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IS-T-829

THERMAL EXPANSION OF GLASSES AT LOW TEMPERATURES

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Date Transmitted: January 1979

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

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by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Physics

Major: Solid State Physics

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1978

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Thermal expansion of glasses at low temperatures

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The linear thermal expansion coefficient ($\alpha = (\partial \ln L / \partial T)_p$) has been measured at temperatures to 1.2K for two very different amorphous solids, fused silica and PMMA (polymethylmethacrylate, plexiglas), using a parallel plate capacitor differential dilatometer. The low temperature expansion coefficients for these solids have the same temperature dependences as the specific heats, and show a contribution which is linear in the temperature and which can be associated with the postulate of a broad distribution of two level states. The Grüneisen parameters which are associated with this contribution are comparable for the two solids ($\gamma \approx -16$), and suggest a further indication of common behavior for amorphous solids at low temperature. Large magnitudes for Grüneisen parameters ($|\gamma| > 5$) generally are associated with tunneling models. While a symmetric double harmonic oscillator tunneling model can be used to understand the sign and magnitude of γ for these solids, this model is inconsistent with other thermal and thermodynamic data for fused silica. The existence of similar negative and large magnitude Grüneisen parameters for these two amorphous solids places an additional constraint on theories for the low temperature properties of glasses.

CHAPTER I. INTRODUCTION

The past 15 years have seen numerous attempts to understand the physics of amorphous solids (glasses) at low temperatures. The low temperature thermal properties of the crystalline and amorphous phases differ radically for materials which can exist in either form. For instance, the measured heat capacities and thermal conductivities are much different for glasses than for crystals. The low temperature heat capacity of nonmagnetic, dielectric crystals is proportional to T^3 and can be understood in terms of the Debye theory (1). Since the low temperature limit of this theory in its most elementary form depends only on the excitation of acoustic waves (phonons) in a solid, it also should apply to glasses. The temperature dependence of the heat capacity of glasses at low temperatures, however, is found to be of the form (2,3)

$$C_V(T) = a_1 T + a_3 T^3 \quad (1-1)$$

The coefficient of the T^3 term (a_3) is slightly larger than would be predicted from sound velocity measurements using Debye theory, while the linear coefficient (a_1) is the same (within a factor of 3) for all materials studied (3). The rest of this chapter will focus on the linear term with the interpretation of the excess contribution to the T^3 term a more complex and possibly different problem.

The low temperature thermal conductivity of nonmagnetic, dielectric crystals is proportional to T^3 and can be interpreted using an equation from the kinetic theory of gases (4),

$$K = 1/3 C_V v_S \ell \quad (1-2)$$

The particles "carrying" the heat are phonons, so, C_V is the phonon heat capacity (proportional to T^3), v_S is the sound velocity (a constant) and ℓ is the phonon mean free path. The phonon mean free path for a high purity crystal at low temperatures is limited by the sample size, so ℓ is a constant and the thermal conductivity is proportional to T^3 . The thermal carriers in glasses also should be phonons, with the mean free path limited by the disorder. This would result in a constant mean free path (smaller than that for a crystal) and a thermal conductivity again proportional to T^3 . The low temperature ($<1K$) thermal conductivity of glasses, however, has the form (2,3)

$$K = AT^\delta \quad (1-3)$$

where $\delta = 1.9 \pm 0.1$. The coefficient (A) appears to be similar in magnitude for all materials studied (3) and smaller than predicted from the disorder. Thus, if phonons are the basic carriers of thermal energy in a glass, the effective mean free path must be inversely proportional to the temperature.

Several theories (5-13) have been proposed to explain the unusual thermal behavior of glasses at low temperature, with the simple postulate of a slowly varying continuous distribution in energy of two level states (14-17) giving the best agreement with existing experimental data. This model and its application to experiments will be discussed in some detail in the following.

Model and Experimental Confirmation

A heat capacity contribution linear in T and a thermal conductivity proportional to T^2 can be derived (14,15) from a uniform distribution in energy of two level states, with only simple arguments needed to obtain these results. The number of excited states is proportional to the number of states per unit energy (n_o , a constant) and $k_B T$ since on the average, only states with an energy equal to or less than $k_B T$ will be excited. The average energy per state is approximately $k_B T/2$, so, the internal energy is to first order $n_o k_B^2 T^2/2$. Therefore, the heat capacity which is the temperature derivative of the internal energy, is given by $n_o k_B^2 T$.

The two level states are stationary and thus, do not contribute to the thermal conductivity except as scattering centers for the phonons. The phonons are absorbed and then reemitted by the two level states, therefore, the two level states determine the phonon mean free paths. The mean free path is inversely proportional to the probability of scattering or to the number of scattering centers (4) ($n_o k_B T$) and also to how well the phonons interact with the two level states (i.e., the matrix elements, $|M^2|$, between a phonon and a two level state). Therefore, the phonon mean free path is inversely proportional to $n_o |M^2| k_B T$ and

$$K \propto \frac{T^2}{n_o |M^2|} \quad (1-4)$$

More elaborate calculations have been done (14,15) but the temperature dependences are the same.

Several other experiments have been performed (mostly on fused silica) which can be understood using a constant distribution in energy of two level states. Most of these low temperature experiments have used GHz acoustic waves since 1 GHz corresponds to a phonon energy/ k_B of 0.05K.

The attenuation of GHz acoustic waves through a glass as a function of intensity (18-20) gives the simplest confirmation of this model. At high intensities, the attenuation is low and at low intensities, the attenuation is high. A small part of a high intensity pulse will saturate all of the two level states having an energy splitting corresponding to the ultrasonic frequency, leaving only a normal low attenuation. A low intensity pulse, on the other hand, will not saturate a sufficient fraction of the corresponding states, so, the wave is scattered by successive absorption and emission and high attenuation occurs. At intermediate intensities, the attenuation varies smoothly with intensity and agrees with theoretical predictions (19). The mean free path calculated at low intensities agrees with that obtained from thermal conductivity experiments (2) and is proportional to $[n_0 |M^2|]^{-1}$.

Another ultrasonic attenuation experiment used two pulses (21). The first pulse of a given frequency and saturation intensity was followed by another pulse of constant intensity but variable frequency. The attenuation of the second pulse was observed as a function of frequency. The attenuation of this pulse was constant in frequency except

at the frequency of the first pulse where the attenuation decreased. This decreased attenuation is interpreted as being due to the decreased number of effective scattering centers at this energy due to the saturation caused by the first pulse.

A few other experiments that have been performed include variations as a function of frequency and temperature of the sound velocity (11, 22,23), the dielectric constant (24) and the far infrared absorption constant (25).

Another ultrasonic experiment, in which phonon echoes (26) were observed, has been used to define the density of states for the thermal transport experiments (thermal conductivity, ultrasonic attenuation and sound velocity). In this experiment, two GHz pulses are injected into one end of a fused silica rod with a time separation, t_s . If the separation (t_s) is small enough, three pulses will be observed at the opposite end, each separated in time by t_s . The data indicate a phase coherence between states over a distance of one micron and give the matrix elements ($|M^2|$) which couple the phonons and the two level states (26). Thus, knowing these matrix elements, the density of states can be calculated for each thermal transport experiment. These agree for the various transport experiments (phonon attenuation, thermal conductivity) but are much smaller than that which is obtained from heat capacity data. This appears to introduce a dilemma, although a possible explanation will be presented later.

In all of the experiments mentioned so far, no information can be obtained about the structure of the two level states. Another experiment,

the thermal expansion, can give information about the volume dependences of the energy differences between the two states (energy splitting).

The next section will show through the Grüneisen theory how this volume dependence is obtained from thermal expansion and heat capacity data and also will postulate a possible model for the two level state.

Grüneisen Theory

The Grüneisen approximation assumes a free energy of the form

$$F(V, T) = \sum_i F_i(V, T) = \sum_i -k_B T \phi(T/\phi_i(V)) \quad , \quad (1-5)$$

where the sum is over all independent contributions and the volume dependence occurs only through the characteristic temperatures, $\phi_i(V)$.

This leads to a heat capacity of the form

$$C_V(T) = \sum_i C_{V_i}(T/\phi_i) \quad . \quad (1-6)$$

The thermal expansion coefficient ($\beta = (\partial \ln V / \partial T)_P$) is related, in this approximation, to the heat capacity per unit volume (C_V/V) as (27)

$$\beta(T) = \sum_i \beta_i(T) = B_T^{-1} \sum_i \gamma_i (C_{V_i}/V) \quad . \quad (1-7)$$

Here, B_T is the isothermal bulk modulus ($B_T = -V(\partial P / \partial V)_T$) and the dimensionless Grüneisen parameter associated with each contribution, γ_i , is given by

$$\gamma_i = - \frac{d \ln \phi_i}{d \ln V} \quad . \quad (1-8)$$

For the Debye contribution, $\phi_i = \Theta_D$ (the Debye temperature) and both C_V

and β are proportional to $(T/\Theta_D)^3$ for $T \ll \Theta_D$. For most physical systems (including the Debye contribution), $\gamma_i = 3 \pm 2$. An example of this would be given by the Leonard-Jones repulsive potential (proportional to r^{-12}) for which $\gamma = 4$. For γ 's much different from these, unusual mechanisms must be postulated. For instance, tunneling is the only mechanism known (28-30) which can give Grüneisen parameters with large magnitudes. This occurs because the characteristic energy depends exponentially on a function of the volume. This volume dependence will be described in the next sections since a tunneling mechanism has been postulated (14-17) for the origin of the two level states. Thus, measurements of the thermal expansion can be used as a test of the applicability of this model to describe the unusual behavior of glasses at low temperatures.

Tunneling Model

A tunneling state occurs when an atom (or molecule) can exist in either of two nearly equivalent sites which are separated by a potential barrier. A single asymmetric tunneling state is shown in Figure 1. The well separation (ℓ) and the asymmetry (Δ) may be different for each state. A two level state occurs from a combination of the asymmetry and the overlap of the single well wavefunctions. In the case of asymmetric wells, the ground state is localized in the lower well and the excited state is localized in the upper well. For symmetric wells ($\Delta = 0$), a two level state results from the symmetric and asymmetric combinations

Figure 1. The potential energy, $V(x)$, plotted as a function of position for an asymmetric double harmonic oscillator with well separation, $2l$, potential barrier, V_0 , and asymmetry 2Δ

of the single well wavefunctions and results in neither state being localized in a single well.

