

Frequency dependence of the density of vibrational states in glasses: Lognormal distribution

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It is shown (for the first time) that the low-energy part of the frequency dependence of the density of vibrational states of the simplest glassy systems satisfies a lognormal distribution. The standard deviation is $\sigma = 1/\sqrt{2}$, the same for all the glasses studied.

The frequency dependence of the density of vibrational states (DVS) in the range $15\text{--}300\text{ cm}^{-1}$, which determines the thermodynamic, spectral, and certain other characteristics of glasses, has lacked an accurate mathematical description. Several models have been offered to explain the DVS. In the elastic-continuum model¹ it is assumed that the DVS $g(\omega)$ has a Debye frequency dependence, $g(\omega) \propto \omega^2$, in glasses. Several experiments, e.g., those of Ref. 2, have revealed a deviation of $g(\omega)$ from a Debye behavior. The fractal model³ and the soft-potential model⁴ are not capable in their present state of predicting an explicit expression for $g(\omega)$ over the entire range of vibrational frequencies specified above. Direct information on the DVS of glasses can be found from experiments on low-frequency Raman scattering and neutron scattering. It follows from Ref. 5 that the intensity $I(\omega)$ of the Stokes part of the low-frequency Raman spectrum is given by

$$I(\omega) = C(\omega)g(\omega)(n(\omega) + 1)/\omega,$$

where $C(\omega)$ is the square of the matrix element of the interaction of the exciting photon with the vibrational states, and $n(\omega)$ is the Bose-Einstein distribution function. Various authors suggest $C(\omega) \propto \omega^p$, where $p = 1$ or 2 . In addition, a more complex expression for $C(\omega)$ has been derived in the model of an elastic continuum under the assumption $g(\omega) \propto \omega^2$.

Our study of glasses by means of low-frequency Raman scattering has revealed that the best approximation of the experimental results is achieved through the use of a lognormal distribution for $g(\omega)$ (Ref. 6). For the case of the DVS we write the lognormal distribution in the form

$$g(\omega) = (\sigma\omega_0\sqrt{2\pi})^{-1} \exp[-\{(\sigma\sqrt{2})^{-1} \ln(\omega/\omega_0)\}^2]. \quad (1)$$

If we assume $C(\omega) \propto \omega^p$, we then find

$$I(\omega) \propto (n(\omega) + 1) \exp[-\{(\sigma\sqrt{2})^{-1} \ln(\omega/\omega_m)\}^2], \quad (2)$$

where $\omega_m = \omega_0 \exp[p \cdot \sigma^2]$. Expression (2) shows that if the DVS is given by (1), then the quantity $I(\omega)/[n(\omega) + 1]$ will be a lognormal distribution, regardless of p . In approximating the experimental curves, we subsequently used $p = 2$.

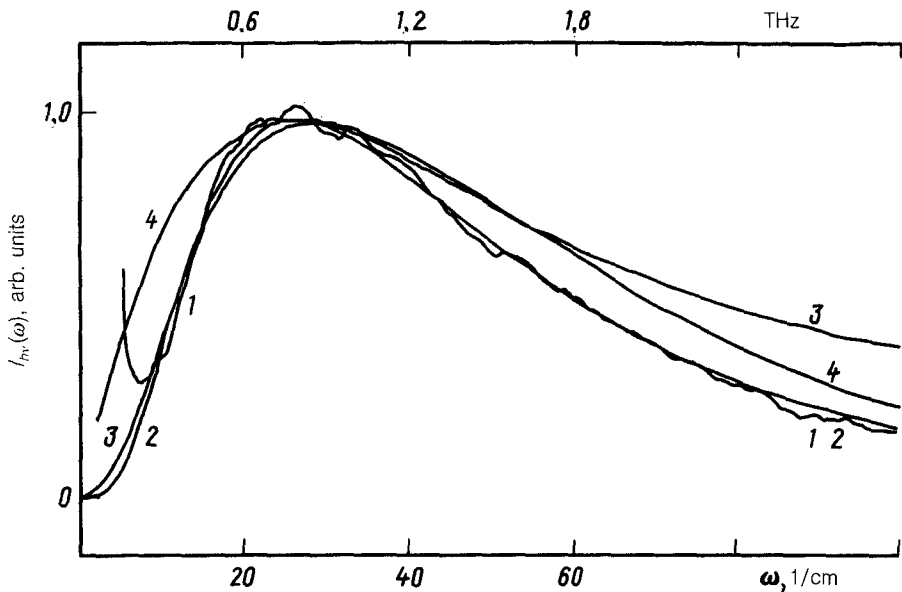


FIG. 1. 1—Low-frequency depolarized vibrational spectrum of glassy B_2O_3 ; 2–4—approximations of this spectrum; 2— $I(\omega) = (n(\omega) + 1)\omega \exp[-\{\ln(\omega/\omega_0)\}^2]$; 3— $I(\omega) = (n(\omega) + 1)\omega^3/(\omega^2 + \omega_1^2)^2$; 4— $I(\omega) = (n(\omega) + 1)\omega^2 \exp[-(\omega/\omega_2)]$.

Figure 1 shows the results of an approximation of the low-frequency Raman spectrum of glassy B_2O_3 with the help of a lognormal distribution. Also shown here are curves 3 and 4 constructed from the equations of Ref. 7 in the elastic-continuum model. A comparison of the curves in Fig. 1 shows that the low-frequency Raman spectrum can be approximated better with a lognormal distribution $g(\omega)$. The discrepancy between the experimental and theoretical curves at $\omega \leq 15 \text{ cm}^{-1}$ results from quasielastic scattering.

