} = C_{11}\chi_T + 1.8(C_1 - 1). \tag{20}$$

$$\frac{dC_{44}}{dP} = C_{44}\chi_T + 0{\cdot}6(C_1 - 1). \tag{21}$$

$$\frac{dC_{12}}{dP} = C_{12}\chi_T + 0{\cdot}6(C_1 - 1). \tag{22}$$

Here

$$C_1 \equiv (dB/dP) \tag{23}$$

and B is the bulk modulus.

It is important to remember that C_1 is related to third order elastic constants [22]. Thus (20)–(22), even though can strictly be used for fluids can help us to estimate the pressure derivatives of the SOECs. Calculations for computing the pressure derivatives of SOECs have been made for vitrous silica at different temperatures using (17)–(22).

C. *Prediction of band absorption spectra of vitrous silica*

It was shown that [23–25]

$$\frac{8A(A + 8C_{11} - 16C_{44})}{(3A - 8C_{11} + 16C_{12})^2} = 1, \tag{24}$$

where

$$A = \omega^2 M/2a. \tag{25}$$

From (24) and (25) it is possible to solve for the frequency and hence predict the position of the absorption band.

From (6) we get

$$\delta = -\beta + \frac{\rho a^2}{2M}\left(\frac{d^2\phi}{dr^2}\right)_{r=a} \tag{26}$$

and we can calculate $(\mathrm{d}^2\phi/\mathrm{d}r^2)_{r=a} \equiv K_1$. With a three-force constant model it is possible to show that for a diamond type of lattice [25]

$$\omega^2 = \frac{4K_1}{M}, \tag{27}$$

and we have $1/\lambda = \omega/2\pi C$ where C is the velocity of light. Hence we can predict the position of the absorption band and can make a comparison of these results with experiment. Such calculations have been made for vitrous silica in these investigations.

D. *Methods of evaluation of acoustic Gruneisen's parameters γ_g^T and γ_g^L*

From (17) we get C_1 associated with γ_g^L the Gruneisen's constant of longitudinal wave while from (18) we get γ_g^T that of the transverse wave. Similarly we use (20) and (21).

The mean acoustic mode Gruneisen's parameter γ_g^{el} can be obtained [6] from the following equation

$$\gamma_g^{el}\left(\frac{\gamma_L}{V_L^3} + \frac{2\gamma_g}{V_L^3}\right)\left(\frac{1}{V_L^3} + \frac{2}{V_T^3}\right)^{-1}. \tag{28}$$

We now give a method of evaluation of γ_g^{el} using (24) and (25). We differentiate (24) with respect to pressure and solve for $(\mathrm{d}A/\mathrm{d}P)_T$. Thus we obtain

$$\begin{aligned}\frac{\mathrm{d}A}{\mathrm{d}P} = \Bigg\{&\frac{\mathrm{d}C_{11}}{\mathrm{d}P}[56A + 128C_{12} - 64C_{11}] - 64A\left(\frac{\mathrm{d}C_{44}}{\mathrm{d}P}\right) + \\ &\frac{\mathrm{d}C_{12}}{\mathrm{d}P}[128C_{11} - 48A - 256C_{12}]\Bigg\}[A - 56C_{11} + 48C_{12} + 64C_{44}]^{-1}.\end{aligned} \tag{29}$$

Now we eliminate $\mathrm{d}C_{12}/\mathrm{d}P$ using the isotropy condition (vide (19)) and finally obtain

$$\begin{aligned}\frac{\mathrm{d}A}{\mathrm{d}P} = \Bigg\{&8\left(\frac{\mathrm{d}C_{11}}{\mathrm{d}P}\right)(3A - 8C_{11} + 16C_{12}) + 16\left(\frac{\mathrm{d}C_{12}}{\mathrm{d}P}\right) \\ &(8C_{11} - 16C_{12} - A)\Bigg\}(A - 24C_{11} + 16C_{12})^{-1}.\end{aligned} \tag{30}$$

Further we have

$$A = K_2\omega^2 \tag{31}$$

where

$$K_2 = M/2a \tag{32}$$

From (31) we get

$$\frac{\mathrm{d}A}{\mathrm{d}P} = \beta_T A\left[2\gamma_g^{el} + \frac{1}{3}\right], \tag{33}$$

where we assumed that $v = kr^3$. Here v is the volume and r is the radius. Hence from (30)–(33) we can solve the mean acoustic mode Gruneisen parameter γ_g^{el}.