Only a small fraction of all the tunneling states will be symmetric wells if the distribution for Δ is sufficiently broad. This fact leads to a possible explanation of the density of states difference obtained from heat capacity and thermal transport experiments. If single phonon excitations are considered, the probability of excitation is much higher for the symmetric wells than for the asymmetric wells (14,15) since the atom's "position" is unchanged in an excitation in the symmetric case. In the thermal transport experiments, phonons interact almost completely with states having a high probability of excitation, or with those which are symmetric. Thus, the density of states which is important for the transport experiments would include only the symmetric states or only a small fraction of the total number of states calculated from heat capacity data. Black and Halperin (31) have postulated two types of two level states to explain this density of states dilemma. The above explanation is consistent with this.

To test the tunneling model, theoretical calculations of the heat capacity and the Grüneisen parameter must be carried out and compared with experimental data. The remainder of this section will calculate the heat capacity and the Grüneisen parameter associated with double harmonic oscillators and will initially be concerned with the symmetric case which can be solved exactly.

The exact solution of the symmetric double harmonic oscillator problem is described in detail in Reference 32. In short, the simple

harmonic oscillator energy states are split due to the possible symmetric and asymmetric combinations of the single well wavefunctions. The amount of splitting is a function of well separation. The four lowest energy states are sketched in Figure 2 as a function of reduced barrier height (σ)

$$\sigma = \frac{2V_0}{\hbar\omega} = \frac{m\omega\ell^2}{\hbar} \quad (1-9)$$

(ω is the characteristic frequency for a single well, V_0 is the barrier height and 2ℓ is the separation.) As can be seen in Figure 2, in the limits of infinite separation and complete overlap (i.e., a single well), the energy states approach those of a single simple harmonic oscillator as is expected. Only the two lowest energy levels are needed to explain the low temperature properties of glasses since the second excited state corresponds to the glass transition temperature (14). A distribution in energy is achieved by assuming a distribution of barrier heights, V_0 (or similarly, a distribution of well separations, ℓ). The energy splitting, $2\Delta_0$, is given for large barrier heights (separations) by (32)

$$2\Delta_0 = 2\hbar\omega \left(\frac{\sigma}{\pi} \right)^{\frac{1}{2}} e^{-\sigma} \quad , \quad \sigma > 2 \quad (1-10)$$

For a two level state, the heat capacity is represented by a Schottky heat capacity (33)

$$C_V(\Delta_0/k_B T) = \frac{\Delta_0^2}{k_B T^2} \operatorname{sech}^2 \left(\frac{\Delta_0}{k_B T} \right) \quad , \quad (1-11)$$

which has a maximum at $\Delta_0 = 1.2 k_B T$.

Figure 2. The energy levels for a symmetric double harmonic oscillator are given by $E_i = \hbar\omega(\nu_i + \frac{1}{2})$. Here, $\nu_i(\sigma)$ is plotted as a function of σ , the reduced barrier height

Using Equations (1-8) and (1-10), the Grüneisen parameter for a single state can be calculated (assuming $\ell^2 \propto V^{2/3}$) to be

$$\begin{aligned}\gamma(\Delta_0) &= - \frac{d \ln \Delta_0}{d \ln V} \\ &= \gamma_\omega (3/2 - \sigma) + 2\sigma/3 - 1/3, \quad \sigma > 2, \quad (1-12)\end{aligned}$$

where $\gamma_\omega (= -d \ln \omega / d \ln V)$ is the single well Grüneisen parameter.

The only free parameter in Equation (1-12) is γ_ω and should be well-behaved; i.e., $\gamma_\omega = 3 \pm 2$. Here, σ must be obtained from Equation (1-10) using a known or assumed value of ω (e.g., the glass transition temperature).

The extension of the above results for one tunneling state to a distribution of states requires the use of the general expressions for both the heat capacity and the Grüneisen parameter,

$$C_V(T) = \int_0^\infty C_V(\epsilon/k_B T) n(\epsilon) d\epsilon \quad (1-13)$$

and

$$\gamma = \frac{\int_0^\infty C_V(\epsilon/k_B T) n(\epsilon) \gamma(\epsilon) d\epsilon}{\int_0^\infty C_V(\epsilon/k_B T) n(\epsilon) d\epsilon} \quad (1-14)$$

In this case, $C_V(\epsilon/k_B T)$ is the heat capacity for a single two level state having an energy splitting, 2ϵ (Equation (1-11)), $\gamma(\epsilon)$ is the Grüneisen parameter associated with a two level state having an energy splitting, 2ϵ , and $n(\epsilon)$ is the number of two level states per unit energy. For the symmetric tunneling states $\epsilon = \Delta_0$ and $\gamma(\epsilon = \Delta_0)$ is

given by Equation (1-12). If $n(\Delta_0)$ is assumed to be a constant, n_0 , Equations (1-11) and (1-13) give

$$C_V(T) = \frac{\pi^2}{12} n_0 k_B^2 T, \quad (1-15)$$

in good functional agreement with experimental data and a previous handwaving derivation. The total tunneling Grüneisen parameter (Equation (1-13)) can be evaluated using the mean-value theorem as

$$\gamma(\Delta_0 = 1.2 k_B T) = \gamma_\omega (3/2 - \sigma) + 2\sigma/3 - 1/3, \quad \sigma > 2. \quad (1-16)$$

The parameter σ must be evaluated using Equation (1-10), this value of $\Delta_0 (= 1.2 k_B T)$ and an estimate of $\hbar\omega$. Because σ now is a function of T , Equation (1-16) suggests a slight temperature dependence for the total tunneling Grüneisen parameter. This may not be observed since the sensitivity of the thermal expansion experiments is limited. The Grüneisen parameter can be estimated using typical values for fused silica ($\hbar\omega/k_B = 1400\text{K}$, $\Delta_0/k_B = 1.5\text{K}$ and $\gamma_\omega = 3$) and $\sigma = 7.26$ as $\gamma(\Delta_0/k_B = 1.5\text{K}) = -12.8$; i.e., $\gamma(\Delta_0)$ is "large" and negative.

The asymmetric double harmonic oscillator problem involves a simple extension of the symmetric double harmonic case. The energy splitting (2ε) for the asymmetric state is given by (14,15)

$$2\varepsilon = 2(\Delta^2 + \Delta_0^2)^{\frac{1}{2}}. \quad (1-17)$$

Therefore, the Grüneisen parameter can be calculated using Equation (1-8) as

$$\gamma(\Delta, \Delta_0) = \frac{\Delta^2}{\epsilon} \gamma_\Delta + \frac{\Delta_0^2}{\epsilon} \gamma(\Delta_0) \quad (1-18)$$

where

$$\gamma_\Delta = \frac{-d \ln \Delta}{d \ln V} \quad (1-19)$$

The Grüneisen parameter associated with the asymmetry, γ_Δ , may be assumed to be "normal" (3 ± 2) since it is a consequence of normal lattice interactions. Thus, the Grüneisen parameter for a single state will depend very much on the relative values of Δ and Δ_0 . When $\Delta_0 \gg \Delta$ (the symmetric case), $\gamma(\Delta, \Delta_0)$ will be approximately $\gamma(\Delta_0)$ (i.e., large and negative). When $\Delta \gg \Delta_0$, $\gamma(\Delta, \Delta_0)$ will be approximately γ_Δ (i.e., 3 ± 2). Hence, the total tunneling Grüneisen parameter for a distribution of tunneling states will depend on the distributions assumed for Δ and Δ_0 .

Phillips (15) has assumed a constant distribution in energy for the asymmetry (Δ) and a constant distribution in energy for σ . The latter results in a distribution in energy for the tunnel splitting (Δ_0) which is approximately proportional to Δ_0^{-1} . This requires that a minimum value of Δ_0 (Δ_{0min}) be adopted to prevent Equations (1-13) and (1-14) from diverging. These distributions for Δ and Δ_0 result in a density of two level states per unit energy (15)

$$n(\epsilon) \propto \ln \left(\frac{2\epsilon}{\Delta_{0min}} \right) \quad , \quad \epsilon \gg \Delta_{0min} \quad (1-20)$$

Equation (1-20) is a slowly varying function of ϵ , so the constant

density of two level states which was initially assumed to explain C_V and K provides a reasonable first approximation.

Equation (1-20) can be substituted into Equation (1-12) to give the heat capacity as

$$C_V(T) \propto k_B^2 T \ln\left(\frac{2.4 k_B T}{\Delta_{\text{omin}}}\right) \quad , \quad k_B T \gg \Delta_{\text{omin}} \quad (1-21)$$

with the same techniques used to obtain Equation (1-16). Equation (1-21) varies slightly faster than T since $\ln(2.4 k_B T / \Delta_{\text{omin}})$ is a slowly varying function of T . Experimental very low temperature heat capacity data for two glasses have been analyzed in terms of a power law (34,35), $T^{\alpha'}$. The effective exponent, α' , can be obtained from Equation (1-21) as

$$\alpha' = 1 + \frac{1}{\ln\left(\frac{2.4 k_B T}{\Delta_{\text{omin}}}\right)} \quad , \quad k_B T \gg \Delta_{\text{omin}} \quad (1-22)$$

Equation (1-22) is a slowly varying function of T , so power law fits should be quite acceptable. Experimental heat capacity data on two different samples of fused silica (35) gave α' 's of 1.22 and 1.30. These α' 's, when substituted in Equation (1-22), give $\Delta_{\text{omin}}/k_B = 2$ mK and 6 mK. The data were taken down to 25 mK without a significant deviation from the power law being observed. In the case of vitreous B_2O_3 , $\alpha' = 1.45$ (34) and $\Delta_{\text{omin}}/k_B = 78$ mK. These data were taken down to 50 mK with a significant deviation from power law behavior appearing at about 60 mK. This deviation, however, appears at a lower temperature than would be

expected from the calculated value of Δ_{omin} , and in a region where Equation (1-22) should not apply.

These heat capacity data are consistent with the density of states given by Equation (1-20). With Phillips' density of states, the total tunneling Grüneisen parameter can be calculated using Equations (1-12), (1-14) and (1-18) as (15)

$$\gamma(T) \cong \gamma_{\Delta} + \frac{\gamma(\Delta_o = 1.2 k_B T) - \gamma_{\Delta}}{\ln\left(\frac{2.4 k_B T}{\Delta_{\text{omin}}}\right)}, \quad k_B T \gg \Delta_{\text{omin}} \quad (1-23)$$

At temperatures much larger than Δ_{omin}/k_B , $\gamma(T)$ will be dominated by γ_{Δ} , and will be normal since the tunnel-splitting contribution is negligible.

