Theory of the Axial Thermal Expansion of Fiber Glass

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Abstract

We study the axial thermal expansion of fiber glass, relate that to the two level tunneling systems inter–coupled via the short range elastic interaction in glass fibers, and compare the result with the experimental finding.

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While many materials have positive thermal expansion coefficients,[1] they can be negative without contradicting fundamental laws of physics. Some of the known negative thermal expansion solids include ZrW_2O_8 and HfW_2O_8, both have approximately cubic crystal structures and negative thermal expansion coefficients at temperatures from 0.5 K to 1,000 K. [2] Many glasses have negative thermal expansion coefficients at low temperatures.[3] The Grüneisen parameter,[4] parameterizing material's thermal expansion, is:

$$\gamma \equiv (\frac{\partial \ln V}{\partial \ln T}) = \frac{3\alpha Y}{c_v} = \frac{\chi Y}{c_v} \tag{1}$$

where α is material's axial thermal expansion coefficient, χ its volume thermal expansion coefficient, Y its Young's modulus, and c_v its volume specific heat. We find $\gamma = -7.5$ for PMMA,[5] $\gamma = -40$ (the part proportional to T) and $\gamma = -7$ (the part proportional to T^3) for vitreous silica,[6] $\gamma = -7.5$ for sodium silicate glass,[7, 8] and $\gamma = -8$ for SiO_2,[9] while most crystals have positive Grüneisen parameters γ between 1 and 2.[10] We have made a qualitative discussion based on the long range elastic dipolar interaction [11] among the two level tunneling systems (TLS) in bulk glass [12] to explain this sign difference in thermal expansions between crystals and glasses. Here we consider the axial thermal expansions of glass fibers.

An entirely harmonic system does not have nonzero thermal expansion. It is also easy to see that in a system where each atom's potential energy is left to right symmetric so that $U(x) = U(-x)$ there will be no thermal expansion. Consider such a system where two neighboring atoms are separated at a distance. When the temperature goes up, each atom's vibrational amplitude will go up. But if that potential is left to right symmetric, each atom's position, time–averaged, will remain at middle unchanged by symmetry so that two neighboring atoms's time–averaged in-between distance will also

remain unchanged; hence no thermal expansion. It is also easy to see that, for that reason, while many materials's thermal expansion coefficients are positive, they can be negative as well, as they are in many glasses. The magnitude of thermal expansion of glasses is also often found to be smaller than what crystals usually have.

Before proceeding to details of the estimate we will first provide a qualitative discussion within classical theory for the low temperature glass thermal expansion following our discussion above. The inter–atomic interaction is approximately harmonic at low temperatures and does not contribute significantly to the low temperature thermal expansion. It is known that the low temperature behaviors of glasses are dominated by the two level tunneling systems (TLS).[12] The TLS are mutually coupled via long range elastic dipolar interactions.[11, 13] In bulk glass, the inter–TLS elastic dipolar interaction potential is: [14]

$$U(r) = \frac{1}{8\pi}\frac{(1+\sigma)(3-4\sigma)}{(1-\sigma)}\frac{\lambda^2}{\rho v_g^2}\frac{1}{r^3} \equiv \frac{A}{r^3} \tag{2}$$

The elastic dipole is a second rank symmetric tensor. Using typical values, we have $\lambda \sim 2\ eV$ for the elastic dipole (there is no such thing as elastic *monopole*) moment of one TLS, $\sigma \sim 0.2$ for the Poisson's ratio, $v_g \sim 4,000\ m/s$ for the speed of sound in glass, and $\rho \sim 2.5\ g/cm^3$ the for glass's density of mass. We have then:

$$A \equiv \frac{1}{8\pi}\frac{(1+\sigma)(3-4\sigma)}{(1-\sigma)}\frac{\lambda^2}{\rho v_g^2} \sim 2.1 eV\mathring{A}^3 \tag{3}$$

and:

$$< U >= \frac{cAn}{d^3} \equiv \frac{cAN}{V} \tag{4}$$

where $N = nV$ is the number of TLS within volume V, $c = \sum_{i=1}^{i=\infty} 1/i^3 \approx 1.19$, and d is the nearest neighbor inter–TLS spacing. Relating the averaged

kinetic energy $< K >$ to the average of the potential energy $< U >$ by virial theorem [15] that $< U >= 2/3 < K >$ and the kinetic energy to temperature T by $< K > \propto \ k_B T$, we have:

$$\gamma = \frac{\partial(\ln V)}{\partial(\ln T)} = -1 \ < 0 \tag{5}$$

We see then, within classical theory, that the thermal expansion of glass is negative, of the same order of magnitude as experimentally observed, and it is therefore plausible to attribute it to the behaviors of the elastically inter–coupled TLS. Because our argument is based on classical mechanics, it does not truly explain the thermal expansion of glass at low temperatures since at low temperatures, the motion of the atom obeys quantum mechanics. It only illustrates the basic cause of the low temperature glass thermal expansion. We note that Dynes [16] has found that, below T_g, the thermal expansion coefficient of glass is often smaller than that in liquid as the molecular orientation and motion contribute less to it. We also note that Klein, Fischer, Anderson, and Anthony [17] proposed, too, a theory to explain the negative thermal expansion of glass, obtaining numeral magnitudes different from experimental. Sheard [18] suggested that the changes in potential barrier heights causing smaller tunneling splittings may lead to negative thermal expansions. Phillips [19] have also considered a connection between TLS and glass thermal expansion. Papouliar [20] proposed a theory to explain the negative glass thermal expansion with results (Grünnesen parameter $\sim -10,000$) vastly different from experimental findings defying the third law of thermodynamics. One part of the glass's thermal expansion comes of course from the anharmonic couplings between the atoms.[26] Its contribution, however, is smaller at lower temperatures as the vibrational amplitudes of the atoms are smaller.

We now consider the thermal expansion of glass fiber. The thermal expansion of a thick fiber is not that different from the thermal expansion of a piece of bulk glass of some particular size and shape. Things might be different in a thin fiber. We have shown that, in a strained glass sample such as a glass fiber, the long range elastic dipole interaction may be screened to become short ranged. [14] It is therefore of interest to examine the axial thermal expansion of a glass fiber along the fiber axis to see if it might be different from that of a bulk glass. There have been studies of the thermal expansions of glass fibers. Hassanzadel–Agham [21] made a micro–mechanical model of the thermal expansion coefficient of unidirectional glass fiber–reinforced polymide composite containing silica nanoparticles. The mechanical and thermal expansion properties of glass reinforced PEEK composites at temperatures from 77 K to room temperature have been examined by Chu and coworkers. [22] Lee and Song [23] applied the Mori–Tanaka model to study the elastic and thermal expansion coefficients of glass fiber reinforced composites. Consider a glass fiber of radius a. Two TLS located on the fiber axis and separated by a distance z interact via the short range elastic interaction: [14]

$$U(z) \approx \frac{\lambda^2}{2aY} \exp(-\beta z/a) \tag{6}$$

where $\beta \approx 1.84$ is the root of a certain Bessel function. We assume that the TLS are uniformly distributed in the fiber. Following virial theorem [15] we relate the average of the potential energy to the average of the kinetic energy proportional to $k_B T$. We realize that the average in virial theorem is an average over time, *i.e.*, over a vibrational period, not an average over space. Within a confined system, however, the two averages are proportional

to each other. We then have:

$$< U >= \frac{\lambda^2}{2aY} \exp(-\frac{\beta z_0}{a}) = \frac{2}{3} k_B T \tag{7}$$

with z_0 proportional to the length of the fiber. From this we determine the axial thermal expansion of a glass fiber:

$$\alpha = [T \ln(\frac{\beta \lambda^2}{2a^3 Y k_B T})]^{-1} \tag{8}$$

At all easily reachable temperatures, the axial thermal expansion coefficient α is negative, though this sign may vary depending on the radius of the fiber and the temperature according to this result. The thermal expansion coefficients for many glass fibers (most around room temperature) can be found at www.Engineering.ToolBox.com. It is known that one part of the glass's thermal expansion comes from the anharmonic couplings among the atoms.[26] We know, however, that the anharmonic effects are more pronounced at higher temperatures with larger atomic vibrational amplitudes, and estimate that at or below room temperature their contribution is no greater than 20% what the interacting TLS have and would therefore not significantly change our result. While our treatment is insufficiently accurate for a quantitative evaluation of the thermal expansion of fiber glass, we hope it can still serve to provide its suggestive estimation. For paraffin–wax, *e.g.*, the experimental result is $\alpha \sim -4.8 \times 10^{-5} K^{-1}$ [27] while our result gives $\alpha \sim -5.3 \times 10^{-5} K^{-1}$ at $T = 300K$ with paraffin–wax's $Y = 2.6 \times 10^{19}$ Pascal, $\lambda = 1.2eV$, and our presumed fiber radius $a = 1mm$. We have been unable to find experimental report for the temperature dependence of fiber glass thermal expansion to check with our result. It will also be of interest to observe what, if any, thermal expansion dependence on the radius of the glass fiber that exists to compare with our result.