3. Results and discussion

As pointed out already an application of the various equations derived above have been applied to vitrous silica. The experimental results used are those of Wang *et al* [6]. In figure 1 we give the phonon frequencies as obtained from (1) and (2) at two different temperatures namely 273 K and 77 K. As pointed out already vitrous silica is a dielectric and hence it is assumed that $K_e = 0$. The β and δ values calculated from (3) and (4) at the four temperatures are given in table 1. The position and maximum values of $\omega_L(k)$ and $\omega_T(k)$ are given in table 2. It may be noted from table 1 that

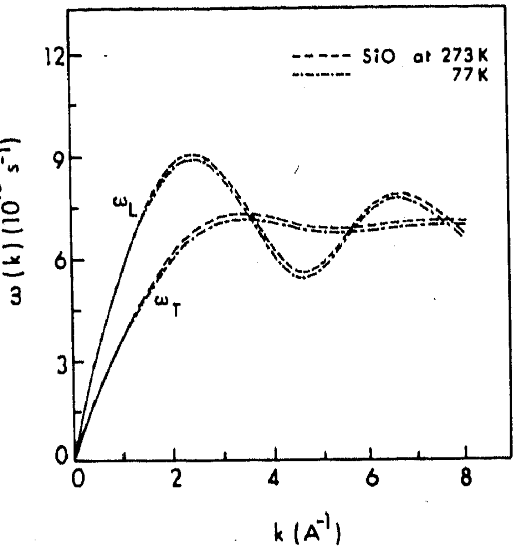

Figure 1. Phonon frequencies at 77 and 273 K.

Table 1. Parameters obtained for β and δ at different temperatures.

Temp. K	$\beta \times 10^{12}$dyn/cm^2	$\delta \times 10^{12}$dyn/cm^2
273	0·0469	0·835
233	0·0406	0·8383
123	0·0380	0·8311
77	0·0352	0·832

$K_e = 0$ and $\rho_w = 2{\cdot}202$ g/cm^3; n_c [11] = 4·3; a [11] = 1·61 Å

Table 2. Characteristics of phonon frequencies at different temperatures.

Temp. (K)	Position and maximum value k Å^{-1}	(ω_L) 10^{13}s^{-1}	Position and maximum values (k) Å^{-1}	ω_T 10^{13}s^{-1}
273	2·4	9·03	3·4	7·3
233	2·4	8·98	3·4	7·24
123	2·4	8·92	3·4	7·19
77	2·4	8·89	3·4	7·1

