

Connection between tunneling and localized configurational relaxations in glasses

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It is postulated that tunneling centers responsible for the low-temperature thermodynamic behavior of a glass are linked with those local regions where thermally excited orientational and/or translational diffusion occurs at $T \leq T_g$ in an otherwise rigid glassy matrix. This postulate is tested by three sets of different experiments, namely, (i) physical aging, (ii) regions created in crystals by neutron irradiation, and (iii) regions created by addition of a second component to a glass, by using results from the literature. These results seem to confirm the postulate. The number of such local regions is $\sim 10^{16}$ per mole of a glass.

I. INTRODUCTION

Despite extensive studies since 1971, the atomic or molecular origin of phonon-assisted tunneling, or localized excitations, responsible for the low-temperature non-Debye behavior of amorphous solids remains unidentified. Hunklinger and Arnold¹ suggested that localized excitations may originate at the defect sites in the microscopically inhomogeneous structure of vitreous SiO₂ and Phillips² showed that rotation of an O-H group bonded to the SiO₂ structure provides an explicit model for the effect of O-H groups on the localized excitations in vitreous silica. The microscopic models of their origin, which apply to all glasses obtained by cooling a liquid, were given by Cohen and Grest³ and by Phillips.⁴ These models predicted that the magnitude of the anomalies in heat capacity, C_p , thermal conductivity, k , etc., of glasses would be greater the lower their glass transition temperature, T_g . As support for their respective views, the authors noted the observations by Raychaudhari and Pohl^{5,6} that when different glasses are studied, the linear term of the C_p - T relation is proportional to the inverse of both their T_g and their fictive temperature, T_f . Recently, McDonald *et al.*⁷ showed that Raychaudhari and Pohl's observations are less satisfactory on experimental grounds and concluded that models developed to explain the localized excitations have no explicit support.

Glasses also have a much higher C_p at $T \leq T_g$ than is expected from phonon contributions alone. This is partly due to the potential energy associated with the thermally excited localized motion, or relaxation, that occurs in them. We postulate that the tunneling centers and localized configurational states available to molecules within an amorphous structure, or that the quantum effects ($T < 1$ K) and the classical (orientational and/or translational) diffusion over short distances, are linked with the same microscopic origin. Thus the tunneling centers may be envisaged as those sites where thermally excited molecular motion occurs at $T \leq T_g$ —the motion being much faster than and different from that which spontaneously relaxes the structure of a glass and densifies it.

The possibility that the tunneling centers and localized

configurational states in vitreous SiO₂ have the same microscopic origin was considered by Hunklinger and Arnold.¹ They noted that the existence of localized structural defects that can occupy different configurations is common to the models given in the literature for the structure of vitreous SiO₂. The ultrasonic peak observed at $T \approx 50$ K in it was then explained in terms of the thermodynamic states associated with the transition between the two sites of a double-well potential that represent the different configurations of the localized structure defect *in vitreous* SiO₂. Phillips² took a similar view and showed that the rotation of O-H groups in impure vitreous SiO₂ provided a precise microscopic model for the extrinsic tunneling states in it. The recent extension of the free-volume theory³ seems to contain the same postulate but for the glassy state in general. However, it leads to a conclusion that, as McDonald *et al.*⁷ noted, has no experimental support. The theory also does not explain the occurrence of secondary relaxations, or the availability of localized configurational states, in the otherwise rigid matrix of a disordered solid, to which the origin of tunneling centers is linked in our postulate.

II. TUNNELING AND LOCALIZED CONFIGURATIONAL STATES

In the explanation for the low-temperature non-Debye behavior of heat capacity of glasses by phonon-assisted tunneling, a certain number, or group, of molecules are assumed to have accessible to them two nearly equivalent equilibrium configurations corresponding to the minima of asymmetric double-well potentials. Tunneling is treated by a model Hamiltonian equation for two-level systems representing the ground states in the two local energy wells^{8,9} and involves a small group of atoms undergoing a local rearrangement. The larger the number of atoms involved the easier it is to find two ground states of equal energy and therefore the number of atoms involved is presumed to be small so that the distance between the states in configurational space is minimized.

The occurrence of localized molecular motions is now considered intrinsic to the disordered structure of all types of glasses despite the varied nature in them of molecular

interactions, from strong electrostatic to the weak van der Waals type, and of the disorder, exclusively orientational or positional, or both.^{10,11} Dielectric and mechanical relaxations, NMR spectroscopy, light scattering, depolarization of fluorescence, and electronic mobilities all show these motions as secondary relaxations which cease to occur on the time scale of one's experiment at $T \ll T_g$. This means that the microscopic configurational state of a glass does not remain fixed on cooling from T_g to 0 K and that the various configurations explored by molecules in local regions in an internal thermodynamic equilibrium within the structure of a glass constitute a degree of freedom, in addition to vibrational, which determines the thermodynamics of a glass.