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References

[1] Indium is the only metallic crystal having a negative thermal expansion.

[2] J. S. O. Evans, T. A. Mary, T. Vogt, M. A Subramatian, and A. W. Sleight, Chemistry of Materials **8**, 2809 (1996).

[3] W. A. Phillips, *Amorphous Solids: Low Temperature Properties*, W. A. Phillips, ed., Springer–Verlag, Berlin (1981).

[4] L. J. Porter, J. F. Justo, and S. Yip, J. Appl. Phys. **82**, 5378 (1997); D. K. C. MacDonald and S. K. Roy, Phys. Rev. **97**, 673 (1955); N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, 493. Hold, Rinchart, and Winston, Philadelphia, PA (1976).

[5] K. G. Lyon, G. L. Salinger, and L. A. Swenson, Phys. Rev. B **19**, 423 (1979).

[6] G. K. White, Phys. Rev. Lett. **34**, 204 (1975).

[7] G. K. White, Cryogenics **4**, 2 (1964).

[8] D. Sanditz, V. Mantatov, and D. Danmmov, Tech. Phys. **54**, 385 (2009).

[9] G. K. White, J. A. Birch, and M. H. Manghnani, J. Non-Crystalline Solids **23**, 99 (1977).

[10] N. W. Ashcroft and N. D. Mermin, *Solid State Physics*. Hold, Rinchart, and Winston, Philadelphia, PA (1976), Table (25.2).

[11] Y. Fu, "Thermal expansion of glass and the two level tunneling systems in glasses", http://www.yaotianfu.org/. (2020).

[12] P. W. Anderson, B. I. Halperin, and C. M. Varma, Phil. Mag. **65**, 1 (1972); W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972). For reviews see *Amorphous Solids: Low Temperature Properties*, W. A. Phillips, ed., Springer Verlag, Berlin (1981); W. A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987). For an up–to–date theoretical discussion on the subject though not about glass thermal expansion see C. C. Yu and H. M. Carruzzo, in *Low–Temperature Thermal and Vibrational Properties of Disordered Solids: A Half–Century of Universal "Anomalies" in Glasses*, M. A. Ramos, ed., World Scientific Press. To appear.

[13] The interaction among two level tunneling systems via phonon couplings has also been discussed by J. Joffrin and A. Levelut, J. Physique **36**, 811 (1975), by J. L. Black an B. I. Halperin, Phys. Rev. B **16**, 2879 (1977), and by M. W. Klein, B. Fischer, A. C. Anderson, and P. J. Anthony, Phys. Rev. B **18**, 5887 (1978).

[14] Y. Fu, Phys. Rev. B **40**, 10056 (1989).

[15] L. D. Landau and E. M. Lifshitz, *Mechanics*, Pergamon Press, Oxford (1964), 23.

[16] J. C. Dynes, Reviews of Modern Physics **70**, 953 (2006).

[17] M. W. Klein, B. Fischer, A. C. Anderson, and P. J. Fischer, Phys. Rev. B **18**, 5887 (1978).

[18] F. W. Sheard, Phil. Mag. **3**, 1381 (1958); F. W. Sheard, *Thermal Expansion 1971*, M. G. Graham and H. E. Hage, eds. AIP Conf. (1972) p. 155.

[19] W. A. Phillips, J. Low Temp. Phys. **11**, 757 (1973).

[20] N. Papouliar, J. Phys. C **5**, 1943 (1972).

[21] M. K. Hassanzadeh–Agham, R. Arsari, and A. Darvizeh, Composites Engineering Part A, Applied Science **96**, 110 (2017).

[22] X. X. Chu, Z. X. Wu, R. J. Huang, Y. Zhu, and L. F. Li, Cryogenics **50**, 84 (2010).

[23] D. Lee and Y. S. Song, Composite Engineering Part B, Applied Science **146**, 98 (2018).

[24] These data are available at www.Engineering.ToolBox.com.

[25] G. Guangfa *et al.*, Physics Procedia **25**, (2012) 339.

[26] C. Kittel, *Introduction to Solid State Physics*, sixth ed., John Wiley and Sons, New York (1986), 114.

[27] A. Haji-Sheikh, J. Efekhar, and D. Y. S. Lou, "Some thermal physical properties of paraffin-wax as a thermal storage medium," osti.gov, 82-0846 (1982).