The Grüneisen parameter associated with a given heat capacity contribution is given by

$$\gamma_l = \frac{\beta_l B_T}{C_{Vl}/V} \quad (1-24)$$

Thus, the experimental determination of the Grüneisen parameter requires heat capacity, thermal expansion and bulk modulus data. In practice, the linear thermal expansion coefficient ($\alpha = (\partial \ln L / \partial T)_p = \beta/3$ for an isotropic solid) is measured instead of the volume thermal expansion coefficient (β). Typical values of α are 10^{-5}K^{-1} at room temperature and 10^{-8}K^{-1} at 4K. An expansion coefficient of 10^{-8}K^{-1} implies that a 1 cm sample will increase in length by 1 Å (the classical diameter of a hydrogen atom) for a 1K temperature change. To obtain one percent data, a resolution of at least 0.01 Å is needed. White and Collins'

dilatometer (29) has this resolution and they have used it to measure the thermal expansion of fused silica down to 1.5K (36). The magnitude of the Grüneisen parameter they calculate from their lowest data point, -47, is very large and suggests a tunneling model.

The purpose of this work was to measure the low temperature thermal expansion of two very different amorphous solids, fused silica and PMMA (polymethylmethacrylate, plexiglas). The next section will explain how very sensitive thermal expansion measurements can be carried out at low temperatures.

Experimental Methods

Several methods have been used to measure thermal expansions. Optical interference methods are not adequate at low temperatures since they only have a resolution of a few angstroms (37). A parallel plate capacitor technique, pioneered by White's group (29,38,39) using a three terminal capacitance bridge, has a resolution of 0.01 Å. Figure 3 shows a capacitance dilatometer (labeled normal) similar to that used by White. The sensitivity arises from the reciprocal relation between the separation (L_g) and the capacitance (C) of two parallel plates,

$$C = \frac{\epsilon_0 A}{L_g}, \quad (1-25)$$

with A the area of the plates and ϵ_0 the permittivity of free space. The sensitivity of the capacitance to a change in the gap is

$$\frac{dC}{dL_g} = -\frac{\epsilon_0 A}{L_g^2}. \quad (1-26)$$

Figure 3. Capacitance dilatometer cells with the normal, inverted and absolute geometries (from Reference 40)

Thus, small separations (gaps) can give high sensitivities. A guarded capacitor configuration is used to reduce edge effects. Figure 3 illustrates three geometries used for capacitance dilatometers.

The "normal" geometry in Figure 3 is used when the length contraction of the sample is less than or approximately equal to that of the cell. Thus, as the cell and sample are cooled, the gap remains the same or becomes smaller. If the sample's contraction were much larger than that of the cell, the gap would become larger at low temperatures and result in a loss of sensitivity. The "inverted" geometry would be used in this case since a small gap will result at low temperature. Since the entire cell changes temperature in these two geometries, a reference material must be used to evaluate the expansion of the sample. Also, the expansion of the sample must be larger than or equal to that of the reference material, otherwise, the reference's expansion must be precisely known. The "absolute" geometry is used to determine a reference material (or to measure very small expansions) since only the sample will change temperature.

Both "normal" and "inverted" geometries will be needed in this work since copper will be used as a reference material. Fused silica has a length contraction from room temperature to 4K (-0.02%) which is much smaller than copper (0.3%) and hence requires that the "normal" geometry be used. PMMA, on the other hand, has a contraction (1%) much larger than copper and requires the "inverted" geometry. The capacitance dilatometer which will be described in the next chapter can be used with either the "normal" or "inverted" geometries.

CHAPTER II. APPARATUS

The cryostat and electrical systems used in the present experiment are described in this chapter. Figure 4 shows the cryostat suspended in a conventional set of stainless steel liquid nitrogen and liquid helium dewars, while the capacitance cell and the vacuum spaces which enclose it are sketched in Figure 5. The inner vacuum space (the sample space) usually contained helium exchange gas (100-200 mT) to insure that the dilatometer was isothermal. The high vacuum (10^{-6} T) in the outer vacuum space isolated the sample space from the helium bath. The radiation shield which surrounds the sample space is attached to the top of the sample space and is intended to reduce thermal gradients along the inner vacuum jacket (sample space vacuum jacket).

The capacitance cell shown in Figure 6 is attached to the base of the helium pot. Four samples (labeled C_1 , C_2 , C_3 , C_c) and three support posts are attached symmetrically to the base plate of the cell as shown in this figure. The top plate is mounted on the three support posts and has four guarded capacitor plates, with one located above each sample. In principle, a knowledge of the thermal expansion of the support posts should be sufficient to define the expansion of the samples. The expansivities of the support posts also determine the type of dilatometer geometry ("normal" or "inverted"). In this experiment, silicon support posts were used for the "normal" geometry with a fused silica center sample, while PMMA support posts were used for the "inverted" geometry with a PMMA center sample. The three outer samples

Figure 4. The cryostat and dewar system

Figure 5. The vacuum spaces, pot and capacitance cell

Figure 6. The capacitance cell

were copper in both cases. The expansivities of these were determined in situ in terms of a silicon center sample in a dilatometer calibration experiment. The fused silica, PMMA and silicon samples all were coated with silver to provide an electrically conducting surface. Figure 7 contains a photograph of the capacitance cell (partly disassembled) with the fused silica sample in the center and with silicon support posts. The three copper rods were used to clamp the silicon posts between the top and base plates. The three copper samples were used as references since a tip of the top plate (and, hence, dilatometer) was observed below 4.2K which was related to the pressure changes in the helium pot as the vapor pressure of the helium was reduced. The "tip" correction which was applied below 4.2K is described in the next chapter.

Cryostat and Electrical Systems

The cryostat (Figure 4) was designed to use the ancillary systems described by Kroeger (40), including the support platform, with nested stainless steel liquid nitrogen and liquid helium dewars (both 30 l capacity) replacing the glass dewars which were used previously (40). Vibrations are not a problem using this cryostat, so a rigid platform mount was used. This also solved another problem which was related to the tipping of the platform (and, hence, cryostat) as a function of time due to the evaporation of liquid nitrogen.

Details of the cryostat vacuum spaces are shown in Figure 5. The brass outer vacuum can is 300 mm tall, 140 mm diameter and 1.6 mm wall thickness. This can is immersed in the liquid helium bath and is

Figure 7. The capacitance cell with a fused silica center sample, three copper samples and three silicon support posts. Also shown are three copper rods for assembling the cell. The top plate is on the left

evacuated with a diffusion pump through a 19 mm diameter stainless steel tube. An indium gasket is used for a vacuum seal.

The copper inner vacuum can which encases the sample space is 180 mm tall, 94 mm diameter and 1.2 mm wall thickness. This space is suspended by five 6 mm diameter stainless steel tubes. Four of these were used for electrical feedthroughs from the bath into the sample space, with a vacuum seal only at the top of each tube. The fifth tube was used with a forepump to evacuate the sample space. An indium gasket also is used to seal this can. The copper radiation shield (0.6 mm thick) is bolted to the top flange of the sample space.

A 100 cm³ helium pot which is used to obtain temperatures below 4.2K is silver soldered under the top flange of the sample space. The pot pumping line is a 19 mm diameter stainless steel tube which is reduced to 6 mm 30 mm above the pot. A 0.8 mm orifice at the top of the pot is used to reduce superfluid helium filmflow effects. The liquid helium is pumped with a 5 hp mechanical pump, with the vapor pressure regulated using a manostat which can control the temperature between 1.4K and 4.2K to slightly better than 1 mK. Below 1.4K the pressure is regulated manually and a minimum temperature of 1.0K is obtained. The capacitance cell, which is attached to the base of the pot, will be described in the next section.

A block diagram of the electrical systems is shown in Figure 8. Most of the present electrical systems are the same as those used by Kroeger (40), so only a brief discussion will be given except where differences exist.

Figure 8. A block diagram of the electrical systems

The ac temperature controller (ACTC) regulates the temperature of the sample space above 4.2K. Figure 9 (from Reference 40) shows a block diagram of the ACTC. A carbon resistor (Speer, $\frac{1}{2}$ watt, $470\Omega \pm 10\%$ at room temperature, 1008Ω at 4.2K) is used for a temperature sensor below 30K while a miniature platinum resistance thermometer (Degussa, 100Ω at 273K) is used above 30K. The sensor resistance is compared to a variable reference resistance box (General Radio decade box (40)) with an ac bridge. The bridge off-balance is connected to a phase-sensitive null detector. The resulting dc output of the detector is connected to the inputs of an integral/proportional/differential controller (C.A.T. (40)) which, in turn, drives a programmable constant voltage power supply. This power supply feeds the cell heater (200Ω , #36 manganin) which is wound noninductively around the helium pot. The ACTC has sufficient sensitivity to maintain the cell temperature stable to ± 0.1 mK. A second heater on top of the sample space can be used with a constant current supply to obtain measurements at elevated temperatures (>150 K). The absolute temperature of the sample space could be determined within 1% below 30K with the carbon sensor and within 0.5K above 30K with the platinum sensor.

The absolute temperature, however, always was determined by comparing the voltage drop across a calibrated resistance thermometer (located in the base of the helium pot) with that across a standard resistor carrying the same current. A standard four-terminal dc potentiometric technique was used (Figure 8), with current reversal to compensate for thermal emf's (40). The germanium (Ge) resistance

Figure 9. A block diagram of the ac temperature controller (ACTC)
(from Reference 40)

thermometer (Cryo Cal, S/N 748, 340Ω at 4.2K) was calibrated locally in terms of T_x , a temperature scale based on paramagnetic salt thermometry (41). The platinum resistance thermometer (Minco, P/N S1055-1, S/N 51) was calibrated locally by Kroeger in terms of IPTS-68. The measuring circuits differ from Kroeger's (40) in that his potentiometer was replaced by a Leeds and Northrup model 7555 type K-5 potentiometer (S/N 1723751). This system allows the measurement of temperatures below 30K with a sensitivity of 0.1 mK and an accuracy of 1 mK, while above roughly 30K, the sensitivity becomes 1 mK and the accuracy 5 mK.

Electrical leads entering the vacuum spaces were sealed in two different ways. Stycast electrical feedthroughs, similar to those of Kroeger (40), were used for all of the leads, except those for the capacitance bridge. The capacitance leads in the form of 0.8 mm diameter stainless steel coaxial cables (type UT-34-SS, Uniform Tubes, Inc., Collegeville, PA) were sealed with Wood's metal solder.

Capacitance Dilatometer and Bridge

The construction of the dilatometer (Figures 6 and 7) can be summarized as follows. The three support posts should maintain the top plate parallel to the base plate, so, in principle, the thermal expansions of each of the four samples can be determined if the thermal expansion of the posts is known. In practice, however, calibration experiments (silicon posts, silicon sample) show that the motion of the top plate is not parallel to the base plate and also does not correspond to the thermal expansion of the post material. The excess motion is due

to constraints on the posts from the mountings to the top and base plates. However, the capacitances between each of the three copper samples and their corresponding guarded areas in the top plate can define the absolute location and hence the plane of the top plate at each temperature. Thus the length change of the center sample can be determined from the known expansion of copper and the temperature-dependent changes in the center sample gaps.