A substantial fraction of the expansivity,¹² heat capacity,¹³ and entropy¹³⁻¹⁵ of a glass at $0 < T < T_g$ is therefore associated with the thermally accessible configurational states of different potential energies available to a group of atoms or molecules, in thermodynamic equilibrium, within local regions, which in turn are distributed in a macroscopically metastable, thermodynamically nonequilibrium structure of a glass. The heat capacity of a glass at $T < T_g$ cannot, therefore, be described by the Debye theory in which the quantity is determined only by the vibrations of atoms or molecules confined to fixed sites in a rigid lattice of a solid treated as an elastic continuum. Such configurational states are accessible to certain groups of atoms or molecules within regions of low density and high entropy in the structure and are figuratively represented by the corrugated bottom of a deep potential well.¹⁰

We suggest that tunneling centers at $T < 1$ K may be related to those local regions where thermally activated molecular motions at $T \leq T_g$ occur and contribute to the C_p of a glass. This means that the low-temperature non-Debye behavior of C_p (or excess C_p) is concomitant with the high-temperature ($T \leq T_g$) non-Debye behavior of C_p (or excess C_p) with T of a glass.

III. CONSEQUENCES OF THE POSTULATE

If the molecules in local regions of loosely packed structure were to be connected with or identified as tunneling centers, one would expect three distinct regions of the variation of C_p with T in the range from 0 K to T_g , namely, (i) a linear increase of C_p with T , (ii) an approximate T^3 dependence according to the Debye equation, and (iii) a rapid increase with temperature beyond the T^3 variation as T_g is approached. This means a change first from the $C_p \propto T$ behavior to an approximate Debye behavior and then a progressive deviation of C_p towards values higher than expected from the Debye behavior, when the degrees of freedom giving rise to potential energy associated with the configurational states become kinetically unfrozen. The observations of the first behavior are well documented in the literature¹⁶ and the excess entropy of glasses and other disordered solids has shown the second and third regions.¹⁰⁻¹⁵

An important consequence of the postulated connection between the high-temperature and the low-temperature non-Debye behaviors is that any procedure that affects the

magnitude of a property in the high-temperature regime would affect qualitatively similarly the property in the tunneling regime. This means that an increase (decrease) in the number of molecules in local high-volume, high-entropy, regions, or in the strength of the secondary relaxation, would increase (decrease) the C_p of a glass both at $T \leq T_g$ and at $T < 1$ K. Therefore, a decrease in configurational C_p at $T \leq T_g$ would also cause a decrease in the linear term of C_p at $T < 1$ K. This consequence can be tested by three types of experiments as follows.

(i) It is known that spontaneous densification on physical aging of a glass lowers the strength of, or the number of molecules involved in, its secondary relaxation¹⁷⁻²² and the number of molecules contributing to its C_p and entropy at $T \leq T_g$.^{13,15} Similar effects appear when the fictive temperature T_f of a glass is decreased by slowly cooling the melt or when two glasses, one obtained by quenching and the other by slow cooling, are measured.²⁰ One would expect that densification of a glass would also reduce the number of tunneling centers, or the density of localized excitations, thereby decreasing its C_p and dielectric loss, increasing its thermal conductivity and affecting changes in the related properties at $T < 1$ K. This means that a glass would approach the Debye behavior or the magnitude of its C_p anomaly would decrease on densification during physical aging, or on lowering of its T_f .

The above given deduction neither agrees with nor opposes the conclusion of other tunneling models^{2,4} which suggest that a high T_g indicates a small concentration of two-site atoms, or tunneling centers, and therefore the amplitude of the C_p anomaly is less in glasses of high T_g . It seems, however, in contrast to the observed approximate inverse relationship between the coefficient of the linear term of C_p and the fictive temperature of vitreous silica,^{5,6} though these findings have been recently also questioned on grounds of experimental interpretation by McDonald *et al.*⁷