$\beta \neq 0$ and hence central forces are not alone operative. Evidently the tetrahedral angular forces are contributing and hence $(\mathrm{d}\phi/\mathrm{d}r)_{r=a} \neq 0$. The position of the maximum phonon frequency does not change with temperature both for $\omega_{\mathrm{L}}(k)$ and $\omega_{\mathrm{T}}(k)$. However with increase in temperature the frequency increases slightly. As expected $\omega_{\mathrm{L}}(k)$ attains a maximum at a small value of k and oscillates showing collective mode propagation for larger values of k while $\omega_T(k)$ attains almost a constant value beyond the maximum. From β and δ given in table 1 and at a temperature 273 K we get $\omega = 11{\cdot}1 \times 10^3\,\mathrm{s}^{-1}$ through the use of (27) and the position of the absorption band should appear at $583\,\mathrm{cm}^{-1}$. The value of A obtained from (24) is $31{\cdot}7 \times 10^{12}\,\mathrm{dyn/cm}^2$ and from (25) we get the absorption band of vitrous silica to appear at $536\,\mathrm{cm}^{-1}$. The observed bands for vitrous silica as reported by Lippincot *et al* and Hass [26, 27] appear between $500\,\mathrm{cm}^{-1}$ and $600\,\mathrm{cm}^{-1}$ which are reasonably close to the calculated values obtained from A and $(\mathrm{d}^2\phi/\mathrm{d}r^2)_{r=a}$. The average value being $560\,\mathrm{cm}^{-1}$. According to Bell and Dean [28] this vibrational mode arises from bond bending vibration in which the oxygen atoms move along the bisectors of Si–O–Si angles. In this connection the absorption band values of $536\,\mathrm{cm}^{-1}$ and $583\,\mathrm{cm}^{-1}$ correspond to a frequency $10 \times 10^{13}\,\mathrm{s}^{-1}$ and $11{\cdot}0 \times 10^{13}\,\mathrm{s}^{-1}$. These values can be considered to be close to each other. From the observed pressure derivatives we obtain (vide (20) and (21)) C_1^L corresponding to $\mathrm{d}C_{11}/\mathrm{d}P$ and C_1^T to $\mathrm{d}C_{44}/\mathrm{d}P$. We now use the well-known Slater's equation [29]

$$C_1^{\mathrm{L,T}} = 2\gamma_g^{\mathrm{L,T}} + \frac{1}{3}. \tag{34}$$

We evaluate γ_g^{L} and γ_g^{T} at 273 and 77 K using (17) and (18) and also from (20) and (21). The values calculated are given in table 3. It is important to stress that γ_g^{L} and γ_g^{T} are related to third order elastic constants [30].

It is known that Bhatia–Singh equation is meant for amorphous solids and gives very good results in agreement with experiment both at low and high temperatures for which results are available. The application of Schofield's equations gives satisfactory results as well. It should be borne in mind that Schofield's equations are meant for liquids and hence the present agreement can be considered as very good.

We can calculate from (30)–(33) the mean acoustic mode Grüneisen's parameter γ_g^{el} at 273 K. Using the experimental values of SOECs we obtain a value of $31{\cdot}7 \times 10^{12}\,\mathrm{dyn/cm}^2$ for A from (24) and finally we get a value for $\gamma_g^{\mathrm{el}} = -2{\cdot}2$ where we used (30)–(33). The experimental value is $-2{\cdot}0$. Thus the agreement is excellent.

Table 3. Gruneisen constants evaluated by different methods at different temperatures.

Temp. K	γ_g^L B.S eq. (17)	γ_g^L Sch eq. (20)	γ_g^L Expt[6]	γ_g^T B.S eq. (18)	γ_g^T Sch eq. (21)	γ_g^T Expt[6]
77	− 5·4	− 5·9	− 5·5	− 2·4	− 3·6	− 2·8
273	− 2·4	− 3·0	− 2·5	− 1·8	− 2·9	− 2·1

4. Conclusions

Using Bhatia–Singh's equation and assuming K_e, the electronic bulk modulus, equal to zero the phonon frequencies have been derived. A change of temperature over a wide range does not effect the position of the maximum while its magnitude decreases only slightly with decreasing temperature. Equations for the pressure derivatives of SOECs have been derived using both Bhatia–Singh's and Schofield's equations. Using the experimental values of the pressure derivatives of the SOECs the longitudinal and transverse Gruneisen's constants have been calculated at two extremely different temperatures for which accurate measurements are available. The results calculated from Bhatia–Singh's parameters give excellent results in agreement with experiment while those obtained from Schofield's equation are also in good agreement with experiment. Using (24) the absorption band spectrum of vitrous silica has been calculated and compared with that obtained from Bhatia–Singh's 'δ' parameter. Both the results are in fair agreement with experiment for SiO_2. Finally we calculate the mean acoustic mode γ_g^{el} from the pressure derivatives of (24). The value obtained is in excellent agreement with experiment.

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