Figure 2 gives an idea of the applicability of the lognormal distribution for describing the DVS of various glassy systems. The DVS curves shown here were calculated from

$$g(\omega) = I_{hv}(\omega)/[\omega(n(\omega) + 1)],$$

where $I_{hv}(\omega)$ is the depolarized spectrum. The best agreement between the experimental and theoretical curves is reached at the value $\sigma = 1/\sqrt{2}$, the same for all the glasses which we studied. Noting the similarity (pointed out in Ref. 7) among the low-frequency Raman spectra for glassy SiO_2 , As_2S_3 , and $Mg_{70}Zn_{30}$, we can draw the conclusion that a lognormal distribution describes the frequency dependence of the DVS of the simplest glassy systems synthesized by a variety of methods. For the width of the function $g(\omega)$ at the 0.5 level we have the following expression (the same for all glasses):

$$\Delta\omega_{0.5}/\omega_m = 2 \sinh(\sqrt{\ln 2}).$$

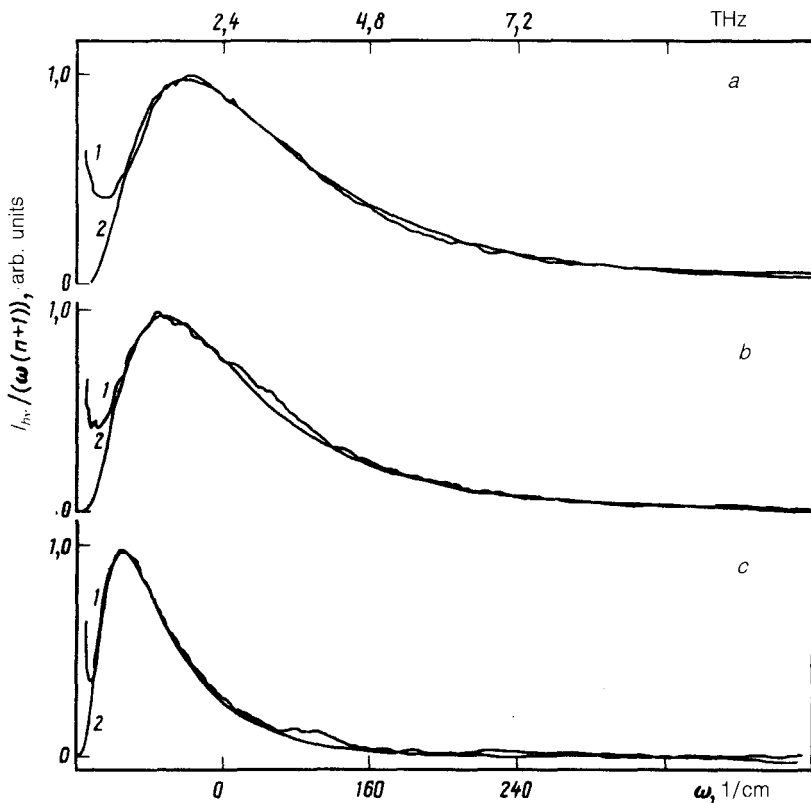


FIG. 2. 1: Experimental profile of the density of vibrational states. 2: Lognormal distribution. *a*— $(\text{Li}_2\text{O})_{0.3}:(\text{B}_2\text{O}_3)_{0.7}$; *b*— SiO_2 ; *c*— B_2O_3 . The lognormal distribution is $g(\omega) = \exp[-\{\ln(\omega/\omega_0)\}^2]$.

In multicomponent systems, $g(\omega)$ may have a more complex shape, which depends on the composition,⁸ and the $g(\omega)$ profile may be represented as a superposition of lognormal curves.

The interpretation of this result can be summarized as follows. In a glassy matrix one can single out groups of atoms for which the binding energy within a group is greater than the binding energy of the outer atoms with the surroundings. The existence of such structural groups has been mentioned in the literature.⁹ With each group we associate an oscillator with a mass equal to the sum of the masses of the atoms in the group and with a stiffness determined by the binding energy of the outer atoms of the group with the surroundings. If it is assumed that the binding energy of the group with its surroundings decreases with increasing scale size (R) of the oscillator as $f \propto 1/R^q$, then we can adopt $\omega \propto 1/R^s$ for the frequency of the oscillator in a first approximation, where s is a real number. When a glass is formed from a melt, for example, a set of groups of the type we have been discussing, with a statistical distribution in R , arises in the structural network. This set determines the statistical distribution of the DVS. It is not difficult to show that with a lognormal distribution $g(\omega)$ the

distribution of structural groups with respect to radius will also be a lognormal distribution, with a standard deviation $\sigma_R = \sigma/s$. If the lognormal distribution is written in the form

$$(\sigma x_0 \sqrt{2\pi})^{-1} \exp\left[-\left\{\left(1/(\sigma x_0 \sqrt{2})\right) \int_{x_0}^x \frac{dx}{x}\right\}^2\right],$$

where x is any random value, one can say that this distribution describes random processes with relative increments.

The results of this study show that the density of vibrational states of glasses of various compositions is described in the range 15–300 cm^{-1} by a lognormal distribution with a single parameter. During the formation of structures (which govern the DVS) during vitrification, a significant role is played by the statistics of the relative changes in the parameters of the structural network of the glass.

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