A search of the literature revealed that only selenium glass has been studied accurately enough over a wide temperature range to provide a test of this consequence. Figures 1, 2, and 3 show the changes in C_p at both $T \leq T_g$ and $T < 2$ K and in the thermal conductivity at $T < 2$ K, respectively, of selenium glass. The high-temperature data in Fig. 1 are taken from Chang and Bestul's work,²³ the low-temperature data in Fig. 2 for C_p from Lasjaunias and others.²⁴ The data in Fig. 3 for thermal conductivity, k , are taken from Calemezcuk.²⁵ These data show (Fig. 1) that aging for 15 months at 278 K decreased by 50% the C_p associated with the tunneling, i.e., after the acoustic T^3 contribution was deducted from C_p .²⁴ At T near T_g , glassy Se obtained by slow cooling the melt has 0.36% lower entropy and 1.5% lower C_p than that obtained by quenching the melt (Fig. 2). In addition, Etienne²⁶ has observed a decrease in the mechanical loss tangent at $T < T_g$ on annealing the selenium glass. Calemezcuk²⁵ has shown (Fig. 3) that thermal conductivity of Se glass at $T < 2$ K increased by $\sim 25\%$ when its fictive temperature was decreased by $\sim 10\%$, or ~ 30 K.

Several other glasses also show this effect. For example, Lasjaunias *et al.*^{27,28} found that densification of silica glass by $\sim 0.1\%$ on aging at 1573 K appreciably de-

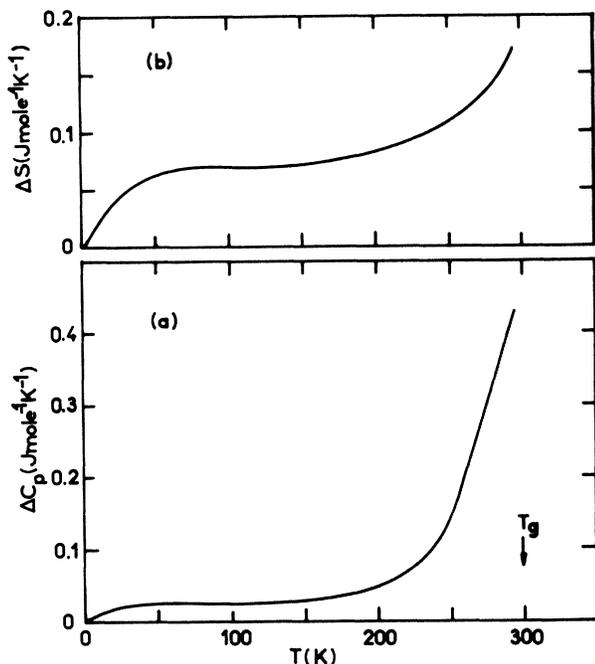


FIG. 1. (a) Excess heat capacity of a melt quenched over a slowly cooled selenium glass plotted against temperature showing the effect of slow cooling the melt on the C_p of its glass. Data are taken from Ref. 23. (b) Excess entropy of the melt quenched over the slow-cooled-melt Se glass.

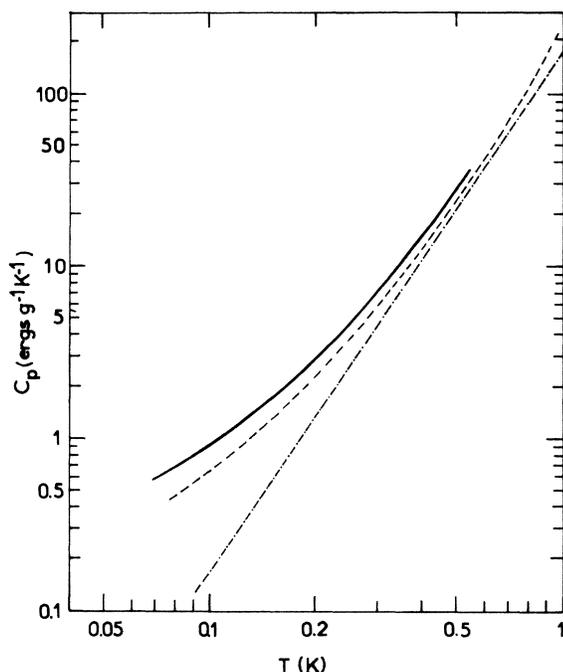


FIG. 2. Heat capacity of Se glass in the tunneling regime. The solid line represents a glass before ageing or annealing and the dashed line represents a glass physically aged for 15 months at 278 K (data from Ref. 24). The dashed-dotted line represents the acoustic contribution to C_p , equal to $T^3 \times 171$ ergs/g K^4 .