The dilatometer was constructed from oxygen-free-high-conductivity (OFHC) copper. All parts were high vacuum (10^{-6} T) annealed several times during the machining, usually at 600°C for one hour. All capacitor and mounting surfaces were ground flat with opposing surfaces parallel (to 3 μm) before being polished to remove scratches.

The base plate, 76.2 mm diameter and 9.5 mm thick, contains fifteen holes (2.9 mm diameter). One hole was drilled in the center to mount the center sample while six were located symmetrically on a 17.5 mm radius circle to mount the copper reference samples and the support posts. Eight more holes were located symmetrically on a 34.9 mm radius circle to attach the base plate to the shell.

The shell, a hollow cylinder 61.0 mm long, 76.2 mm outer diameter and 6.4 mm wall thickness, was attached at one end to the base plate with a 0.13 mm mylar gasket and three nylon screws. Two stainless steel screws and spring washers were used to attach the other end of the shell to the base of the helium pot. Two spacers (0.13 mm copper) were used to reduce the transmission to the cell of possible distortions of the helium pot due to pressure changes.

The mylar gasket is used to insulate electrically the base plate from the shell which is at ground potential. This enables the electrically conducting samples to be connected to the high voltage side of the capacitance bridge with only one connection to the base plate. The low side of the bridge (see below) is connected to the guarded capacitor plates in the top plate.

The top and base plates, ideally, are constrained at only three points on each plate which are associated with the two ends of each support post. Problems can arise, however, if the posts have flat ends and an expansivity different from the copper support plates, since additional non-symmetric support points may exist and the top plate may move in an unusual manner with temperature. The ends of the silicon support posts were rounded to prevent multiple contacts with the support plates, but, unfortunately, the ends of the PMMA support posts were left flat and an anomalous motion of the top plate was observed.

Another constraint problem was associated with the silicon support posts. Since silicon is so hard, holes could not be tapped in the ends for mounting screws. Instead, spring-loaded copper rods (Figure 7) were inserted to clamp the support posts between the top and base plates and these resulted in an anomalous apparent expansion of the silicon support posts. The differential expansion between the copper rods and the silicon posts changes the compression of the springs as a function of temperature, therefore changing the constraint forces. In addition, the spring constant itself is a function of temperature.

A heating problem at liquid nitrogen temperatures was found to be the result of the relatively low resistance of the silicon support posts (2-3k Ω at room temperature due to a thin layer of SiO₂ on the surface of a 500 Ω post) and the 50 V rms voltage across the posts. To cure this, thin mylar sheets (0.013 mm) were placed under each silicon post to provide electrical insulation. The effects of the mylar and the constraints, however, are not serious for these experiments since data for the three copper samples were used to define the location of the top plate above the center sample for each temperature.

The 57.2 mm diameter top plate contains four capacitor plates (Figures 6 and 7), one in the center and three on a 17.5 mm radius circle. A guarded capacitor configuration insulates electrically the capacitor plates from the top plate and defines the areas of the plates accurately.

We in the past have used two designs for guarded capacitor plates. One of these used epoxy joints (39), while the second involved mylar insulated tapered joints (40). The first top plates which were constructed for this experiment used epoxy joints which did not work properly at low temperatures. Close examination revealed very small cracks in the epoxy and some failure to bond to the surfaces.

After this problem, the following simpler and much more satisfactory construction was adopted. The upper plate has one 2.9 mm diameter hole for each capacitor plate (Figure 6) while the bottom (guard) plate has a matched precisely machined hole which is 0.25 mm greater in diameter than the actual 10.45 mm diameter capacitor plate. Figure 10 shows the

Figure 10. The detailed construction of a single capacitor plate

construction of a single plate. Each capacitor plate is insulated with mylar from the grounded upper plate as shown. The capacitor plates were mounted in the top plate with a 0.13 mm mylar cylinder wedged in the guard gap and the bottom surface was ground flat (to 3 μm) and polished. The top plate then was taken apart, cleaned, annealed and reassembled. After final assembly, the mylar in the guard gaps was removed and the capacitor plates were found to be level with the surface to within 10 μm . Electrical connections to the capacitor plates from the coaxial cables are made with #36 manganin wires onto which gold pin connectors had been soldered.

The capacitances were measured using a three-terminal capacitance bridge (39), without which measurements of the thermal expansion would be very difficult. This type of bridge allows a precise measurement of a capacitance independent of cable and other shunt capacitances.

A simplified schematic drawing of this bridge is shown in Figure 11. The ratio transformer (a step-wise adjustable ideal auto-transformer) is used to adjust the voltage input to the standard capacitor (C_s in Figure 11) until the currents in the two arms of the bridge are equal. The balance condition (Figure 11) shows that the unknown capacitance (C_x) is directly proportional to the ratio transformer setting.

The detailed circuit of the bridge used here is shown in Figure 12. The major additions from Figure 11 are the use of two ratio transformers (one five decade and one seven decade) and standard capacitors in parallel to obtain higher resolution, and a small circuit to balance the resistive component. The 100 pF standard capacitor and the five

$$\text{AT BALANCE } V_x j\omega C_x = V_s j\omega C_s \Rightarrow C_x = C_s \frac{V_s}{V_x}$$

----- SHIELD

Figure 11. The basic three-terminal capacitance bridge. C_x is the unknown capacitor and C_s is the standard capacitor (from Reference 40)

SHIELDS ARE NOT SHOWN

Figure 12. The detailed capacitance bridge circuit (from Reference 40)

decade ratio transformer provide a stable, "rough" balance, while the 0.1 pF standard capacitor and the seven decade ratio transformer provide the precise balance and are used at low temperatures to resolve small capacitance changes. The standard capacitors are placed in a temperature-controlled box to give a bridge stability of 10^{-8} pF or better. Kroeger's null detector (40) was replaced with a Princeton Applied Research Model 186 synchro-het lock-in amplifier (S/N 5111) to obtain higher resolution. With this detector, a capacitance as large as 11 pF could be measured with a stability and sensitivity of 10^{-8} pF.

Each capacitor plate in turn can be connected to the low side of the bridge while the base plate and samples are all connected to the high side (47 V rms, 1 kHz). (The base plate was insulated electrically from the grounded shell with a mylar gasket.) While measuring one capacitor plate, the other three all are grounded, with the active plate at balance being at virtual ground. Therefore, the total electrostatic force on the top plate is always the same when the bridge is balanced. At one time, irreproducible effects were observed which were traced to changes in the forces which occurred when switching from one plate to another with the bridge slightly out of balance for the second measurement. These effects disappeared when care was taken that the entire top plate always was at or extremely near ground potential when switching. This was accomplished by grounding the detector input immediately after measuring a capacitance. The estimated value of the next capacitance then was set on the bridge, the selector switch changed, and the detector

ground removed. With the present cell constraints, this effect probably is not important but the above switching procedure was used as a precaution.

Samples

This section contains information about the samples and support posts which were used in this experiment. All of the samples and support posts were machined to final lengths which would insure that the gaps at 4K were between 0.08 mm and 0.13 mm for the various sample and post configurations. Gaps larger than these result in a loss of sensitivity while smaller gaps cause the capacitance to become increasingly sensitive to the width of the guard gap and to the relative tip between each capacitor plate and the corresponding sample surface. The copper samples and the silicon and PMMA support posts were machined, ground and polished in special jigs to insure that the three samples in each set were the same length with ends flat and parallel to $3\text{ }\mu\text{m}$.

The fused silica sample (Spectrosil) was obtained from Thermal American Fused Quartz Co. (Montville, NJ). According to the manufacturer, this material contains approximately 0.1 ppm metallic impurities and 0.1% by weight of hydroxyl ions. This material corresponds closely to the material used by White for measurements of the heat capacity (42) and thermal expansion (36) of fused silica. The material was supplied in the form of a 16 mm diameter solid rod, 610 mm long. The sample which was used (37.46 g mm long at room temperature) had a 3.18 mm diameter hole drilled about 4 mm into the center of the base for the

purpose of mounting it to the base plate. A thin coat ($<3 \mu\text{m}$) of silver was chemically deposited on the side of the sample while $0.4 \mu\text{m}$ of silver was evaporated on each end in a high vacuum (10^{-7} T). A copper wire (0.23 mm diameter) was varnished (GE-7031) into the hole and a copper screw was soldered to the wire to seat the sample firmly to the base plate using a spring washer and a nut.

The PMMA samples were obtained from a 15.9 mm diameter commercial plexiglas rod. Three support posts were cut from the rod and machined to lengths of 38.04 mm at room temperature. Holes were drilled and tapped (4-40) in the center of each end of each post for attaching it to the top and base plates. A fourth piece of PMMA was cut from the same rod to be used as a center sample. This sample is 37.89_2 mm long (at 296K) and has a similar hole to that for the posts drilled and tapped in its base. Silver ($0.4 \mu\text{m}$) was evaporated on each end and in a longitudinal strip along the side to connect electrically the two ends. Stainless steel screws with spring washers were used to mate the PMMA to the base and top plates and only two to three threads of the screws were used.

The copper (reference) samples were prepared from a long 9.53 mm diameter copper rod (99.999+% pure) which was obtained from American Smelting and Refining Company (ASARCO), as was Kroeger's copper (40,43). This rod was electron-beam-melted (to remove dissolved gasses and some impurities) into a 19.1 mm diameter ingot which was swaged into a 15.9 mm diameter rod. This rod then was high vacuum (10^{-6} T) annealed at 650°C for one hour. Three samples were cut from this rod, and a hole

was drilled and tapped (4-40) in the base of each sample. The samples again were annealed in a high vacuum at 450°C for one hour before the final 0.4 mm finishing cuts and polishing were done. After this, the three samples again were high vacuum annealed at 600°C for one hour. The final room temperature length of each sample is 37.51₆ mm. The copper samples were seated to the base plate using OFHC copper screws and spring washers.

The silicon support posts were cut from an 8 mm diameter single crystal rod obtained from Dow Corning (Crystal F 2110209). This p-type silicon, according to the manufacturer, had a room temperature resistivity of 62 ohm cm. The three posts were cut and then ground to final room temperature lengths of 37.57₂ mm each. The ends were rounded slightly as previously discussed.