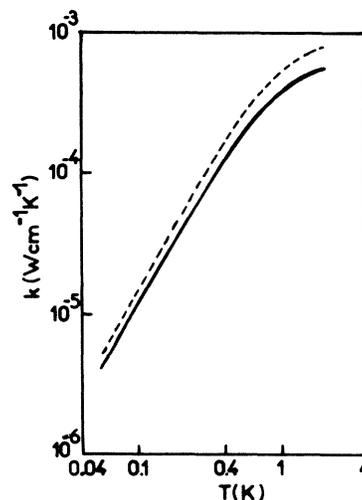


FIG. 3. Thermal conductivity of Se glass in the tunneling regime. The solid line represents melt-quenched glass and the dashed line represents an annealed glass (data from Ref. 25). The increase reported is $\sim 25\%$ for $\sim 10\%$, or ~ 30 K, decrease in the fictive temperature.

creased its C_p at $0.5 < T < 1$ K and by $\sim 10\%$ at $0.1 < T < 0.5$ K, the temperature range for the tunneling-center excitations. The same group²⁷ also showed that, conversely, expansion of B_2O_3 glass on thermal treatment above its fictive temperature increased its C_p by $\sim 10\%$ at $T < 1$ K. Aging or annealing of sputtered amorphous films of metallic alloys seems to cause the largest known decrease in their C_p and increase in their thermal conductivity.²⁹ Since the authors³⁰ have independently confirmed that aging densified the sputtered amorphous films, in particular of $Zr_{76}Cu_{24}$, we suggest that densification reduced the number of local regions identified here as tunneling centers.

(ii) Neutron and electron irradiation of certain crystals causes them to acquire an anomalous behavior of their C_p and k at $T < 2$ K. As a consequence of our view, such crystals should also acquire a secondary relaxation at $T \gg 0$ K. For example, neutron irradiation of synthetic quartz has been found to introduce local excitations in the crystal and the consequent anomalies in the temperature dependence of both its thermal conductivity^{31,32} and low-temperature heat capacity.³² Concomitant with the appearance of these anomalies, as Stevels³³ has found, is an increase in the number of atoms involved in localized motions in its crystal at $T \approx 50$ K, which appears as a pronounced increase in the height of its dielectric relaxation peak at 50 K measured at 32 kHz. Thus neutron-irradiated synthetic quartz behaves like an amorphous solid in both its low- and high-temperature regimes.

(iii) Addition of a second component to a glass occasionally increases the density of localized excitations or the magnitude of its C_p anomaly. As a consequence of our view it should also increase the strength of its secondary relaxation. In a careful study of the effect of the addition of K_2O to SiO_2 glass, McDonald *et al.*⁷ noted that

the addition of K_2O increased the low-temperature anomalous C_p or the density of the localized excitations of the SiO_2 glass. Stevels³³ has found that the height of the secondary relaxation peak at ~ 60 K measured at 1 MHz is increased by $\sim 50\%$ on addition of K_2O to SiO_2 glass and that further addition of K_2O increased the height of the peak further.

Phillips² has already shown that small addition of OH groups to vitreous SiO_2 , which chemically bonds to its network structure affected both its C_p and thermal conductivity. He used these observations to develop an explicit microscopic model in which the rotation of chemically bonded O-H groups in vitreous SiO_2 provided a quantitative account of the impurity-induced extrinsic tunneling states.

Thus the above-mentioned three experiments seem to confirm the postulated connection between the localized states involved in tunneling and those involved in configurational relaxations of a glass. We have observed^{11,15} that nearly 10–30% of the total polarization is associated with the secondary relaxations of a glass. Since only one in $\sim 10^6$ molecules is involved in dielectric relaxations at the low electric fields generally used, it means that the total number of molecules in localized regions is $\sim 10^{16}$ per mole and that the number of localized regions containing

this number of molecules is appreciably less than $\sim 10^{16}$ per mole.

IV. CONCLUSIONS

The tunneling centers at $T \approx 1$ K may be connected in origin with those local regions where thermally activated molecular motion at $T \leq T_g$ occur and contribute to the C_p of a glass. If so, the low-temperature C_p anomaly is concomitant with the high-temperature ($T \leq T_g$) non-Debye behavior. Aging of a glass decreases both these anomalies. The decrease has been observed in both the heat capacity and dielectric measurements. The thermal conductivity at $T < 2$ K is increased on lowering the fictive temperature of a glass.

Aging causes a glass to spontaneously approach a structure with the properties of an isotropic elastic continuum. Its C_p would tend towards the Debye behavior in the entire range of $0 < T \leq T_g$, when the contributions from the tunneling effects at low temperatures together with the thermally activated transitions at $T \leq T_g$ gradually cease to dominate. It follows that if Hunklinger and Arnold's¹ suggestion was analogous to our postulate, annealing of vitreous SiO_2 would also reduce the ultrasonic peak observed at $T \approx 50$ K. This can be experimentally tested.

¹S. Hunklinger and W. Arnold, in *Physical Acoustics*, edited by W. P. Mason and R. N. Thurston (Academic, New York, 1977), Vol. 12, p. 155.

²W. A. Phillips, *Philos. Mag. A* **43**, 747 (1981).

³M. H. Cohen and G. S. Grest, *Phys. Rev. Lett.* **45**, 1271 (1980).

⁴J. C. Phillips, *Phys. Rev. B* **24**, 1744 (1981).

⁵A. K. Raychaudhuri and R. O. Pohl, *Solid State Commun.* **37**, 105 (1980).

⁶A. K. Raychaudhuri and R. O. Pohl, *Phys. Rev. B* **25**, 1310 (1982).

⁷W. C. McDonald, A. C. Anderson, and J. Schroeder, *Phys. Rev. B* **31**, 1090 (1985).

⁸P. W. Anderson, B. I. Halperin, and C. M. Varma, *Philos. Mag.* **25**, 1 (1972).

⁹W. A. Phillips, *J. Low Temp. Phys.* **7**, 351 (1972).

¹⁰G. P. Johari, in *Plastic Deformation in Amorphous and Semicrystalline Materials (Les Houches Lectures 1982)* (Les Editions de Physique, Les Ulis, France, 1982), p. 109.

¹¹G. P. Johari, *J. Chim. Phys.* **82**, 283 (1985).

¹²R. Simha, J. M. Roe, and V. S. Nanda, *J. Appl. Phys.* **43**, 4312 (1972).

¹³M. Goldstein, *Ann. N.Y. Acad. Sci.* **279**, 68 (1976).

¹⁴M. Goldstein, *J. Chem. Phys.* **64**, 4767 (1976).

¹⁵G. P. Johari, *Ann. N.Y. Acad. Sci.* **279**, 102, 117 (1976); *Philos. Mag.* **41**, 41 (1980).

¹⁶R. O. Pohl, *Phase Transitions* **5**, 239 (1985).

¹⁷M. Frank and H. A. Stuart, *Kolloid Z.* **225**, 1 (1968).

¹⁸L. Guerdoux and E. Marchal, *Polymer* **22**, 1199 (1981).

¹⁹G. P. Johari and M. Goldstein, *J. Chem. Phys.* **53**, 2372 (1970).

²⁰G. P. Johari, *J. Chem. Phys.* **77**, 4619 (1982).

²¹S. Etienne, J. Y. Cavaille, J. Perez, and G. P. Johari, *Philos. Mag. A* **51**, L35 (1985).

²²S. E. B. Petrie, *J. Macromol. Sci. Phys.* **12**, 225 (1976).

²³S. S. Chang and A. B. Bestul, *J. Chem. Thermodyn.* **6**, 325 (1974).

²⁴J. C. Lasjaunias, B. Picot, A. Ravex, and M. Vandorpe, in *Extended Abstracts of the Second Conference of the Condensed Matter Division of the European Physical Society on Dielectrics and Phonons, Budapest, 1974* (European Physical Society, Budapest, 1974), p. 199.

²⁵R. Calemezcuk, Thésé, Docteur des Sciences, L'Université Scientifique et Médicale et L'Institut National Polytechnique de Grenoble, 1983, p. 133.

²⁶S. Etienne, Ph. D. thesis, Université de Lyon, France, 1985.

²⁷J. C. Lasjaunias, G. Penn, A. Ravex, and M. Vandorpe, *J. Phys. Lett.* **41**, L131 (1980); *J. Non-Cryst. Solids* **57**, 157 (1983).

²⁸J. C. Lasjaunias, G. Penn, and M. Vandorpe, in *Phonon Scattering in Condensed Matter*, edited by H. J. Maris (Plenum, New York, 1980), p. 25.

²⁹J. C. Lasjaunias, A. Ravex, D. Laborde, and O. Bethoux, *Physica* **126B**, 126 (1984).

³⁰A. Ravex, J. C. Lasjaunias, and O. Bethoux, *J. Phys. F* **14**, 329 (1984).

³¹R. Berman, *Proc. R. Soc. London, Ser. A* **208**, 90 (1951).

³²J. W. Gardner and A. C. Anderson, *Phys. Rev. B* **23**, 474 (1981).

³³J. M. Stevels, *J. Non-Cryst. Solids* **40**, 69 (1980).