An additional silicon sample was used for calibration purposes. This sample was obtained from a 38.1 mm diameter polycrystalline rod (obtained from Dow Corning) which had a room temperature resistivity of 36,000 ohm cm. Absolute expansivities for this material have been determined in another experiment (44). A section of this rod was cut and polished to a final room temperature length of 37.41₉ mm, after which it was longitudinally quartered. One of the quarters then was silvered in the same manner as the fused silica. A 0.8 mm diameter hole was ultrasonically drilled into the base and a mounting similar to that for the fused silica sample was used.

CHAPTER III. PROCEDURES AND ANALYSIS

The samples were mounted firmly to the base plate and the top plate was attached, after which the rest of the cryostat was assembled. The capacitances then were measured to be sure that the gaps were as expected. After checking the vacuum seals, the dilatometer was cooled slowly to 4.2K, first using liquid nitrogen and then liquid helium. The temperature of the cell was controlled with an automatic temperature controller (ACTC) above 4.2K, while below 4.2K it was controlled by regulating the pressure in the filled helium pot. When the temperature and capacitances were constant, they were recorded. The temperature then was changed and the measurements repeated. A pot pressure-related tip correction, as determined in an isothermal experiment, was applied to the data taken below 4.2K. The temperatures, corrected capacitances and the effective thermal expansions of the copper samples (determined in a calibration experiment) were used to determine the linear thermal expansion coefficient of the center sample. Various polynomials were fit to the raw thermal expansion data so that corrections could be made for the use of finite temperature intervals (i.e., $(\Delta L/\Delta T)_p$ not $(\partial L/\partial T)_p$).

Experimental Procedure

After firmly (but not tightly) mounting the samples to the base plate with spring washers (see Figure 6), the posts and the top plate were installed. The mountings (and constraints) were different for the silicon and PMMA support posts as was described in the last chapter.

The cell then was attached to the helium pot after which the capacitances were measured. This provided a check to determine that the cell had been assembled properly with the lengths and gaps adding up correctly ($\pm 3 \mu\text{m}$). The vacuum cans then were attached and the cryostat was placed in the dewar system. The vacuum and sample spaces were evacuated before liquid nitrogen was added to the helium and nitrogen dewars. Exchange gas ordinarily was used in the vacuum space (500 mT helium) to cool the system faster. In most cases, the dilatometer was cooled from room temperature to 77K overnight. The cooling was accomplished more slowly for the PMMA experiments because of long term 4.2K length drifts which were observed in these samples when the cooling to 77K was done overnight. In this case, no exchange gas was used and three days were taken to cool from room temperature to 77K. After stabilizing at 77K, the exchange gas (if any) was removed and a few data points were taken to check the electronics and assembly of the cell. The liquid nitrogen then was removed from the helium dewar and liquid helium was added. The cell was at 4.2K after about two hours, and was allowed to remain at this temperature overnight before any data were taken.

Data points were taken below 4.2K at regular temperature intervals of 0.5K, while at higher temperatures the increments varied from 1K just above 4K to 25K near room temperature. The temperature was controlled and stabilized using the ACTC above 4.2K and the manostat below 4.2K. Shortly after the controller had locked in, the temperature and capacitances would stabilize and after a period of time they were

recorded. The times necessary for the cell to stabilize ranged from a few minutes below 10K to several hours above 100K.

The cell was calibrated by taking data for a center sample of known thermal expansivity (silicon (44)), with the average thermal expansion of the copper samples, " α_{Cu} ", as the unknown parameter. This parameter may differ from the "true" thermal expansion of copper because of sample differences or due to effects inherent in the construction of the dilatometer. The effective thermal expansion of the copper samples agreed with the measured thermal expansion of copper (43) to 1% above 16K. Below 16K, a systematic deviation was observed and detailed data were taken. Kroeger and Swenson (43) comment on apparent sample-dependent differences in the low temperature thermal expansion of copper, with the present data as reliable as any others.

The measured thermal expansions of the three copper samples were identical above 4.2K ($\pm 1.5 \times 10^{-10} \text{K}^{-1}$), with, however, the data for the three samples suddenly beginning to disagree below 4.2K. An isothermal experiment showed that these differences were related to the pressure in the helium pot and hence must be related to a tipping of the cell with changing pressure. The abrupt appearance below 4.2K is related to the pot pressure changes which occur below that temperature as liquid helium is pumped to reduce the temperature. The cause of this effect is not known. After the first set of fused silica data, a bellows was inserted in the vacuum space pumping line 150 mm below the main flange. This hopefully would prevent a tipping of the dilatometer due to a

compression of the pot pumping line as it was evacuated. This, however, did not seem to have an effect on the tip.

A correction for this effect for each sample was determined empirically for each cooldown and all of the raw data below 4.2K have had a "tip correction" applied. This correction was determined at 6.3K (stable to 1 mK) by noting the changes in all the capacitances as gaseous helium at one atmosphere was added to an initially evacuated pot. The assumption that the capacitance changes were linear in pressure was confirmed by a preliminary experiment. A further check was given by the requirement that for a pure tip the average of the three outer gap changes should be the same as that of the center. The tip of the top plate with respect to the base plate was about 10^{-7} radians/atmosphere, with the axis of rotation differing slightly between different cooldowns. Table 1 gives the tip corrections used in the present experiment.

Table 1. Tip corrections used in the present experiments. Fused silica (1) and (2) refer to two different cooldowns.

Sample	dC_1/dp	dC_2/dp	dC_3/dp	dC_c/dp (10^{-5} pF/atm)
Si	1.563	-1.578	0.641	0.118
fused silica (1)	1.313	-2.252	0.877	-0.378
fused silica (2)	1.052	-1.827	0.827	-0.103
PMMA	1.219	-1.303	0.796	0.425

These tip corrections need to be known to 10^{-6} pF/atmosphere to obtain

1% data for fused silica and PMMA and were easily obtainable to this accuracy.

Thus, each capacitance value at a given temperature below 4.2K was corrected to a reference pressure (usually the first point of a sequence of data points) by using the pot pressure as calculated from helium vapor pressure tables (45). Figure 13 shows the tip-corrected calibration data (the average of the three copper samples) below 10K, along with Kroeger's results (43). Figure 14 shows the individual measured thermal expansions of the three copper samples at five points before the tip correction was applied. This figure also shows the tip-corrected calibration data below 4K. After the tip corrections were applied, the scatter of the data for these three copper samples was less than the size of the circles ($\pm 1.5 \times 10^{-10} \text{ K}^{-1}$).

The calibration data are presented in Appendix A. The deviations of the data from Kroeger's results (43) were smoothed graphically so that a resolution of 10^{-11} K^{-1} was obtained below 4K. At each point of the calibration, the tip-corrected expansions of the three copper samples agreed to $\pm 1.5 \times 10^{-10} \text{ K}^{-1}$. The average of the data for the three copper samples scattered about a smooth curve from $\pm 3 \times 10^{-11} \text{ K}^{-1}$ below 2K (corresponding to the resolution of the capacitance bridge) to $\pm 10^{-10} \text{ K}^{-1}$ ($\pm 0.3\%$) near 10K. The three copper samples and their mountings were not disturbed after the calibration.

Figure 13. The cell calibration data below 10K. Also shown is the measured thermal expansion of copper (43)

Figure 14. The low temperature cell calibration data. The open circles are the individual measured expansions of the three copper samples at five points before the tip correction was applied. After the tip correction is applied, the difference between the three copper samples is smaller than the size of the circles which represent "average" data

Data Analysis

The magnitudes of the gaps above each sample (L_{gi} , $i = 1-3, c$) are determined from the capacitances using

$$L_{gi} = \frac{\epsilon_0 A}{C_i}, \quad i = 1-3, c \quad (III-1)$$

where A is the effective area of a capacitor plate. The first approximation to the effective area is to assume that the diameter of the guarded plates extends half way across the guard gap. A more accurate determination (38) shows that the actual effective area is about 0.3% smaller than this and results in $\epsilon_0 A = 0.0776$ pF cm at room temperature for each capacitor plate. This effective area then is corrected for contractions when cooling by using

$$A(T) = A(T_0) \left[1 + \left(\frac{\Delta L}{L_0} \right)_T \right]^2 \quad (III-2)$$

where $(\Delta L/L_0)_T$ (<0) is the relative length change of copper as compared to $T_0 = 20^\circ\text{C}$ (43).

The gaps and the identical lengths of the copper samples (L) determine in principle the position of the capacitor plates (X_i) in the top plate relative to the base plate since

$$X_i = L + L_{gi}, \quad i = 1-3 \quad (III-3)$$

The lengths of the copper samples are those corresponding to the temperature of the dilatometer (43). These data for the copper samples are used to determine the position of the center capacitor plate as

$$\begin{aligned}
 x_c &= \frac{1}{3} \sum_{i=1}^3 x_i \\
 &= L + \frac{1}{3} \sum_{i=1}^3 L_{gi}
 \end{aligned}
 \tag{III-4}$$

because of the symmetry. The length of the center sample then can be written as

$$\begin{aligned}
 L_c &= x_c - L_{gc} \\
 &= L + \frac{1}{3} \sum_{i=1}^3 L_{gi} - L_{gc}
 \end{aligned}
 \tag{III-5}$$

Therefore, the length change of the center sample with a change in temperature is given by

$$\Delta L_c = \Delta L + \frac{1}{3} \sum_{i=1}^3 \Delta L_{gi} - \Delta L_{gc}
 \tag{III-6}$$

The average linear thermal expansion coefficient of the center sample then is given by

$$\begin{aligned}
 \bar{\alpha}_c &= \frac{1}{L_c} \frac{\Delta L_c}{\Delta T} \\
 &= \frac{L}{L_c} \alpha_{Cu} + \frac{1}{L_c \Delta T} \left(\frac{1}{3} \sum_{i=1}^3 \Delta L_{gi} - \Delta L_{gc} \right)
 \end{aligned}
 \tag{III-7}$$

The effective thermal expansion of the copper samples, " α_{Cu} ", was obtained in the cell calibration experiment. Various polynomials in T were fit to the data for $\bar{\alpha}_c$ using a least squares technique so that a finite interval correction (40) could be applied.

Error Analysis

Both systematic and random errors occur in the measurement of the thermal expansion coefficient. The systematic errors result from the measurements of the sample lengths, the capacitance plate areas, the effective thermal expansion of the copper samples, and the accuracy of the standard capacitors. Random errors result from the resolution of the capacitance bridge, the measured change in temperature, the possibly nonreproducible tipping of the top plate, and the differential expansion between the samples and the base plate.

The lengths of the copper samples and the diameters of the capacitor plates were measured with micrometers accurate to $3\text{ }\mu\text{m}$. Thus the lengths of the 37.52 mm long samples at room temperature are known to better than 0.03%. The diameters of the plates varied between them by $\pm 6\text{ }\mu\text{m}$ while the holes in the guard plate varied by $\pm 8\text{ }\mu\text{m}$. Effects on the measured capacitances due to rounded corners on the capacitor plates and guard plate are not known, but are believed to be comparable to the uncertainty of the measured areas, so the average effective area of the four plates should be known to better than 1%. The ratio $L(T)/L_0$ is known to 1 ppm (43) and does not contribute a detectable error. The calibration of the cell can contribute a systematic error which is unknown but is believed to be small compared to the thermal expansions of fused silica and PMMA. A systematic error also is due to the uncertainty of the standard capacitors, $\pm 0.01\%$ for the 100 pF standard and $\pm 0.1\%$ for the 0.1 pF standard (40).

The capacitance bridge also contributes a random error at low temperatures due to its resolution, 10^{-8} pF. The accuracy of the measurement of temperature changes is limited to about 0.03% due to nonlinearities of the potentiometer or 0.1 mK, whichever is greater. An error in the calculated gaps occurs when the two capacitor plates are not parallel (46). However, using the present method with three copper reference samples, these errors will cancel to first order and should result in uncertainties which are less than the resolution of the capacitance bridge or 0.1%, whichever is greater. The support points between the center sample and the base plate can change as a function of temperature due to the differential thermal expansion between the sample and the plate, with friction playing a role. This can result in an anomalous motion of the center sample and will cause a scatter in the thermal expansion data which should scale with the differential expansion.

The scatter of the data in the calibration experiment agrees well with the above analysis since the scatter below 2K ($\pm 3 \times 10^{-11} \text{ K}^{-1}$) is predicted from the resolution of the capacitance bridge, while the scatter around 10K ($\pm 10^{-10} \text{ K}^{-1}$) corresponds to 0.3% of the measured thermal expansion, and is temperature-independent. This scatter probably is due to the sample-base plate joint effect which was described above. Similar scatter was observed in data taken at higher temperatures. The major factor which limits the accuracy of the present results at high temperatures (1%) is due to the uncertainty in the effective areas of the capacitor plates, as described above.

CHAPTER IV. RESULTS

The experimental low temperature expansivity data are expected to be of the form

$$\alpha(T) = b_1 T + b_3 T^3 \quad (IV-1)$$

since this is the form of the low temperature heat capacity. If Equation (IV-1) is written as

$$\alpha/T = b_1 + b_3 T^2, \quad (IV-2)$$

a plot of α/T versus T^2 should give a straight line with a slope b_3 and an intercept b_1 on the vertical axis. Figures 15 and 16 present our low temperature data for fused silica and PMMA in this form. The observed expansivities are negative for fused silica and positive for PMMA. Both samples, however, show a negative value of b_1 , with b_3 negative for fused silica and positive for PMMA. Both sets of data show deviations from Equation (IV-1) (at higher temperatures for PMMA) which are similar to those found in the heat capacity (42,47).

As was mentioned in the Introduction, the coefficient of the T^3 term for the low temperature heat capacity, a_3 , is larger than that predicted from low temperature sound velocity measurements using Debye theory. As a result, a_3 should be written as $a_{3D} + a_{3exc}$, where a_{3D} is the coefficient predicted from sound velocities using Debye theory and a_{3exc} is an excess contribution. The pressure dependence of the sound velocities can be used to predict the Debye contribution to the

Figure 15. The low temperature ($T < 4\text{K}$) linear thermal expansion data for fused silica plotted as α/T versus T^2

Figure 16. The low temperature ($T < 2.4\text{K}$) linear thermal expansion data for PMMA plotted as α/T versus T^2

thermal expansion. The coefficient of the T^3 term of the thermal expansion (b_3) therefore should be written as $b_{3D} + b_{3exc}$. Calculations of a_{3D} and b_{3D} from sound velocity data are described in Appendix B with the results for fused silica and PMMA given in Table 2. Also given in this table are the coefficients of the heat capacity and thermal expansion and the bulk modulus for fused silica and PMMA.

The parameters listed in Table 2 are used to determine the Grüneisen parameter for each contribution using

$$\gamma_i = \frac{3b_i B_T}{a_i} \quad (1-24)$$

The Grüneisen parameter associated with the linear term, γ_1 , is large and negative (-16) for both solids while the behavior of the Grüneisen parameter associated with the excess T^3 term, γ_{3exc} , is very puzzling, being large and negative for fused silica and very small for PMMA.

Fused Silica

The data for fused silica which are plotted in Figure 15 and tabulated in Appendix A, agree with White's results (36) above 2.5K. Initially, however, data taken below 2.2K showed considerable scatter (Figure 17) which was associated with the use of helium exchange gas (100 mT, 4.2K), and which only was important below the lambda point in the superfluid helium temperature region ($T_\lambda < 2.2K$). The data plotted in Figure 15 (and also shown in Figure 16) which were taken without exchange gas are smooth and continuous through 2.2K. White's data (36) (also shown in Figure 17) were obtained using exchange gas, and appear

Table 2. A summary of various parameters (Equations (I-1), (I-24), (IV-1), (IV-3)) which are used to calculate the final results of this experiment, together with these results which are expressed as the Grüneisen parameters, γ_1 , γ_{3exc} , γ_5

parameter (units)	fused silica (T < 4K)		PMMA (T < 2.4K)	
	value	reference	value	reference
B_T (10^{10} N m ⁻²)	3.50	48	0.82	50
a_1 (J m ⁻³ K ⁻²)	3.04	42	5.28	51
a_3 (J m ⁻³ K ⁻⁴)	2.53	42	32.2	51
a_{3D} (J m ⁻³ K ⁻⁴)	1.69	49, App. B	21.5	50, App. B
a_{3exc} (J m ⁻³ K ⁻⁴)	0.84	-	14.6	-
a_5 (J m ⁻³ K ⁻⁶)	0.217	42	-	-
γ_{3D}	-2.29	48, App. B	4.25	50, App. B
b_1 (10^{-9} K ⁻²)	-0.441	-	- 3.52	-
b_3 (10^{-9} K ⁻⁴)	-0.206	-	3.83	-
b_{3D} (10^{-9} K ⁻⁴)	-0.034	App. B	3.72	App. B
b_{3exc} (10^{-9} K ⁻⁴)	-0.172	-	0.11	-
b_5 (10^{-11} K ⁻⁶)	-0.419	-	-	-
γ_1	-15.2±0.8	-	-16.4±2.1	-
γ_{3exc}	-21.5±1.2	-	0.2±0.6	-
γ_5	- 2.0±0.4	-	(>0)	-

Figure 17. The low temperature linear thermal expansion data for fused silica as taken with and without exchange gas. White's (36) data are shown also

to exhibit the same problems we observe below the lambda point. Fused silica is known to absorb helium and the absorbed helium alters the heat capacity (52), although the heat capacity data show no discontinuous effects at 2.2K.

A three term odd power series,

$$\alpha = b_1 T + b_3 T^3 + b_5 T^5 \quad , \quad (IV-3)$$

was fit to the no exchange gas data below 4K since this type of series best fits the heat capacity data (42) in the same temperature region. The resulting Grüneisen parameters associated with each contribution are given in Table 2. The magnitude of γ_1 (-15.2) is much smaller than that calculated by White (36) (-47) but is more reliable because of the assumed effects of exchange gas on his low temperature data. The magnitude of γ_{3exc} (-22) is very surprising, but possibly could arise because we have no direct heat capacity data for our sample.

Data which were taken for fused silica up to 10K agreed well with White's results (36) above 2.5K, so no additional data were taken. A five term power series similar to Equation (IV-3) was fit to the present data (without exchange gas below 4.2K and with exchange gas from 4.2K to 10K) to generate Table 3. The coefficients and root mean square deviations (rmsd's) of these fits are given in Table 4. A linear interpolation in Table 3 is good to 1% above 4K while the three term fit (Equation (IV-3)) should be used below 4K.

Table 3. The linear thermal expansion coefficient for fused silica. A linear interpolation is accurate to one percent above 3.5 K, while the fit equation (see Table 4) should be used for lower temperatures.

T (K)	α (K^{-1})
1 K	$-0.65 \times 10^{-9} \text{ K}^{-1}$
1.5	-1.40
2	-2.66
2.5	-4.73
3	-7.92
3.5	$-1.26 \times 10^{-8} \text{ K}^{-1}$
3.75	-1.54
4	-1.85
4.5	-2.64
5	-3.62
5.5	-4.83
6	-6.25
7	-9.69
8	$-1.37 \times 10^{-7} \text{ K}^{-1}$
9	-1.79
10	-2.24

Table 4. The coefficients used to generate Table 3
 for $\alpha = \sum_n b_n T^n$
 (odd)

$$T \leq 3.5K$$

$$b_1 = -4.4101 \times 10^{-10} K^{-2}$$

19 points, 1.2K to 3.8K

$$b_3 = -2.0621 \times 10^{-10} K^{-4}$$

$$\text{rmsd} = 1.1 \times 10^{-10} K^{-1}$$

$$b_5 = -4.1877 \times 10^{-12} K^{-6}$$

$$3.5K \leq T \leq 10K$$

$$b_1 = -3.92233 \times 10^{-10} K^{-2}$$

$$b_3 = -2.26872 \times 10^{-10} K^{-4}$$

$$b_5 = -3.13956 \times 10^{-12} K^{-6}$$

36 points, 1.2K to 10.1K

$$b_7 = 5.59624 \times 10^{-14} K^{-8}$$

$$\text{rmsd} = 5 \times 10^{-10} K^{-2}$$

$$b_9 = -2.38532 \times 10^{-16} K^{-10}$$

PMMA

The data for PMMA from 1.2K to 300K are given in Appendix A, with the low temperature ($T < 2.4\text{K}$) data shown in Figure 16. The data taken with and without helium exchange gas agreed, so, most of the data were taken with exchange gas. High temperature (2.4K to 300K) data shown in Figures 18 and 19 agree with other, less accurate, results (53,54).

A two term series (Equation (IV-1)) was fit to the data below 2.4K since above 2.4K an Einstein mode, which is seen in the heat capacity (47), becomes important. The coefficients and their associated Grüneisen parameters are given in Table 2.

Various polynomials in overlapping temperature regions were fit to the data taken above 2.4K to generate Table 5. The coefficients and rmsd's of the fits are listed in Table 6. A linear interpolation in Table 5 is good to 1% except below 2.4K where the fit equation should be used.

Conclusions

The asymmetric tunneling model as discussed in the first chapter was used to explain both the heat capacity and the thermal transport experiments, as well as to explain the observed differences in the densities of states derived from these two types of experiments. This model then was extended to include the thermal expansion, again using the distributions for Δ (the asymmetry parameter) and Δ_0 (the tunnel splitting) assumed by Phillips (15). The prediction from this model, as given by Phillips (15), was that γ_1 should be approximately equal to

Figure 18. The linear thermal expansion data for PMMA below 11K plotted as α/T versus T^2

Figure 19. The linear thermal expansion data for PMMA from 11K to 300K

Table 5. The linear thermal expansion coefficients for PMMA. A linear interpolation is accurate to one percent above 2.4 K, while the fit equation (see Table 6) should be used below 2.4 K.

T (K)	α (K^{-1})	T (K)	α (K^{-1})
1 K	$(0.031) \times 10^{-8} K^{-1}$	25	$1.13 \times 10^{-5} K^{-1}$
1.5	0.77	30	1.37
2	2.36	35	1.59
2.75	7.47	40	1.80
3	1.02×10^{-7}	45	1.98
3.25	1.346	50	2.14
3.5	1.73	60	2.41
4	2.69	70	2.64
4.5	3.87	80	2.83
5	5.28	90	3.01
5.5	6.89	100	3.17
6	8.68	120	3.48
6.5	1.065×10^{-6}	140	3.75
7	1.29	160	4.01
7.5	1.502	180	4.35
8	1.74	200	4.86
9	2.25	220	5.56
10	2.79	240	6.34
12	3.93	260	7.06
14	5.07	280	7.68
16	6.29	290	7.90
18	7.46	295	7.95
20	8.61	300	(8.00)

Table 6. The coefficients used to generate Table 5 from

$$\alpha = \sum_n b_n T^n$$

<u>T ≤ 2.4K</u>	
$b_1 = -3.157 \times 10^{-9} K^{-2}$	23 points, 1.2K to 2.4K
$b_3 = 3.831 \times 10^{-9} K^{-4}$	rmsd = $4.5 \times 10^{-10} K^{-1}$
<u>2.4 ≤ 13K</u>	
$b_0 = 5.898591247 \times 10^{-9} K^{-1}$	$b_7 = -9.419034183 \times 10^{-11} K^{-8}$
$b_1 = -4.514905600 \times 10^{-8} K^{-2}$	$b_8 = 5.265995984 \times 10^{-12} K^{-9}$
$b_2 = 7.947381800 \times 10^{-8} K^{-3}$	$b_9 = -1.652121428 \times 10^{-13} K^{-10}$
$b_3 = -6.341356128 \times 10^{-8} K^{-4}$	$b_{10} = 2.227103257 \times 10^{-15} K^{-11}$
$b_4 = 2.930105648 \times 10^{-8} K^{-4}$	
$b_5 = -7.094006739 \times 10^{-9} K^{-7}$	51 points, 12K to 14.6K
$b_6 = 1.033332909 \times 10^{-9} K^{-7}$	rmsd = $1.0 \times 10^{-9} K^{-1}$
<u>13K ≤ T ≤ 22K</u>	
$b_0 = 8.19047 \times 10^{-9} K^{-1}$	
$b_1 = -1.68315 \times 10^{-7} K^{-2}$	16 points, 4.9K to 25.5K
$b_2 = 6.52369 \times 10^{-8} K^{-3}$	rmsd = $7.6 \times 10^{-9} K^{-1}$
$b_3 = -2.37215 \times 10^{-9} K^{-4}$	
$b_4 = 3.03186 \times 10^{-11} K^{-5}$	
<u>22K ≤ T ≤ 300K</u>	
$b_0 = -4.812791894 \times 10^{-6} K^{-1}$	$b_7 = 4.658063062 \times 10^{-18} K^{-8}$
$b_1 = 8.420185021 \times 10^{-7} K^{-2}$	$b_8 = -1.428535986 \times 10^{-20} K^{-9}$
$b_2 = -1.247561788 \times 10^{-8} K^{-3}$	$b_9 = 2.386463528 \times 10^{-23} K^{-10}$
$b_3 = 3.125641672 \times 10^{-10} K^{-4}$	$b_{10} = -1.673558269 \times 10^{-26} K^{-11}$
$b_4 = -7.301391831 \times 10^{-12} K^{-5}$	
$b_5 = 1.048747091 \times 10^{-13} K^{-6}$	30 points, 10.6K to 300K
$b_6 = -8.992469167 \times 10^{-16} K^{-7}$	rmsd = $1.4 \times 10^{-7} K^{-1}$

γ_{Δ} , the Grüneisen parameter which is associated with Δ ($\gamma_{\Delta} = -d \ln \Delta / d \ln V$). Since γ_{Δ} is the result of "normal" microscopic interactions, the magnitude of γ_1 was predicted to be of the order of 3. The large, negative Grüneisen parameters obtained here certainly are not "normal".

The present data agree, however, with the results of a calculation which assumes a uniform distribution of symmetric wells. For this model, the Grüneisen parameter, γ_1 , is given by Equation (1-16) as

$$\gamma_1(\Delta_0 = 1.2 k_B T) = \gamma_{\omega}(3/2 - \sigma) + 2\sigma/3 - 1/3 \quad (1-16)$$

Since the model gives σ directly (Equation (1-10)), the only free parameter is γ_{ω} , the Grüneisen parameter for a single well. For fused silica (using $\hbar\omega/k_B = 1400K$ and $T = 2.5K$), Equation (1-16) gives $\gamma_{\omega} = 3.83$, while for PMMA ($\hbar\omega/k_B = 430K$ and $T = 1.7K$), it gives $\gamma_{\omega} = 4.79$. Both γ_{ω} 's are in the "normal" range, thus, the Grüneisen parameters (γ_1) are consistent with the assumption of a distribution of symmetric tunneling states. As was discussed in the first chapter and briefly at the beginning of this chapter, however, this model is inadequate for an understanding of the low temperature thermal and thermodynamic properties of amorphous solids.

A dilemma now arises for which there is no apparent resolution. Thermal expansion is a bulk thermodynamic property to which all states of energy comparable with $k_B T$ must contribute, just as for the heat capacity. The large magnitude, negative Grüneisen parameters which we report can be understood if most of these states are related to

symmetric double harmonic oscillators. The pulsed phonon and thermal conductivity experiments suggest (26), however, that not more than 4% of the states contributing to the heat capacity can be of this type, with the remaining "anomalous" states possibly corresponding to asymmetric double harmonic oscillators. These latter states, in any model, will have a Grüneisen parameter which is small in magnitude. Hence, there seems to be no way to use a tunneling model in a consistent fashion to "understand" the heat capacity, pulsed phonon, thermal conductivity, and thermal expansion measurements. Phillips (15) suggests, and we agree, that his general conclusion for both heat capacity and thermal expansion are reasonably insensitive to the distributions which he assumes.

The major contribution of the present research is that two very different amorphous solids, fused silica and PMMA, have been shown to have very similar large, negative Grüneisen parameters which are associated with a continuous distribution of two level systems. The origins of these results are not clear. They cannot be explained in terms of a tunneling model which applies to other thermal and thermodynamic properties for these systems, so another model, one which has extreme volume sensitivity for the characteristic energy levels, must be found. Indeed, the existence of low temperature Grüneisen parameters for amorphous solids which are similar to these we report, places great constraints on any model for the low temperature properties of glasses.

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ACKNOWLEDGEMENTS

The author wishes to thank several individuals who have contributed to the completion of this thesis. Special acknowledgements are due to:

Dr. Clayton A. Swenson who supervised this work, for his invaluable and timely advice;

Dr. Gerhard L. Salinger who suggested the thesis topic and who supervised the initial work during the sabbatical absence of Dr. Swenson;

Dr. Guy K. White for making his thermal expansion data for fused silica (36) available;

And Iowa State University's Department of Athletics for the change of pace and additional income while the author coached the men's varsity tennis team.

APPENDIX A. EXPERIMENTAL DATA

The individual thermal expansion data points are given in the following tables. Table A1 gives the data used to calibrate the cell. Tables A2 and A3 give the data for the fused silica and PMMA samples, respectively.

The tables are divided into four columns. The first column gives the 8 digit data number for each data point. The first six digits are the date (month, day, year) the data point was taken while the last two digits number the data point for the day. The second and third columns give the average temperature and the change in temperature, respectively, for each data point. The fourth column gives the measured linear thermal expansion. The thermal expansion is not known to better than 1% or $6 \times 10^{-11} \text{K}^{-1}$ whichever is greater, and an additional digit is usually included. The data which were taken without helium exchange gas are marked with an asterisk (*).

The PMMA data for February 1977 were taken by measuring the average of three PMMA support posts against three copper samples. This was done in a geometry similar to the one described in the text except without the center sample and center capacitor plate. The data which were taken in this geometry below 90K were not consistent with the present data and are not included in the table because they are believed to be incorrect.

Table A1. The measured thermal expansion of the copper samples with respect to a silicon center sample. These data were used to calibrate the cell

Data #	T (K)	ΔT (K)	α (K ⁻¹)
11157701	84.662	4.930	$8.94 \times 10^{-6} \text{K}$
11167701	5.179	1.0252	0.443×10^{-8}
11167702	6.198	1.0127	0.746
11167703	7.265	1.1206	1.141
11167704	8.483	1.3154	1.799
11167705	10.209	2.1373	3.121
11167706	12.305	2.0549	5.452
11167707	14.435	2.2046	9.002
11167708	16.499	1.9230	1.382×10^{-7}
11227701	3.739	0.5007	0.184×10^{-8}
11227702	3.243	0.4929	0.155
11227703	2.768	0.4557	0.122
11227704	2.300	0.4812	0.112
11227705	1.811	0.4961	0.097
11227706	1.346	0.4346	0.063
11237703	2.764	0.4710	0.108
11237704	2.275	0.5064	0.112
11237705	1.760	0.5230	0.081
11237707	1.372	0.4188	0.066
11237708	1.840	0.5174	0.084
11237710	1.540	0.5990	0.075
11237711	1.484	0.4860	0.076
11237712	1.981	0.5089	0.097
11237713	2.477	0.4828	0.108
11237714	2.959	0.4802	0.145
11237716	4.816	1.1640	0.394
11237717	5.885	0.9741	0.643

Table A2. The experimental thermal expansion data for fused silica. Data taken without helium exchange gas are marked with an asterisk (*)

Data #	T (K)	ΔT (K)	α (K ⁻¹)
12017701	84.668	4.933	$-5.70 \times 10^{-7} \text{K}^{-1}$
12027701	5.146	1.0159	-4.032×10^{-8}
12027702	6.155	1.0027	-6.795
12027703	7.211	1.1092	-1.047×10^{-7}
12027704	8.416	1.3014	-1.538
12027705	10.124	2.1137	-2.297
12027706	4.670	0.8254	-3.019×10^{-8}
12027707	5.592	1.0018	-5.167
12027708	6.634	1.0807	-8.390
12027709	7.763	1.1776	-1.270×10^{-7}
12027710	9.179	1.6545	-1.871
12037702	3.681	0.3851	-1.400×10^{-8}
12037703	3.251	0.4746	-1.004
12037704	2.780	0.4673	-0.617
12037705	2.302	0.4905	-0.393
12037707	1.326	0.5004	-0.235
12037708	1.216	0.2810	-0.251
12037709	1.564	0.4144	-0.227
12037710	1.922	0.3021	-0.318
12037711	1.769	0.6086	-0.273
12037712	1.371	0.1874	-0.175
12037713	1.169	0.2150	-0.162
12037714	1.263	0.4031	-0.184
12047702	3.469	0.4460	-1.231
12047703	3.010	0.4722	-0.773
12047704	2.547	0.4538	-0.533
12047706	1.612	0.4811	-0.272

Table A2. Continued

Data #	T (K)	ΔT (K)	α (K ⁻¹)
12047707	1.221	0.3005	-0.189
12047708	1.291	0.4389	-0.193
12047709	1.748	0.4760	-0.246
12047710	2.230	0.4873	-0.385
12047711	1.773	1.4010	-0.277
12047712	1.276	0.4065	-0.233
12057701	1.316	0.4772	-0.129
12057702	1.903	0.6972	-0.346
12047703	2.083	0.3386	-0.386
12057704	1.669	0.4883	-0.229
12067701	1.795	0.6295	-0.223
12077701	1.525	0.5347	-0.151
12097703	5.195	0.4321	-3.874
12097705	6.171	0.6121	-6.778
12097706	6.807	0.6613	-8.973
12097707	3.362	0.3599	-1.194
12097709	2.482	0.4982	-0.462
12097710	2.164	0.1364	-0.347
12097711	1.812	0.5681	-0.299
12137701	84.670	4.932	-5.49×10^{-7}
12147701	4.587	0.3896	-2.768×10^{-8}
12147702	5.010	0.4563	-3.623
12147703	5.485	0.4934	-4.671
12147704	5.996	0.5283	-6.271
02097803*	1.490	0.5704	-0.141
02097804*	1.551	0.4474	-0.141
02097805*	1.551	0.4465	-0.138
02097806*	1.938	0.3283	-0.265
02097807*	1.837	0.5314	-0.223

Table A2. Continued

Data #	T (K)	ΔT (K)	α (K ⁻¹)
02097808*	1.773	0.4046	-0.224
02097809*	1.721	0.5091	-0.187
02097810*	1.689	0.4449	-0.166
02107801*	3.760	0.5108	-1.577
02107802*	3.264	0.4805	-1.003
02107803*	2.794	0.4600	-0.652
02107804*	2.325	0.4774	-0.396
02107805*	1.788	0.5977	-0.209
02107806*	1.250	0.4780	-0.117
02107807*	1.242	0.4625	-0.122
02117801*	3.461	0.5471	-1.228
02117802*	2.991	0.3921	-0.781
02117803*	2.498	0.5929	-0.447
02117804*	2.009	0.3870	-0.264
02117805*	1.603	0.4242	-0.161
02117806*	1.219	0.3437	-0.090

Table A3. The experimental thermal expansion data for PMMA. Data taken without helium exchange gas are marked with an asterisk (*)

Data #	T (K)	ΔT (K)	α (K^{-1})
01157801	3.750K	0.4962K	$2.171 \times 10^{-7} K^{-1}$
01157802	3.266	0.4723	1.362
01157803	2.805	0.4487	7.964×10^{-8}
01157804	2.353	0.4565	4.174
01157806	1.567	0.4587	0.965
01157807	1.183	0.3089	0.167
01157808	1.268	0.4779	0.392
01157809	1.758	0.5030	1.446
01157810	1.805	0.4105	1.547
01157811	1.409	0.3808	0.598
01157812	1.467	0.4962	0.711
01157813	1.883	0.3365	1.864
01157814	2.220	0.3382	3.327
01167801	3.872	0.3020	2.431×10^{-7}
01167802	3.618	0.2148	1.952
01237801	3.869	0.3578	2.403
01237802	3.501	0.3794	1.737
01237803	3.127	0.3684	1.178
01237804	2.747	0.3909	7.337×10^{-8}
01237805	2.311	0.4818	3.912
01237806	1.855	0.4297	1.672
01237809	1.721	0.4084	1.328
01237810	2.120	0.3894	2.995
01237811	2.517	0.4040	5.489
01247801	3.423	0.3920	1.612×10^{-7}
01247802	3.024	0.4049	1.068
01247803	2.649	0.3450	6.488×10^{-8}
01247804	2.182	0.5899	3.253

Table A3. Continued

Data #	T (K)	ΔT (K)	α (K^{-1})
01247806	2.076	0.5215	2.688
01247807	1.894	0.8859	1.933
01247808	1.259	0.3844	0.361
01247809	1.421	0.7091	0.605
01247810	2.024	0.4973	2.431
01247811	2.470	0.3948	5.114
01247812	2.950	0.5640	9.628
01257801	4.901	0.5280	4.995×10^{-7}
01257802	5.488	0.6457	6.859
01257803	6.182	0.7432	9.388
01257804	6.943	0.7789	1.254×10^{-6}
01257805	7.743	0.8200	1.619
01257806	8.620	0.9342	2.048
01257807	9.556	0.9374	2.548
01257808	10.612	1.175	3.127
01257809	11.860	1.321	3.845
01257810	13.160	1.280	4.598
01257811	14.603	1.605	5.448
01257812	16.355	1.899	6.485
01257813	18.353	2.097	7.659
01257814	20.545	2.287	8.925
01257815	22.922	2.467	1.023×10^{-5}
01257816	25.462	2.613	1.160
01257817	28.127	2.718	1.293
01267801	35.078	11.096	1.605
02167802	45.685	10.117	1.992
01267803	55.593	9.700	2.288
01277801*	3.285	0.4959	1.383×10^{-7}
01277802*	2.810	0.4529	8.095×10^{-8}

Table A3. Continued

Data #	T (K)	ΔT (K)	α (K^{-1})
01277803*	2.332	0.5027	4.149
01277804*	1.846	0.4706	1.777
01277805*	1.306	0.6090	0.387
01287801	61.342	10.418	2.441×10^{-5}
01297801	71.436	9.770	2.666
01297802	80.093	7.543	2.844
01297803	88.784	9.839	2.985
02197804	98.650	9.893	3.162
01307801	111.907	16.622	3.369
02137702	91.205	7.508	3.017
02147701	99.664	9.424	3.176
02147702	113.891	19.030	3.370
02157701	133.044	19.275	3.626
02157702	154.889	24.415	3.961
02157703	179.451	24.709	4.376
02167701	204.291	24.971	4.967
02167702	229.441	25.329	5.955
02167703	254.865	25.519	6.863
02177701	280.470	25.691	7.676
02177702	298.812	10.994	7.905

APPENDIX B. DEBYE CONTRIBUTION

The Debye heat capacity and thermal expansion contributions for fused silica and PMMA can be calculated from measured sound velocities and their volume (or pressure) dependences. The Debye heat capacity per unit volume is given by (1)

$$\frac{C_{V,D}}{V} = \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar v} \right)^3 = a_{3D} T^3, \quad (B.1)$$

where

$$\frac{3}{v^3} = \frac{1}{v_\ell^3} + \frac{2}{v_t^3}. \quad (B.2)$$

Here, v is the "average" velocity of sound while v_ℓ and v_t are the measured low temperature longitudinal and transverse sound velocities. The Debye heat capacity for a volume V can be written in terms of a characteristic temperature, ϕ_D , as

$$C_{V,D} = \frac{2\pi^2}{5} k_B \left(\frac{T}{\phi_D} \right)^3 \quad (B.3)$$

where

$$\phi_D = \frac{v^{1/3}}{k_B \hbar} \quad (B.4)$$

The Debye Grüneisen parameter depends on this characteristic temperature, ϕ_D , and is defined as

$$\gamma_{3D} = \frac{-d \ln \phi_D}{d \ln V} \quad (B.5)$$

using Equation (I-8). Substituting Equation (B.4) results in

$$\gamma_{3D} = \frac{1}{3} - \frac{d \ln v}{d \ln V} \quad (B.6)$$

This can be written in terms of the longitudinal and transverse sound velocities as

$$\gamma_{3D} = \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right)^{-1} \left(\frac{\gamma_l}{v_l^3} + \frac{2\gamma_t}{v_t^3} \right) \quad (B.7)$$

where

$$\gamma_{l,t} = \frac{1}{3} - \frac{d \ln v_{l,t}}{d \ln V} = \frac{1}{3} + \frac{d \ln v_{l,t}}{d \ln \rho} \quad (B.8)$$

with $\rho (= m/V)$ being the density. Equation (B.8) can be written in terms of the longitudinal and shear moduli (C_{11} and G) as

$$\gamma_l = \frac{B_T}{2C_{11}} \frac{dC_{11}}{dP} - \frac{1}{6} \quad (B.9)$$

$$\gamma_t = \frac{B_T}{2G} \frac{dG}{dP} - \frac{1}{6} \quad (B.10)$$

since (48,55)

$$v_l^2 = C_{11}/\rho \quad (B.11)$$

$$v_t^2 = G/\rho \quad (B.12)$$

and

$$B_T = C_{11} - \frac{4}{3} G \quad (B.13)$$

The Debye thermal expansion contribution now can be calculated as

$$b_{3D} = \frac{\gamma_{3D} a_{3D}}{3B_T} \quad (1-24)$$

The above can be used to calculate the Debye contribution for the heat capacity and thermal expansion using experimental sound velocity measurements. The results (with references) are given in Table B1.

Table B1. The various parameters used to calculate the Debye contributions

Parameter (units)	PMMA ⁵⁰	Fused Silica ^{48,49}
ν_l (m s^{-1})	3.182×10^3	5.8×10^3
ν_t (m s^{-1})	1.591×10^3	3.8×10^3
ν (m s^{-1})	1.785×10^3	4.2×10^3
a_{3D} ($\text{J m}^{-3} \text{K}^{-4}$)	21.5	1.69
γ_l	5.24	-2.78
γ_t	4.19	-2.23
γ_{3D}	4.25	-2.29
B_T (N m^{-2})	8.20×10^9	3.50×10^{10}
b_{3D}	3.72×10^{-9}	-3.4×10^{-11}